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Date: June 7, 2024

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- 'WO2005086251A2 (Werner).pdf'

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(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
September 15, 2005 (09/15/2005)

PCT

(10) International Publication Number
WO 2005/086251 A2

(51) International Patent Classification⁷: **H01L 51/00**

(21) International Application No.: PCT/DE2005/000372

(22) International Filing Date:
March 3, 2005 (03/03/2005)

(25) Filing Language: German

(26) Publication Language: German

(30) Priority Data:
10 2004 010 954.0 March 3, 2004 (03/03/2004) DE

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(81) Designated States (unless otherwise indicated, for every available national protection type): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every available regional protection type): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK,

[Continued on the next page]

(54) Title: USE OF A METAL COMPLEX AS N-DOPANT FOR AN ORGANIC SEMICONDUCTING MATRIX MATERIAL, ORGANIC SEMICONDUCTOR MATERIAL, AND ELECTRONIC COMPONENT, AS WELL AS DOPANT AND LIGAND AND METHOD FOR PRODUCING THE SAME

(57) Abstract: The invention relates to the use of a metal complex as n-dopant for doping an organic semiconducting matrix material for modifying the electrical properties of the same, wherein the compound represents an n-dopant with regard to the matrix material. The aim of the invention is to provide n-doped organic semiconductors for matrix materials that have little reduction potential while achieving high conductivities. According to the invention, a neutral electron-rich metal complex having a central atom as the preferably neutral or charged transition metal atom having a valence electron number of at least 16 is used as the dopant compound. The complex can especially be multinuclear and comprises at least one metal-metal bond. At least one ligand can form a pi-complex with the central atom, or can be a bridging ligand, especially hpp, a borate, carborane or triazacycloalkane or comprise at least one carbanion carbon atom or a bivalent atom selected from the group including C (carbene), Si (silylene), Ge (germylene), Sn, Pb. The invention also relates to novel n-dopants and methods for producing them.

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EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG). *For explanations of the two-letter codes and other abbreviations, refer to the explanations ("Guidance Notes on Codes and Abbreviations") at the beginning of each regular issue of the PCT Gazette.*

Published:

— *without international search report and to be republished upon receipt of the report*

**Use of a metal complex as n-dopant for an organic
semiconducting matrix material, organic semiconductor
material, and electronic component, as well as dopant and
ligand and method for producing the same**

The invention relates to the use of a metal complex as a dopant
for doping an organic semiconducting matrix material to modify its
electrical properties, wherein the compound acts as an n-dopant
with respect to the matrix material. It also involves an organic
semiconducting material containing an organic matrix material and
a metal complex as an n-dopant, as well as an electronic device
with an organic semiconducting material doped with a metal complex
as an n-dopant. The invention further relates to n-dopants and
ligands and methods for producing them.

It is known that organic semiconductors can be modified in their
electrical properties, especially their electrical conductivity,
through doping, similar to inorganic semiconductors like silicon
semiconductors. By generating charge carriers in the matrix
material, an increase in initially low conductivity and a change

in the Fermi level of the semiconductor, depending on the type of dopant used, is achieved. Doping increases the conductivity of charge transport layers, reduces ohmic losses, and improves the transition of charge carriers between contacts and the organic layer. Inorganic dopants are often disadvantageous for organic matrix materials due to their high diffusion coefficients, which can impair the function and stability of electronic devices. It is also known to release dopants through chemical reactions in the semiconducting matrix material to provide dopants. However, the oxidation potential of such released dopants is often insufficient for various applications, especially for organic light-emitting diodes (OLEDs). Additionally, the release of dopants generates other compounds and/or atoms, such as atomic hydrogen, which can adversely affect the properties of the doped layer or the corresponding electronic device.

Furthermore, organic compounds used as dopants often do not have sufficiently low oxidation potential for the respective application.

The invention has the object of specifying metal complexes as n-dopants for doping an organic semiconducting matrix material, in particular for producing electronic devices that in particular have sufficiently low oxidation potentials for producing electron transport materials for organic light-emitting diodes (OLEDs) without adverse effects on the matrix material, effectively increasing the number of charge carriers in the matrix material, and being relatively easy to handle. Another object of the invention is to provide suitable ligands and methods for producing the dopants.

These objects are achieved by the features of the independent claims, in particular by using neutral electron-rich metal complexes. Additionally, the object is achieved by providing an organic semiconducting material with a compound of such a neutral electron-rich metal complex as an n-dopant. Preferred embodiments

are derived from the dependent claims.

By using a neutral electron-rich metal complex as an n-dopant for the organic semiconducting matrix material, a much stronger donor is present than previously known organic donor compounds. Moreover, by providing a neutral electron-rich metal complex compared to other n-dopants in the form of organic compounds, the donor properties of the compound can be varied by selecting a suitable central atom and thus its oxidation potential. The n-dopants according to the invention thus preferably have a very low oxidation potential. The complex preferably has at least one organic ligand, without being limited to this. Specifically, the n-dopants according to the invention can significantly increase the conductivity of charge transport layers and/or substantially improve the transition of charge carriers between contacts and the organic layer when used as an electronic device.

The metal complexes used in the invention preferably represent isolated molecules, which are thus preferably present in the respective semiconducting layer as isolated molecules that are not fixed to each other and/or to a matrix and/or another component by chemical bonds. The valence electrons of the metal central atoms, apart from the valence electrons directly attributable to the metal atom of the complex, are thus provided essentially or entirely by the ligands of the complex and the metal atoms of the complex, which are arranged within the preferably substantially closed coordination sphere formed by the ligands. Preferably, all metal atoms of the complex or all metal atoms of an outer sphere of the metal complex are coordinated to non-metallic ligands, preferably organic ligands. It is understood that individual metal complexes can each be bonded to each other or to other components such as the matrix material to immobilize the metal complexes if necessary. For this purpose, the ligands can have suitable functional groups that can be connected to each other, such as unsaturated groups that can react with each other to form a linear or branched oligomer or polymer.

The complexed central atom can have a formal valence electron count (VE) of 16 or more, for example 18 or 19 or 20 or 21 or more valence electrons. The central atom can in particular be a metal atom from the first transition metal period, a metal atom from the second transition metal period, or a metal atom from the third transition metal period. Independently or in combination, the complexes according to the invention can be at least dinuclear complexes with at least one metal-metal bond between the central atoms, providing particularly electron-rich metal complexes with a high electron density at the central atom of the metal complex.

A neutral or charged transition metal atom is particularly preferred as the central atom of the electron-rich metal complex.

The central atom can, for example, be a metal atom from the group of the first transition metal period (scandium to zinc), or a metal of the second transition metal period (yttrium to cadmium), such as rhodium, palladium, silver, and cadmium, or a metal of the third transition metal period, including the lanthanides and actinides.

The central atom can in particular be a metal from groups 7 to 10. The transition metal of the at least one central atom can also be any of the following elements: V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Nd, Ta, Mo, W, Rh, Ir, Pd, Pt. Particularly preferred is the transition metal atom selected from the group Mn, Fe, Co, Ni, Cu, Zn, for example selected from the group Fe, Co, Ni. Additionally, the transition metal atom can be selected from the group Cr, Mo, W. The transition metal atom can also be selected from the group V, Nb, Ta, or from the group Ir, Pt, Au, Hg. For various application purposes, metal complexes with a lower formal valence electron count at the metal central atom of the complex or with a lower electron density at the metal central atom can also be used.

The transition metal atom in the neutral metal complex used according to the invention can be present as a neutral atom or as a charged transition metal atom, preferably with a formal charge of 0 to 3, for example a formal charge of 0, 1, or 2, wherein the central atom can in particular be an atom of the first transition

metal period. The charge of the central atom, which can be an atom of the first, second, or third transition metal period, can also be different from 0.

At least one, two or more, or all ligand atoms (donor atoms) binding to the central atom can be different from an aromatic nitrogen atom that is part of an aromatic 6-membered ring, in which the nitrogen atom has a double bond to a neighboring atom, especially a carbon atom. Ligands such as pyridine, pyrimidine, pyridazine, or pyrazine are often used in complex chemistry. At least one, two or more, or all ligand atoms binding to the central atom may also be different from an aromatic nitrogen atom of a 5-membered ring, such as a pyrrole or imidazole ring. The aromatic ring of the substituent may, in these cases, have a non-coordinating nitrogen atom or a substituent with an N-atom. In particular, at least one ligand atom binding to at least one central atom may be different from the nitrogen atom of pyridine, 2,2';6',2''-terpyridine, or 2,2'-bipyridine, in particular different from 4,4',5,5'-tetramethyl-2,2'-bipyridine. The above can apply to both substituted and unsubstituted ligands. This may in particular apply to Cr or Ru complexes. It should be understood, however, that such ligands are not generally excluded from the invention, and one, two or more, or all donor atoms may have the properties mentioned above.

In particular, at least one ligand may be at least bidentate or tridentate, and at least one, two, or more donor atoms of the ligand binding to a central atom can be different from nitrogen.

At least one, two, or more donor atoms of at least one ligand, or 1, 2, 3, or 4 or more, or all donor atoms of the complex can, for example, be an sp^3 -configured nitrogen atom, such as the nitrogen atom of a substituted or unsubstituted alkylamine residue not covered by the above. Optionally, one, two, or more, for example 3, 4, or all of the ligand atoms binding to at least one central atom of the neutral metal complex can be different from an aromatic

nitrogen atom or generally different from nitrogen. Independently or simultaneously, one, two, three, four or more, or all donor atoms of at least one or all central atoms of the complex can be different from oxygen, without this being mandatory.

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Preferably, at least one ligand atom binding to the central atom is selected from the group consisting of B, Al, Ga, In, C, Si, Ge, Sn, Pb, P, As, Sb, Bi, S, Se, Te, and possibly also O, wherein 2, 3, 4 or more, or all ligand atoms binding to the central atom can be selected from this group. Preferably, at least 1, 2, 3, or 4 or more, or all donor atoms are selected from the group consisting of B, C, Si, Ge, Sn, S, P, Se, As, Sb, Te (possibly including N), in particular selected from the group B, C, S, P, Se (possibly including N). It should be understood that at least one ligand atom can additionally be selected from the group Si, Ge, Sn, As, Sb, Te.

At least 1, 2, 3, or 4 or more, or preferably all ligand atoms binding to the central atom may have a lower electronegativity than nitrogen (electronegativity according to Allred-Rochow for N: 3.07).

It should be understood that the above statements regarding ligand atoms binding to the central atom (donor atoms) apply to mononuclear metal complexes, but also to multinuclear metal complexes, in which the ligand atom binding to the central atom can bind to only one central atom but also to two or three central atoms in the case of a multinuclear complex. The respective ligand can be a monodentate ligand or a bidentate, tridentate, or polydentate ligand, with different ligand atoms binding to different metal atoms of the metal complex according to the invention, potentially forming bridging ligands. It should also be understood that in the case of multinuclear metal complexes with preferably two, but also three or more central atoms, which are preferably transition metal atoms, neutral or charged, metal-metal bonds can exist between two or more central atoms. These metal-

metal bonds can formally correspond to a single bond or a metal-metal multiple bond with respect to valence electrons, although a metal-metal bond can already be present if the electron density between the metal atoms is less than that for a metal-metal single bond. It should be understood that the additional metal atoms of a multinuclear metal complex are not considered ligand atoms in the sense of the invention.

At least 1, optionally 2, 3, or 4 or more, or all donor atoms of the metal complex can be part of a heterocyclic unsaturated ring, wherein preferably the heteroatom is the atom binding to the central atom of the metal complex. The heteroatom can in particular be an N, S, P, or Se atom, but also possibly an O atom, without being limited to this. Optionally, the heterocyclic unsaturated ring can have additional heteroatoms, which can also be different from the first heteroatom. The metal complex can have 1, 2, 3, 4 or more, or all ligand atoms as part of such a heterocyclic unsaturated ring. The heterocyclic unsaturated ring can have 5, 6, or 7 ring atoms, without being limited to this.

Preferably, 1, 2, 3, 4 or more, or all donor atoms of the complex are part of an aromatic ring or a conjugated, for example mesomeric, system of the ligand, wherein the donor atom can bind to one or two multiply bonded atoms.

The following are some advantageous classes of compounds described in more detail:

Pi-complexes

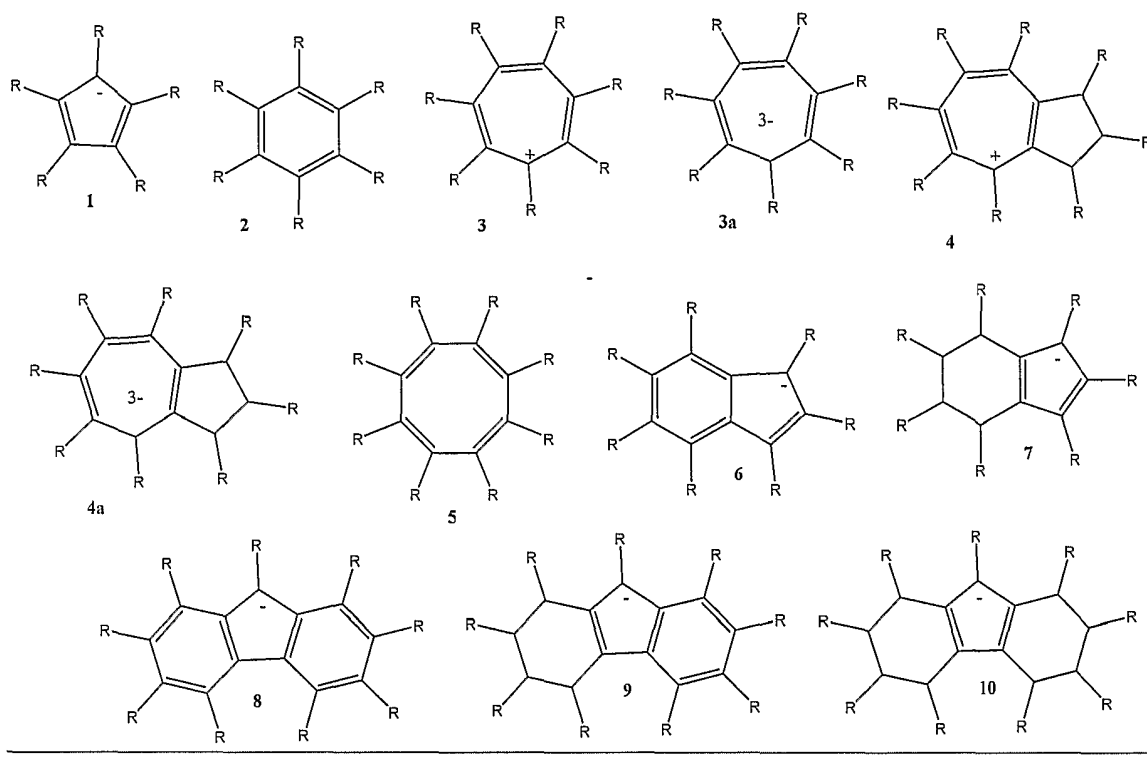
According to an advantageous embodiment, at least one ligand of the neutral metal complex forms a pi-complex with the central atom. The ligand of the pi-complex can coordinate to the central atom with a multiple bond, i.e., a double bond or a triple bond, wherein the multiple bond can represent, for example, a C-C, C-O, C-N, S-O, N-O bond, without being limited to these. The ligand forming the pi-complex can have a mesomeric or aromatic system that the

pi-complex forms with the central metal atom. The pi-complex can include, for example, a 2-electron donor such as a double or triple bond, a 3-electron donor such as an allyl group or an η^3 -1-3-cyclohexenyl group, a 4-electron donor such as a butadiene or cyclobutadiene group, a 5-electron donor such as an η^5 -1-5-cyclohexadienyl group, or in particular a 6-electron donor group such as a benzene ring, a cyclopentadienyl anion, a cycloheptatrienyl cation, a cycloheptatrienyl trianion, a cyclooctadienyl dianion, or the like. It should be understood that the complex can also have two or more ligands that form a pi-complex with the central atom. In particular, the complex can include two ligands forming a pi-complex with the central atom, which can in particular coordinate the central atom linearly. It should be understood that the pi-complex can also include other ligands that do not coordinate with the central atom through a pi-electron system. Such ligands can be, for example, carbonyl, phosphine, or the like, without being limited to these. It should also be understood that the pi-complex can have two or possibly more ligands coordinating with the central atom through a pi-bonding system, wherein these ligands are different from each other, in particular regarding the number of electrons of the pi-electron system and/or the number of coordinating atoms, in particular the number of ring atoms in the case of aromatic pi-complexes. For example, the central atom can be coordinated by a pi-benzene ligand and/or a pi-cyclopentadienyl ligand or by two pi-cyclopentadienyl ligands or two pi-benzene ligands such as dibenzene iron, which are differently substituted, or by a cyclopentadienyl or benzene ligand on the one hand and a ligand complexing through a double or triple bond on the other hand, wherein the double or triple bond may also have a heteroatom. The biscyclopentadienyl complexes can be η^5 -complexes as pi-complexes, without being limited to this.

Generally, one or more or all ligands of the complex can be selected from the group **1-10** (with compound **5** in particular as a singly or doubly charged anion or cation).

In the base compounds **1-10**, one or more or possibly all C, CR, CR₂, C⁻, CR⁻, CR₂⁻ groups can be substituted isoelectronically or non-isoelectronically by corresponding same or different heteroatoms.

5 In particular, one or more of the CR or C⁻ groups can be replaced by P. Simultaneously or alternatively, one or more of the CR₂ or C⁻ groups can be replaced by S. The following elements can be used as heteroatoms: B, Al, Ga, In, N, P, As, Sb, Bi, Si, Ge, Sn, Pb, O, S, Se, Te, possibly also without O. In particular, the
10 heteroatoms can be selected from the group B, Al, Ga. Furthermore, the heteroatoms can be selected in particular from the group N, P, As, Bi, preferably selected from the group N, P, As. Furthermore, the heteroatoms can be selected from the group Si, Ge, Sn, Pb, in particular from the group Si, Ge. Additionally, the heteroatoms
15 can be selected from the group O, S, Se, Te, in particular from the group O, S, Se. In particular, the heteroatoms from the mentioned groups can also each be atoms of the third main group period (atomic numbers in particular between 13 and 16) or the fourth main group period (atomic numbers in particular between 31
20 and 34).



The residues R in the base compounds **1-10** can be the same or different, be open-chain or part of a ring or ring system, and are preferably selected from: alkyl, including cycloalkyl, aryl, the above heteroatoms. The alkyl or aryl groups can be fully or partially substituted with one or more, same or different heteroatoms from the above list. It should be understood that the above residues R can also generally be residues according to the invention with a +I effect and/or +M effect on an unsaturated or aromatic ring (or P instead of N). Generally, the residues R in the inventive compounds can also have unsaturated groups, e.g., with C=C, C=N bonds, or the like.

The central atom of the complexes can be selected from the group Mn, Fe, Co, Ni, Cu, Zn, or selected from the group Cr, Mo, W, particularly preferably selected from the group Fe, Co, Ni, for example, complexes with Fe or Co. The central atom can also be another metal atom from groups 6 or 7 to 10.

In particular, one, two, or all of the ligands can be cyclopentadienyl or benzene or selected from the group of compounds

3, 4, and 5, or selected from the group of compounds 6, 8, and 9, in particular also compound 8, or selected from the group of compounds 7, 10, wherein the ligands can be substituted or unsubstituted.

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Paddlewheel complexes and multinuclear complexes in general

According to an advantageous embodiment, the metal complex according to the invention is a multinuclear metal complex. In particular, the metal complex can be a multinuclear metal complex with at least one, two, three, or four, or possibly more ligands binding to at least two central metal atoms. The metal complex can also have one, two, or more metal-metal bonds, which can each be metal-metal single bonds or metal-metal multiple bonds. The multinuclear complex can have two, three, or four or more central metal atoms. Preferably, the complex contains no more than 20, no more than 10, no more than 6, or no more than 4, in particular no more than 3 metal atoms. The metal complexes are preferably isolated molecules. Multinuclear complexes can in particular be carbonyl or cyclopentadienyl complexes.

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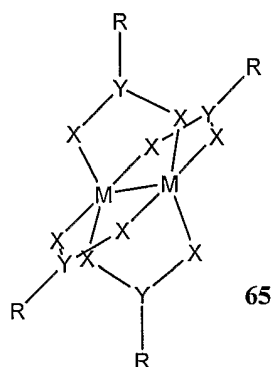
The metal atoms of multinuclear metal complexes are preferably predominantly or entirely transition metal atoms, in particular from groups 6 or 7 to 10, for example selected from the group Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, W.

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Such a metal complex can, for example, be a so-called paddlewheel complex, in which two central metal atoms, in particular transition metal central atoms, are bridged by 1, 2, 3, 4, or more bidentate ligands, each binding one ligand atom to both central metal atoms.

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The metal atoms are usually 4-fold or possibly 5-fold or more coordinated:



One or both central metal atoms M can optionally also each independently be complexed with at least one additional ligand, such as carbonyl, phosphine, or others, which can be arranged axially (terminally) to the M-M bond.

In particular, the multinuclear metal complexes can include at least one atom from the group Mn, Fe, Co, Ni, Cu, Zn, in particular an atom from the group Fe, Co, Ni, or at least one atom selected from the group Cr, Mo, W, in particular Mo, W, wherein preferably all central atoms of the neutral metal complex are identical. Generally, M can be any metal atom, in particular a transition metal atom, for example a transition metal atom from the first, second, or third transition metal period or an atom from groups 6 or 7 to 10 of the transition metals. Both metal atoms M can be the same or different from each other.

Instead of the bidentate, bridging ligand RYX_2 connecting both central metal atoms, one or more of the bridging ligands can be replaced by monodentate ligands, for example by carbonyl, RCN, substituted or unsubstituted phosphines, or others, wherein the substituent R can be any organic residue including hydrogen, in particular also a hydrocarbon residue or a substituted or unsubstituted alkyl residue, in particular an alkyl residue with C1 to C10, especially C1 to C4, or up to C6.

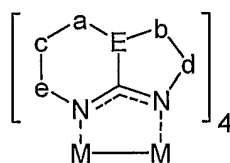
At least one, several, or all of the ligand atoms X binding to the

metal atom can be selected from the group F, Cl, Br, I, O, S, Se, N, P, for example halogen, preferably selected from the group O, S, Se, N, P, particularly preferably selected from the group S, Se, N, P, wherein at least one, two, three, or four or all ligand
5 atoms can be different from N. However, X can also be another suitable atom. The various atoms X binding to the metal atom can be the same or different within a ligand or within the complex. Thus, different ligands L, L' can also be used as bidentate ligands bridging the two metal atoms. The atom Y is preferably a main group
10 element, in particular a two, three, or four-binding main group element. The atom Y is preferably selected from the group B, C, N, O, Si, P, S, As, Se, Sb, Te, particularly preferably selected from the group O, S, Se, N, P, C, in particular selected from the group S, Se, N, P (possibly also O), without being limited to these.

15 Preferably, at least one ligand, two, several, or all ligands are selected from the group of halides, carboxylates, formamidinates, pyrimido-pyrimidines, including their anions, in particular substituted or unsubstituted pyrimido[1,2-a]pyrimidines or their
20 anions, in particular hpp (hpp: anion of 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidine), and guanidines, possibly also diketonates. The ligands can each be the same or different from each other. In particular, at least one ligand is a carboxylate, a formamidine, a pyrimido-pyrimidine, in particular hpp, or a
25 guanidine. In particular, all ligands of the complex are each a carboxylate, a formamidine, a pyrimido-pyrimidine, in particular hpp, or a guanidine, wherein all ligands of the complex are preferably the same. Particularly preferred are the ligands selected from the group of carboxylates, formamidinates, pyrimido-
30 pyrimidines, and guanidines. The groups Y but also X, specifically the carboxylates, formamidinates, pyrimido-pyrimidines, and guanidines, possibly also diketonates, can each be substituted or unsubstituted, for example having substituted or unsubstituted alkyl residues or hydrocarbon residues, for example
35 each with C1 to C10 or higher, in particular C1 to C6 or C2 to C4, or other substituents.

At this point, but also generally within the scope of this invention, the term "alkyl residue" also includes cycloalkyl residues, in particular cycloheptyl, cyclohexyl, or cyclopentyl residues.

From the above enumeration, the structure types 65a, 65b, 65c, and 65d are preferred, which are described in more detail below:



Type 65a

wherein

- the structural elements a-e can have the meanings: a = -CR₁R₂-, b = -CR₃R₄-, c = -CR₅R₆-, d = -CR₇R₈-, and e = -CR₉R₁₀-, where R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, and R₁₀ can be H, alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl, -NR₂ or -OR, either simultaneously or independently of each other. Preferably, R₁, R₃, R₅, R₇, R₉ = H and R₂, R₄, R₆, R₈, R₁₀ = alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl, -NR₂, or -OR, or
- optionally, a or b or e or d can be NR with R = alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl, or
- optionally, a and d or b and e can be NR with R = alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl, or
- at c, C is replaced by Si,
- wherein the bonds b-d and c-e or b-d and a-c can be unsaturated simultaneously or independently of each other,
- wherein the bonds b-d, a-c, and c-e can be part of a saturated or unsaturated ring system simultaneously or

independently of each other, which can also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or

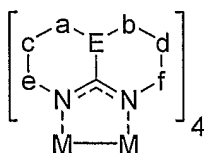
- wherein the bonds b-d, a-c, and c-e can be part of an aromatic or condensed aromatic ring system simultaneously or independently of each other, which can also contain the heteroelements O, S, Se, N,

- wherein the atom E is a main group element, preferably selected from the group N, P, As, Sb, without being limited to these,

- wherein the structural element a-E-b can optionally be part of a saturated or unsaturated ring system, which can also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or

- the structural element a-E-b can optionally be part of an aromatic ring system, which can also contain the heteroelements O, S, Se, N,

- wherein the metal M is a transition metal, preferably W or Mo;



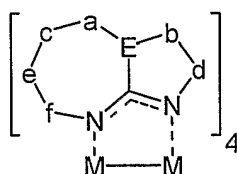
Type 65b

wherein

- the structural elements a-f can have the meanings: a = -CR₁R₂-, b = -CR₃R₄-, c = -CR₅R₆-, d = -CR₇R₈-, e = -CR₉R₁₀-, and f = CR₁₁R₁₂, where R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, R₁₀, R₁₁, and R₁₂ can be hydrogen, alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl, -NR₂, or -OR, preferably R₁, R₃, R₅, R₇, R₉, R₁₁ = H and R₂, R₄, R₆, R₈, R₁₀, R₁₂ = alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl, -NR₂, or -OR, except for structure 65b where

$R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, R_{10}, R_{11},$ and $R_{12} = H$, or

- at the structural elements c and/or d, C can be replaced by Si, or
- optionally, a or b or e or f can be NR with R = alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl, or
- optionally, a and f or b and e can be NR with R = alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl,
- wherein the bonds a-c, b-d, c-e, and d-f, but not simultaneously a-c and c-e, and not simultaneously b-d and d-f, can be unsaturated,
- wherein the bonds a-c, b-d, c-e, and d-f can be part of a saturated or unsaturated ring system, which can also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- the bonds a-c, b-d, c-e, and d-f can be part of an aromatic or condensed aromatic ring system, which can also contain the heteroelements O, S, Se, N,
- wherein the atom E is a main group element, preferably selected from the group N, P, As, Sb, without being limited to these,
- wherein the structural element a-E-b can optionally be part of a saturated or unsaturated ring system, which can also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- the structural element a-E-b can optionally be part of an aromatic ring system, which can also contain the heteroelements O, S, Se, N,
- wherein the metal M is a transition metal, preferably W or Mo;



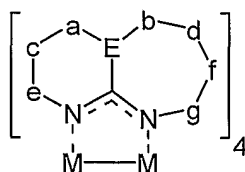
Type 65c

5 wherein

- the structural elements a-f can have the meanings: a = -CR₁R₂-, b = -CR₃R₄-, c = -CR₅R₆-, d = -CR₇R₈-, e = -CR₉R₁₀-, and f = CR₁₁R₁₂, where R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, R₁₀, R₁₁, and R₁₂ can simultaneously or independently be H, alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl, -NR₂, or -OR; preferably R₁, R₃, R₅, R₇, R₉, R₁₁ = H and R₂, R₄, R₆, R₈, R₁₀, R₁₂ = alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl, -NR₂ or -OR,
- or
- at c or e, C can be replaced by Si, or
- optionally, a or b or d or f can be NR with R = alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl, or
- optionally, a and d or b and f can be NR with R = alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl,
- wherein the bonds a-c, c-e, e-f, and b-d, but not simultaneously a-c, c-e, and e-f, and not simultaneously a-c and c-e, and not simultaneously c-e and e-f, can be unsaturated,
- wherein the bonds a-c, c-e, e-f, and b-d can be part of a saturated or unsaturated ring system, which can also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- the bonds a-c, c-e, e-f, and b-d can be part of an aromatic or condensed aromatic ring system, which can also contain the heteroelements O, S, Se, N,
- wherein the atom E is a main group element, preferably

selected from the group N, P, As, Sb, without being limited to these,

- wherein the structural element a-E-b can optionally be part of a saturated or unsaturated ring system, which can also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- the structural element a-E-b can optionally be part of an aromatic ring system, which can also contain the heteroelements O, S, Se, N,
- wherein the metal M is a transition metal, preferably W or Mo; or



Type 65d

- wherein the structural elements a-g can have the meanings:
 $a = -CR_1R_2-$, $b = -CR_3R_4-$, $c = -CR_5R_6-$, $d = -CR_7R_8-$, $e = -CR_9R_{10}-$, $f = CR_{11}R_{12}$, and $g = CR_{13}R_{14}$, where $R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, R_{10}, R_{11}, R_{12}, R_{13}$, and R_{14} can simultaneously or independently be H, alkyl with C_1-C_{20} , cycloalkyl with C_1-C_{20} , alkenyl with C_1-C_{20} , alkynyl with C_1-C_{20} , aryl, heteroaryl, $-NR_2$, or $-OR$; preferably $R_1, R_3, R_5, R_7, R_9, R_{11}, R_{13} = H$ and $R_2, R_4, R_6, R_8, R_{10}, R_{12}, R_{14} =$ alkyl with C_1-C_{20} , cycloalkyl with C_1-C_{20} , alkenyl with C_1-C_{20} , alkynyl with C_1-C_{20} , aryl, heteroaryl, $-NR_2$, or $-OR$, or
- at c, d, and f, but not d and f simultaneously, C can be replaced by Si, or
- optionally, a or b or e or g can be NR with R = alkyl with C_1-C_{20} , cycloalkyl with C_1-C_{20} , alkenyl with C_1-C_{20} , alkynyl with C_1-C_{20} , aryl, heteroaryl, or
- optionally, a and g or b and e can be NR with R = alkyl

with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀,
alkynyl with C₁-C₂₀, aryl, heteroaryl,

- wherein the bonds a-c, c-e, b-d, d-f, and f-g, but not simultaneously a-c and c-e, and not simultaneously b-d, d-f, and f-g, and not simultaneously b-d and d-f, and not simultaneously d-f and f-g, can be unsaturated,
- wherein the bonds a-c, c-e, b-d, d-f, and f-g can be part of a saturated or unsaturated ring system, which can also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- the bonds a-c, c-e, b-d, d-f, and f-g can be part of an aromatic or condensed aromatic ring system, which can also contain the heteroelements O, S, Se, N,
- wherein the atom E is a main group element, preferably selected from the group N, P, As, Sb, without being limited to these,
- wherein the structural element a-E-b can optionally be part of a saturated or unsaturated ring system, which can also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- the structural element a-E-b can optionally be part of an aromatic ring system, which can also contain the heteroelements O, S, Se, N,
- wherein the metal M is a transition metal, preferably W or Mo.

For the residues R in the structures 65a-65d, the definitions for structure 65, as described above, can be applied.

According to the invention, the ligands used to produce the structures 65a-65d are also disclosed.

Further complex ligands

Preferably, at least one, two or more, or all of the ligands are selected from the group of borates, carboranes, triazacycloalkanes, triazacycloalkenes, pyrroles, thiophenes, pyrazoles, imidazoles, thiazoles, oxazoles, pyridines,

pyridazines, pyrimidines, pyrazines. In particular, at least one, two or more, or all ligands are selected from the group of borates, carboranes. At least one, several, or all of the ligands can be selected from the group of triazacycloalkanes, triazacycloalkenes, and possibly other amines. At least one, two or more, or all of the ligands can be selected from the group of pyrroles, thiophenes, pyrazoles, imidazoles, thiazoles, and possibly oxazoles. At least one, two or more, or all of the ligands can be selected from the group of pyridines, pyridazines, pyrimidines, pyrazines. The ligands can each be the same or different and can be selected from one or more of the mentioned groups. In particular, when a ligand is selected from the group of borates and carboranes, another ligand can be an aryl- or aryl-pi-ligand, such as a substituted or unsubstituted cyclopentadienyl, benzene, or cycloheptatrienyl ion.

The central atom of each complex can be selected from the group Mn, Fe, Co, Ni, Cu, Zn or selected from the group Cr, Mo, W, particularly preferably selected from the group Fe, Co, Ni, for example complexes with Fe or Co. The central atom can also be another metal atom from groups 6 or 7 to 10.

Carboranes

Preferred carboranes are those of the type $[R_2C_2B_4]^-$, $[R_2C_2B_9H_9]^{2-}$, $[R_2C_2B_{10}H_{10}]^{2-}$, where R can be any substituents, in particular alkyl substituents, in particular lower alkyl substituents with C₁₋₆. The substituents R can be the same or different.

Borates

If the ligand is a borate anion, the borate preferably has the general structure 15 (Table 2), where R is any substituent, preferably H, alkyl, in particular lower alkyl with C₁₋₆ or aryl, in particular benzyl, or generally a hydrocarbon residue. It is understood that the substituent R can also contain heteroatoms, in particular N, O, or halogen. R' is any substituent, preferably alkyl, in particular lower alkyl with C₁ to C₆ or aryl, where R' can contain heteroatoms, in particular N, O, or halogen. R' can

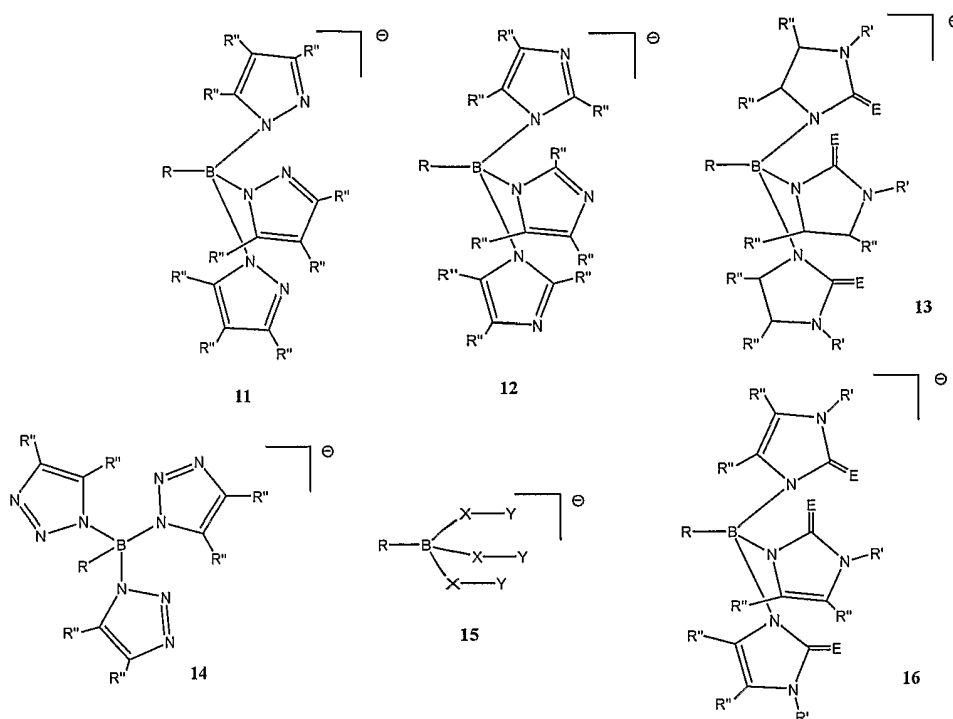
also be a pure hydrocarbon. The descriptions for R apply to R'. The various substituents R, R', or R' can be the same or different. Two substituents R' can be part of a ring system, in particular part of the same ring system, preferably part of a ring system condensed onto the main structure. The ring system can be saturated, unsaturated, in particular aromatic. E is at least a two-bonded atom and can be selected from the group O, S, Se, Te, optionally selected from the group O, S, Se or selected from the group S, Se, and Te. The group E of the various ring systems can be the same or different. X represents a "spacer," where 1, 2, or 3 of the groups X may be absent in compound 15. X can be a branched or unbranched alkyl chain with or without heteroatom substituents, in particular an alkyl chain with 1 to 6, in particular C₁ to C₄ or C₁ to C₂, an aryl substituent, including a hetero-substituted aryl substituent, a condensed aryl substituent with or without heteroatoms, an alkylaryl substituent with or without a heteroatom, or a heteroatom. The heteroatom is preferably selected from the group N, P, S, Se, Ge, Sn, without being limited to these. The various groups X in compound 15 can be the same or different. Preferably, X is an alkyl chain, particularly preferably a lower alkyl chain with C₁ to C₆. Y is a donor-capable hetero- or carbon atom, preferably selected from the group N, P, S, Se, Ge, Sn, optionally selected from the group N, P, S, Se or selected from the group P, S, Se, Ge, Sn. The various donor atoms Y in compound 15 can be the same or different. Y can be part of a ring or ring system, in particular an unsaturated ring or ring system, including an aromatic or heteroaromatic ring system. The ring containing the donor-capable hetero- or carbon atom Y preferably includes 5 to 7 ring atoms, for example 5 or 6. The ring containing the donor atom Y can have several heteroatoms, which can be the same or different, for example two or three. The heteroatoms can each, for example, be N atoms or contain at least one N atom.

In particular, the borate can have fewer than three, fewer than two, or no oxygen donor atoms.

In particular, the borate can be one of compounds 11, 12, 13, 14, or 16, where the metal complex can also have different borate ligands, in particular different borate ligands from the mentioned group of compounds 11, 12, 13, 14, 16.

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Here, as in general with borates, in particular borates according to compound 15, the atom Y can also be part of a pyrrole, indole, carbazole, furan, benzofuran, thiophene, benzothiophene, pyrazole, imidazole, thiazole, or oxazole ring. One or more of the atoms Y can also be part of a pyridine, quinoline, isoquinoline, acridine, pyridazine, pyrimidine, pyrazine, quinoxaline, pteridine, or purine ring, where the donor atom Y binding to the central atom can be part of a 5- or 6-membered ring. Generally, Y can be part of a (hetero) aromatic ring. The mentioned rings can also be partially or fully saturated. Generally, Y can be part of a 3- to 8-membered, in particular 3- to 6-membered, in particular 5- or 6-membered ring. Y can, in particular as a ring, contain the heteroatoms O, N, P, S, Se, Ge, Sn, in particular the heteroatoms O, N, P, S. C can form a carbanion; C, Ge, and Si can form carbenes (C(II)), germylenes (Ge(II)), and silylenes (Si(II)). Preferably, the ring has one or two multiple bonds in conjugation with the donor atom Y.



It is understood that the residues Y in compound 15 can be the same or different.

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Optionally, the borate based on compound 15 or one of compounds 11, 12, 13, 14, or 16 can also be merely a bidentate or even a monodentate ligand, where one or two of the X-Y groups are each replaced by a substituent R, independently of each other, including H, where two substituents R can also form a saturated or unsaturated ring. The tridentate borate ligands can in particular coordinate facially to the central atom.

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Optionally, in compound 15, the B atom can also be replaced by an Al or a Ga atom.

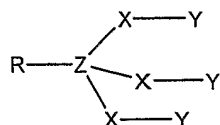
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The central atom of the carborane or borate metal complexes, in particular of compounds 11, 12, 13, 14, 16, can preferably be selected from the group Cr, Mn, Fe, Co, Ni, Cu, Zn, in particular from the group Fe, Co, Ni. The metal atom can also be selected from the group Cr, Mo, W, for example, Cr, Mo, or W, or represent a metal from transition metal groups 7 to 10.

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Tripod ligands

According to another advantageous embodiment, at least one, two, or all of the ligands of the neutral metal complex can be tripod ligands 18, which thus have three ligand atoms,

**18**

which bind to at least one central metal atom of the respective complex and bind to a central atom via additional atoms or groups that function as spacers. Compounds according to formula 15 represent such tripod ligands. It is understood, however, that, for example, the central B atom of compound 15 can be replaced by a C, Si, P, or As atom, without being limited to these. Generally, the tripod ligand according to formula 18 can have a suitable central atom Z, which can be a main group element or a transition metal atom. Regardless, Z can be a metal atom, in particular a main group metal atom. Z is at least a trivalent atom. Preferably, Z is carbon, but it can also be B or P in particular. Otherwise, the descriptions of the groups R, X, and Y apply as mentioned above for borates. In particular, the groups -X-Y can also be configured according to compounds 11, 12, 13, 14, and/or 16.

In particular, in the tripod ligand, Y is generally a donor-capable atom, which can be a heteroatom or a carbon atom. At least one, several, or all heteroatoms of the tripod ligand are preferably selected from the group N, P, S, Se, Ge, Sn, possibly also Si, without being limited to these. The donor atom can carry a charge, in particular a negative charge, for example a carbanionic carbon. The donor atom can also appear in a lower valence than its maximum valence, for example a carbene carbon atom, a germylene germanium atom, a silylene silicon atom, an Sn(II), or even a Pb(II) atom. Preferably, at least one donor atom of the ligand is a carbanionic carbon or an atom with a lower than maximum valence, in particular

C, Ge, Si, and this particularly preferably applies to all donor atoms of the ligand. Optionally, Y can also be part of a ring or ring system. Preferably, the donor atoms of the tripod ligand are the same, but they can also be different from each other.

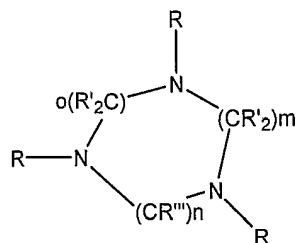
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Preferably, the ligand has at least one or two donor atoms binding to at least one central metal atom as carbanionic carbon atoms or, related to the ligand, a formally divalent or bivalent atom selected from the group C (carbene), Si (silylene), Ge (germylene), possibly also Sn or Pb, which are each part of an aromatic or non-aromatic, preferably unsaturated ring, wherein the multiple bond can be in conjugation with the free electrons of the donor atom. Preferably, the ring containing the donor atom has at least one or two additional heteroatoms, preferably selected from the group N, P, As, S, Se, or Te, in particular N, S, Se, which can be the same or different from each other.

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Triazacycloalkanes



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One, two, several, or all of the ligands of the metal complex according to the invention can be triazacycloalkanes, in particular those of the general formula 17, where m, n, o are integers, preferably independently integers from 0 to 6, preferably from 0 to 4, particularly preferably independently 1 or 2. m, n, and o can be the same or different from each other. Substituents R can be any residues, preferably alkyl residues, in particular lower alkyl residues with C1 to C6, or aryl residues, including hydrogen. The alkyl or aryl residues can be substituted or unsubstituted. The residues can be the same or different. All or several of the substituents R can have free electron pairs, whereby the ligand

formally receives one or more negative charges. The residues R' can be any substituents, preferably hydrogen, alkyl, or aryl, where the descriptions for the residue R apply accordingly. The various residues R' can be the same or different. It is understood that one or more of the N atoms of the triazacycloalkanes can also be replaced by an atom selected from the group P, As, Sb. Preferred in this case are triphosphacycloalkanes.

Furthermore, it is understood that if m, n, and/or o are integers of 2 or greater, the mentioned groups between the heteroatoms of the cyclic ligand can also be unsaturated, for example forming triaza(hetero)cycloalkenes, -dialkenes, -trialkenes, or the like. The alkyl or aryl residues of the substituents R and/or R' can each also contain heteroatoms.

Fullerenes

Preferred are complexes where at least one, two, or all of the ligands are Buckminster fullerenes that bind to the central atom of the complex. The Buckminster fullerenes can in particular be C₆₀ and/or C₇₀ fullerenes. Derivatives of these fullerenes, especially substituted fullerenes, are also included. The fullerenes here ultimately represent substituted cyclopentadienyl ligands, as they complex the central metal atom via the cyclopentadienyl ring.

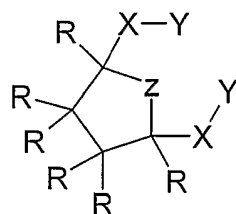
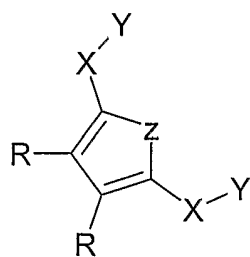
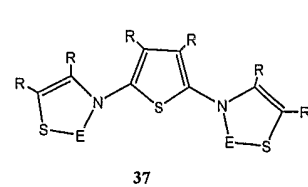
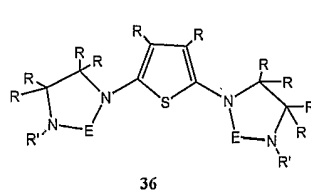
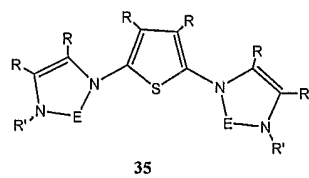
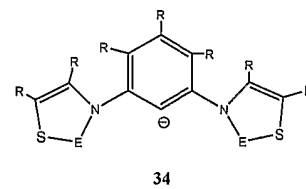
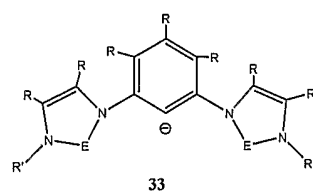
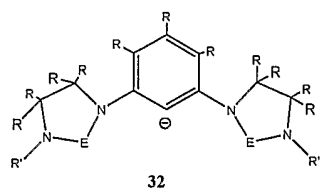
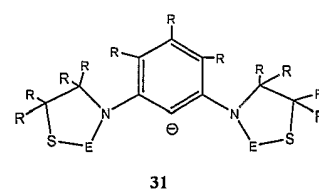
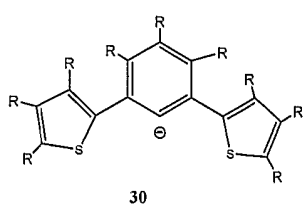
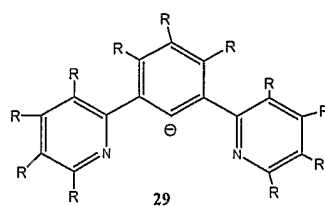
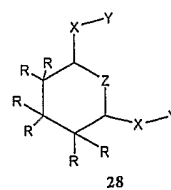
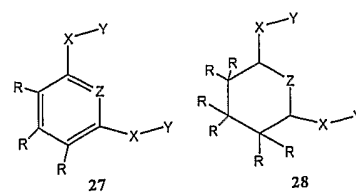
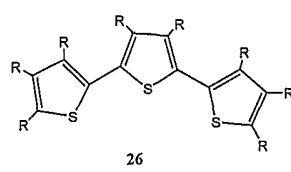
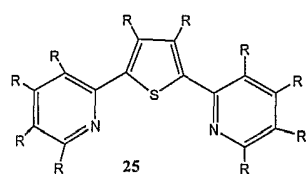
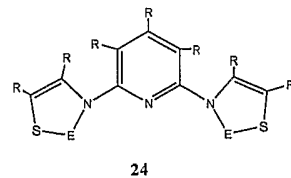
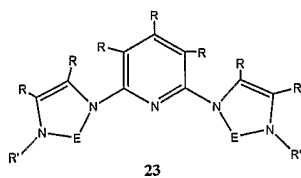
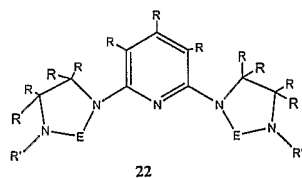
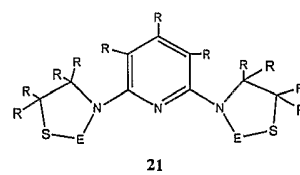
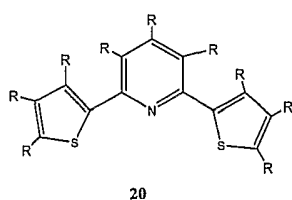
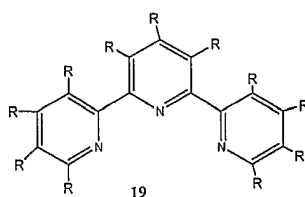
Pincer ligands

Also particularly preferred are so-called pincer ligands, which act as tridentate ligands towards the central metal atom of the complex. In particular, such pincer ligands can be bound meridionally to the central atom. The pincer ligands can in particular be 6-electron donors. The (formally uncomplexed) pincer ligands can be neutral or charged, preferably negatively charged.

Preferably, one, two, or all of the pincer ligands of the complex have one of the general structures 27, 27a, 28, or 28a according to the formulas below, for example, one, two, or all pincer ligands

of the complex have one of the structures 27 or 28, or 27a or 28a. In particular, all ligands of the complex can have one of the structures 27 or 27a or 28 or 28a. It is understood that the pincer ligands of a complex can be the same or different. The pincer ligands thus have a central ring with a heteroatom Z or C atom (carbanion), which binds to the central metal atom, as well as two other ligand atoms Y, which are connected to the ring containing the heteroatom Z via bridging atoms or bridging atom groups X. Optionally, one or more of the groups X in the ligand according to compounds 27, 27a, 28, or 28a may be absent. The groups X and/or Y within the ligand 27, 27a, 28, or 28a can each be the same or different. In particular, the ring bearing the central ligand atom of the pincer ligand can be a 5-membered or 6-membered ring, which may optionally contain one or more heteroatoms, one of which can be a donor atom. One or both of the X-Y groups can also be rings or parts of ring systems, in particular parts of 5- or 6-membered rings, which can each have additional heteroatoms besides the atom Y. The atom Y can also be a carbon atom. At least one, two, or three donor atoms Y, Y', and Z of the pincer ligand or one, two, three, or more of the donor atoms of the complex containing at least two pincer ligands can be different from nitrogen. The pincer ligand can have at least one or two or more rings each containing a ligand atom, with a number of ring atoms different from 6, in particular a 5-membered ring. This ring can be the ring containing the central ligand atom Z or form one of the X-Y groups. All donor atoms can be part of a 5-membered ring, which can be unsaturated or aromatic.

28



One, two, or more donor atoms of the ligand or all donor atoms of the complex can each be part of an aromatic ring or a conjugated, unsaturated system. This is in particular true for donor atoms S, C(II) (carbene), C(carbanion), Si(II), and/or Ge(II). In the case of low-valence donor atoms, such as divalent donor atoms like carbene, germylene, silylene, the donor atom can also be adjacent to one or two heteroatoms with a free electron pair such as N, P, As, Sb, S, Se, Te, which preferably stands in conjugation with empty or not fully occupied orbitals of the donor atom. This can apply to both the pincer ligands and the below en- or bidentate ligands.

In compounds 27, 27a, 28, 28a, Y is a donor-capable hetero- or carbon atom, preferably selected from the group N, P, O, S, Se, Te, C, Si, Ge, Sn, Pb, for example selected from the group C, N, P, O, S, Se, without being limited to these. The atom Y can be different from N. The two atoms Y can be the same or different. Y can be part of a ring or ring system. In particular, Y can be a carbon atom, such as a carbanion or carbene carbon atom, or a Ge atom, in particular a germylene (Ge(II)), or a Si atom, in particular a silylene (Si(II)), or a sulfur atom.

Z is a donor-capable heteroatom or carbon atom, preferably selected from the group C, N, P, O, S. If at least one of the atoms Y is an N atom, Z can be different from N. In particular, Z can be a carbon atom, such as a carbanion or carbene carbon atom, or a Ge atom, in particular a germylene (Ge(II)), or a Si atom, in particular a silylene (Si(II)), or a sulfur atom.

X represents a "spacer" and can be any at least bivalent atom or atomic group. In particular, X can be a branched or unbranched alkyl chain, in particular a lower alkyl chain with C1 to C6, preferably C1 to C4, or one or two atoms, where X can have no heteroatoms or one or more heteroatoms. The heteroatoms can be part of the bridge. X can be an aryl substituent, including a

condensed aryl substituent with or without heteroatoms, including an alkylaryl substituent with or without a heteroatom. X can also be a single heteroatom, such as O, S, N, P, or the like. R can be any substituent, preferably H, alkyl, in particular lower alkyl
5 with C1 to C6, or aryl. The alkyl or aryl residue can be substituted or unsubstituted and may contain one or more heteroatoms. The individual substituents R can be the same or different. Two substituents R can be part of a ring, which can be saturated, unsaturated, including aromatic, and preferably part of a ring
10 system condensed onto the main structure. The descriptions for R apply to R', where R' is in particular an atom or atomic group different from hydrogen. The substituents R' can be the same or different from each other.

E can be an atom selected from the group C, Si, Ge, Sn, Pb, preferably selected from the group C, Si, Ge, in particular C or Ge, for example, each in oxidation state (II). The donor atom E can form a carbene, germylene, or silylene ligand, preferably two donor atoms E each form a biscarbene, bisgermylene, or bissilylene
20 ligand or mixed ligands with these donor atoms. The ring of the pincer ligand containing an E atom preferably has, aside from E, at least one or two additional heteroatoms, which are preferably each part of a ring, preferably an unsaturated or aromatic ring. The additional heteroatom(s) preferably bind to the atom E,
25 possibly through an unsaturated system such as a double bond. Heteroatoms can in particular be N or S. The ring containing the donor atom E (in particular as carbene C(II), Ge(II), Si(II)) can have two additional N atoms, two S atoms, or one N and one S atom.

The complex with at least one, several, or exclusively pincer ligands preferably has at least one central atom selected from the group Cr, Mn, Fe, Co, Ni, Cu, Zn, preferably selected from the group Mn, Fe, Co, Ni, particularly preferably selected from the group Fe, Co, Ni, possibly including Mn. The at least one central
30 atom can be selected from the group Cr, Mo, W, and for example Mo or W, possibly also Cr. The central atom can also generally be an

atom of the 7th to 10th transition metal group; it can be different from Cr or Ru, without this being mandatory.

In particular, compounds 20 to 26 and 29 to 37 can have the
5 aforementioned central atoms, which can be different from Cr or Ru. However, compounds 20 to 26 and 29 to 37 can also have another central atom selected from the group of the first, second, or third transition metal period.

10 The ligand can be selected from the group of compounds 20 to 24, where one or more of the atoms S or N of the terminal five-membered rings can also each be replaced by Se, Te, or possibly O or P, As, or Sb. One or more of the double bonds of the five-membered rings of compounds 20 to 24 can also be saturated. E can each in
15 particular be carbene carbon C(II), Ge(II) (germylene), or Si(II) (silylene), possibly also O.

The pincer ligand can also be selected from the group of compounds 25 or 26, where the S atom of the central 5-membered ring or one
20 or both of the S atoms of the terminal 5-membered rings of compound 26 can be a Se or Te atom, possibly also O. One or more of the double bonds of the system can also be saturated. E can each in particular be carbene carbon C(II), Ge(II), or Si(II).

25 For example, the ligand can be selected from the group of compounds 29, 30, 31, where one or more of the atoms S can be replaced by Se or Te, possibly also O, and one or more of the atoms N can be replaced by P, As, or Sb. E can each in particular be carbene carbon C(II), Ge(II), or Si(II).

30

The pincer ligand can be selected from the group of compounds 32 to 34, where E can in particular be a bivalent C (carbene), Si (silylene), or Ge (germylene) atom. One or more of the atoms N can be replaced by P, As, or Sb. One or more of the atoms S can be
35 replaced by Se or Te, or possibly O.

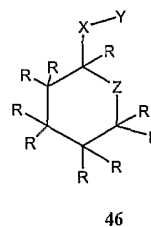
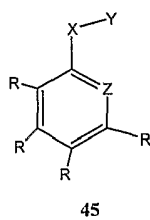
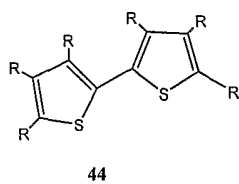
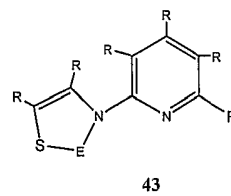
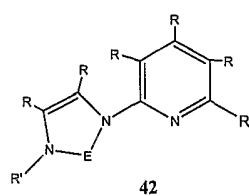
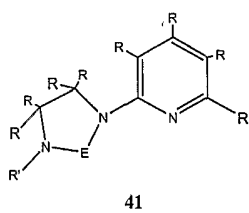
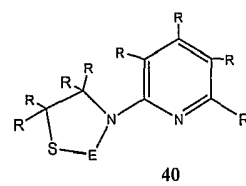
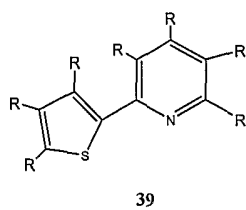
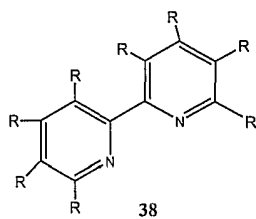
The pincer ligand can also be selected from the group of compounds 35, 36, or 37, where E is preferably a bivalent carbon atom (carbene), Si(II), or Ge(II). At least one of the atoms N can be replaced by P, As, or Sb. At least one of the atoms S can be replaced by Se or Te, or possibly O.

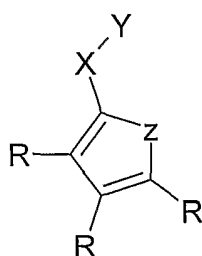
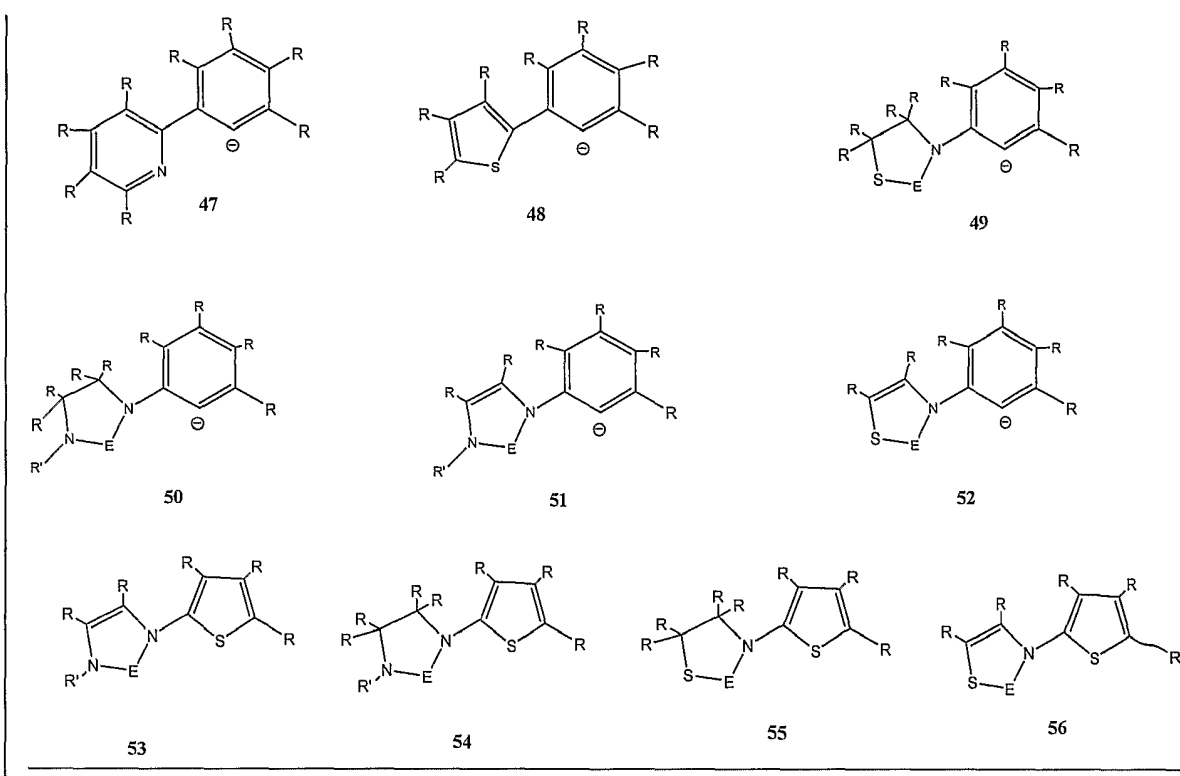
If the ligand from the group of compounds 19 to 26 and 29 to 37, in particular compounds 20 to 26 and 29 to 37, has a bivalent ligand atom E selected from the group C, Si, Ge, Sn, Pb, in particular selected from the group C, Si, Ge, then the central atom of the complex is preferably cobalt, in particular Co(II), or Ru, in particular Ru(0).

Furthermore, the ligand can be a bidentate ligand of the general structure 45, 45a, 46, 46a. The X-Y group can in particular form a heterocyclic ring with Y as a heterodonor atom, where the ring is preferably a 5- or 6-membered ring. Regarding the atoms or atom groups Z, X, and Y as well as the substituents R and R', the above descriptions for the pincer ligands apply.

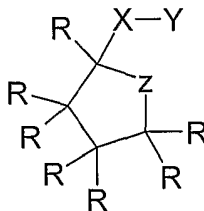
In particular, one, two, or all ligands of the complex can be selected from the group of compounds 45, 45a, 46, 46a, for example a compound 45 or 45a or 46 or 46a, where the above descriptions for the groups Z, X, Y apply to the pincer ligands.

In particular, one, two, or all of the ligands of the complex can be selected from the group of compounds 38 to 44 and 47 to 56, in particular from the group of compounds 39 to 44 and 47 to 56, where the above descriptions for the groups R and E apply to the pincer ligands. In particular, the ligand can also have a ring with a bivalent donor atom S, C, Si, Ge, Sn, Pb, in particular a donor atom C, Si, Ge, so that corresponding carbanions, carbenes, silylenes, or germylenes are present.





45a



46a

5 In particular, a ligand with one of the general structures 27, 27a, 28, 28a, 45, 45a, 46, 46a can have an atom Z with C⁻ (carbanion) or C(II) (carbene). In particular, one or both of the ligand atoms Y can then be an atom E selected from the group C, Si, Ge, Sn, Pb, in particular selected from the group C, Si, Ge, where E (within
10 the ligand) is bivalent.

In particular, the donor atom Y of one of compounds 27, 27a, 28, 28a, 45, 45a, 46, 46a can be the sulfur atom of a thiophene ring, which can optionally also be replaced by Se or Te, possibly also
15 by O.

Furthermore, the ligand can be selected from the group of compounds 40, 41, 42, 43, where N can each also be replaced by P, As, or Sb, and S can each be replaced by Se, Te, possibly also O.

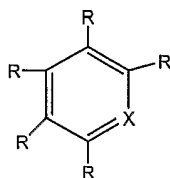
- 5 Furthermore, the ligand can be selected from the group of compounds 47, 48, 49, 50, 51, 52, in particular also from the group of compounds 49, 50, 51, 52, where S can each be replaced by Se or Te or possibly also O, and N can be replaced by P, As, Sb.
- 10 The ligand can also be selected from the group of compounds 53, 54, 55, and 56, where S can be replaced by Se, Te, or possibly O, and N can be replaced by P, As, or Sb, where E is preferably C(II) (carbene), Si(II) (silylene), or Ge(II) (germylene).
- 15 Furthermore, at least one, several, or all of the ligands can be selected from the group of compounds 57 to 64, in particular selected from the group of compounds 59 to 64, where the descriptions for E and R, R' apply to the pincer ligands. For X as a carbon or heterodonor atom, the descriptions for Y or Z regarding
- 20 the pincer ligands apply. In particular, compound 58 can be a, possibly substituted, cyclopentadienyl anion, thiophene, pyrrole, selenophene, phosphine, or furan. E is preferably a bivalent or divalent atom from the group C (carbene), Si (silylene), Ge (germylene), Sn, Pb, preferably selected from the group C, Si, Ge.
- 25 E can in particular also be C⁻ (carbanion). Optionally, one or more double bonds of compounds 57 to 64 can be saturated.

In compounds of type 27, 27a, and 28, 28a, and especially in compounds 19 to 26 and 29 to 37, in particular 20 to 26 and 29 to

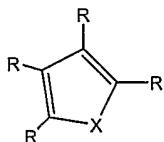
30 37, as well as in compounds 45, 45a, 46, 46a, especially in compounds 38 to 44 and 47 to 56, 39 to 44 and 47 to 56, as well as in compounds 57 to 64, in particular in compounds 59 to 64, preferably at least one, several, or all of the rings containing a donor atom have a hydrocarbon group with 1, 2, or 3 or more,

35 preferably 4 or more carbon atoms, preferably an unsubstituted alkyl group or also a substituted alkyl group. The number of C

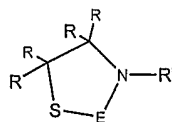
atoms in the group is preferably from 4 to 20 or 4 to 10, for example 4 to 6. Preferably, at least one, two, or each of the rings is substituted with at least one substituent that has a stronger +I effect and/or a +M effect compared to hydrogen or a methyl group. Preferably, at least one, two, or each donor atom is associated with a +M substituent that is in conjugation with it. Preferably, one, two or more, or each ring is substituted with at least one alkyl group or a group with an equal or stronger +I effect. It is understood that at least one, several, or all rings can also have +M substituents, for example, N-alkyl or N-dialkyl substituents (or P instead of N), where the above applies to alkyl.



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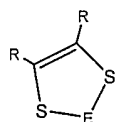
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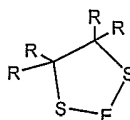
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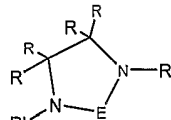
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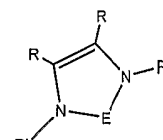
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64

It is understood that if at least one or all central atoms have several substituents, two or all substituents can belong to the same substituent type or be the same.

Ionization potential/oxidation potential

Preferably, the metal complex according to the invention has an ionization potential in the gas phase of ≤ 6.4 eV, preferably ≤ 6 eV, in particular ≤ 5.5 eV. In particular, the ionization potential of the complex in the gas phase can be ≤ 5.0 eV or ≤ 4.5 eV.

The gas phase ionization potential I_{pg} of the compounds usable according to the invention can, for example, be determined relative

to tetrathiafulvalene (TTF), which is: $I_{pg} = 6.4$ eV (see R. Gleiter, E. Schmidt, D. O. Cowan, J. P. Ferraris, J. Electr. Spec. Rel. Phenom. 2, 207 (1973)).

- 5 The oxidation potential of TTF is $E_{1/2(ox)} = -0.09$ V relative to Fe/Fe⁺ (ferrocene/ferrocenium) (M. Iyoda, T. Takano, N. Otani, K. Ugawa, M. Yoshida, H. Matsuyama, Y. Kuwatani, Chem. Lett., 1310 (2001)). Based on this reference point, the redox potential of the n-dopants according to the invention can be ≤ -0.09 V relative to
10 ferrocene/ferrocenium, preferably ≤ -0.6 V, particularly preferably ≤ -1.1 V, for example ≤ -1.6 V or ≤ 2.1 V, without being limited to this.

The oxidation potential relative to ferrocene/ferrocenium can, for
15 example, be determined by cyclic voltammetry. The potential is largely independent of the chosen electrolyte system and can be determined according to IUPAC recommendations (Gritzner, G.; Kuta, J. Pure Appl. Chem. 1984, 56, 461-466). The electrolyte system must have a sufficiently large electrochemical window and
20 sufficient solubility of the donor compound. Suitable electrolyte systems include acetonitrile/1M LiClO₄/Pt electrodes, although other suitable electrolyte systems can also be used.

Vapor pressure

- 25 The vapor pressure of the complex used according to the invention can be in particular $< 10^{-3}$ Pa at 30°C, for example $\leq 5 \times 10^{-4}$ Pa or $\leq 1 \times 10^{-4}$ Pa.

The n-dopants and/or complexes used according to the invention can
30 each be air-stable; if appropriate, they can also each be air-unstable.

Synthesis of the n-dopant complexes and their ligands

35 General

The synthesis of the n-dopant metal complexes according to the

invention can, for example, be carried out by direct synthesis of the compounds or by reduction of salts, where the resulting neutral metal complex is present as a cation in the salt. The anion can be any suitable anion, such as halogen, perchlorate, sulfate, or the like. The reduction can be carried out, for example, electrochemically or chemically, without being limited to this. The reduction can be carried out, for example, by electrocrystallization, where the product obtained can be harvested at the working electrode and subsequently purified. However, the production of the complexes according to the invention can also be carried out without using such an electrocrystallization step.

Synthesis procedures

The complexes according to the invention can be synthesized by known methods, and some are also commercially available. The synthesis of the ligands of the complexes according to the invention and the complexes themselves are described, for example, in the following literature references, which are hereby fully incorporated by reference into the application. It is understood that the mentioned literature references are only given as examples and the ligands and complexes can usually also be synthesized by other suitable methods.

Paddlewheel complexes

The paddlewheel complexes can be prepared either by ligand substitution from other paddlewheel complexes (F. A. Cotton, J. G. Norman Jr., J. Coord. Chem. 1 (1970) 161-72; F. A. Cotton, D. J. Timmons, Polyhedron 17 (1998) 179-84), by salt metathesis from the metal halide and an anionic ligand (F. A. Cotton, D. J. Timmons, Polyhedron 17 (1998) 179-84), by reduction of a cationic paddlewheel complex (F. A. Cotton, P. Huang, C. A. Murillo, X. Wang, Inorg. Chem. Commun. 6 (2003) 121-6), or in a redox reaction from a metal compound and the ligand (T. A. Stephenson, E. Bannister, G. Wilkinson, J. Chem. Soc. (1964) 2538-41).

Furthermore, a new method has been developed to efficiently produce

paddlewheel complexes of type 65a-d in a one-step synthesis. For this, a corresponding inorganic metal salt is heated to reflux with free bases of the ligands indicated in 65a-d and a suitable strong reducing agent in a suitable organic solvent until the reaction is complete. Suitable solvents are preferably those in which the formed complexes exhibit sufficient stability, preferably dialkyl ethers, cyclic ethers, cyclic and acyclic polyethers such as 1,4-dioxane, dimethoxyethane, etc., aromatics, and mixtures thereof.

Suitable reducing agents are, for example, base metals, preferably alkali metals such as sodium, potassium, and cesium.

The complexes are isolated by separating the inorganic by-products through crystallization, precipitation, or sublimation.

The novel one-step synthesis offers a time- and resource-saving approach to complexes of the type W_2L_4 .

The following are examples:

Synthesis of ligands and their precursors

Example 1:

1. Imidazo[1,2-a]pyrimidine hydroperchlorate

The preparation was carried out according to a method described in the literature (M. Künstlinger, E. Breitmaier, Synthesis 1983 (2), 161-162). Deviating from this, the product was isolated as imidazo[1,2-a]pyrimidine hydroperchlorate by adding perchloric acid.

Mp. 195°C

^1H -NMR (500 MHz, CD_3CN) [ppm]:

8.99-8.96 (m, 2H); 7.98 (d, 1H); 7.93 (d, 1H); 7.58 (dd, 1H)

MS: m/z = 119 $[\text{M}]^+$

2. 5,6,7,8-Tetrahydro-imidazo[1,2-a]pyrimidine

4.2 g of imidazo[1,2-a]pyrimidine hydroperchlorate were heated in acetic acid solution with palladium on activated charcoal for 8 hours under a hydrogen atmosphere. Subsequent filtration, removal of the solvent, and addition of diethyl ether yielded 5,6,7,8-tetrahydro-imidazo[1,2-a]pyrimidine hydroacetate as colorless crystals, which were recrystallized from ethanol.

Yield: 3.21 g

Mp. 65°C

¹H-NMR (500 MHz, DMSO-d₆) [ppm]:

6.97 (d, 1H); 6.91 (d, 1H); 3.90 (t, 2H); 3.25 (t, 2H); 1.98 (quint., 2H)

The release of 5,6,7,8-tetrahydro-imidazo[1,2-a]pyrimidine was achieved in alkaline ethanol solution.

Yield: 3.08 g

Mp. 110°C

¹H-NMR (500 MHz, DMSO-d₆) [ppm]:

6.51 (d, 1H); 6.36 (d, 1H); 6.09 (s, 1H); 3.80 (t, 2H); 3.16 (t, 2H); 1.90 (quint., 2H)

MS: m/z = 123 [M]⁺

Example 2:

1. 2-Amino-4,6-dimethyl-1,4,5,6-tetrahydropyrimidine

1 g of 2-amino-4,6-dimethylpyrimidine was heated in hydrochloric acid solution (2 M HCl) with palladium on activated charcoal as a catalyst for 14 hours under a hydrogen atmosphere. Subsequent filtration, removal of the solvent, and addition of diethyl ether yielded 2-amino-4,6-dimethyl-1,4,5,6-tetrahydropyrimidine

hydrochloride, which was recrystallized from i-propanol/diethyl ether and dried in vacuum.

Yield: 1.03 g

5 Mp. 129°C

¹H-NMR (500 MHz, DMSO-d₆) [ppm]:

8.14 (s, 2H); 6.81 (s, 2H); 3.48 (m, 2H); 1.98 (d, 1H); 1.14 (d, 6H); 1.10 (d, 1H)

10 The release of 2-amino-4,6-dimethyl-1,4,5,6-tetrahydropyrimidine was achieved in alkaline ethanol solution.

¹H-NMR (500 MHz, DMSO-d₆) [ppm]:

3.46 (m, 2H); 1.98 (m, 1H); 1.13 (d, 6H); 1.10 (d, 1H)

15

2. 2,4-Dimethyl-3,4-dihydro-2*H*-pyrimido[1,2-*a*]pyrimidine hydroperchlorate

20 0.66 g of 2-amino-4,6-dimethyl-1,4,5,6-tetrahydropyrimidine was heated to reflux in methanolic solution with the addition of perchloric acid and an equimolar amount of 1,1,3,3-tetramethoxypropane. Removal of the solvent and overlaying the residue with diethyl ether yielded 2,4-dimethyl-3,4-dihydro-2*H*-
25 pyrimido[1,2-*a*]pyrimidine hydroperchlorate, which was filtered and dried in vacuum.

Yield: 0.46 g

¹H-NMR (500 MHz, DMSO-d₆) [ppm]:

30 9.86 (s, 1H); 8.75 (dd, 1H); 8.55 (dd, 1H); 6.99 (dd, 1H); 4.43 (m, 1H); 3.76 (m, 1H); 2.29 (m, 1H); 1.69 (quar., 1H); 1.57 (d, 3H); 1.27 (d, 3H)

35 3. 2,4-Dimethyl-1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine

0.5 g of 2,4-dimethyl-3,4-dihydro-2H-pyrimido[1,2-a]pyrimidine hydroperchlorate was heated in acetic acid solution with palladium on activated charcoal for 8 hours under a hydrogen atmosphere. Subsequent filtration, removal of the solvent, and addition of diethyl ether yielded 2,4-dimethyl-1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidine hydroacetate as colorless crystals, which were recrystallized from ethanol.

Yield: 0.37 g

10 Mp. 101°C

¹H-NMR (500 MHz, DMSO-d₆) [ppm]:

7.47 (s, 1H); 7.09 (s, 1H); 3.50-3.55 (m, 1H); 3.43-3.39 (m, 1H); 3.35-3.21 (m, 3H); 3.05-3.03 (m, 1H); 2.11 (m, 1H); 1.95-1.91 (m, 1H); 1.78-1.71 (m, 1H); 1.37-1.30 (quar., 1H); 1.24 (d, 3H); 1.14 (d, 3H)

The release of 2,4-dimethyl-1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidine was achieved in alkaline ethanol solution.

20

Yield: 0.1 g

Mp. 133°C

¹H-NMR (500 MHz, DMSO-d₆) [ppm]:

3.24-3.16 (m, 3H); 3.16-3.14 (m, 1H); 3.09-2.93 (m, 1H); 2.86-2.83 (m, 1H); 1.89-1.85 (m, 1H); 1.77-1.73 (m, 1H); 1.65-1.58 (m, 1H); 1.17-1.10 (m, 4H); 0.97 (d, 3H)

MS: m/z = 167 [M]⁺

30

Example 3:

1. Benzimidazo[1,2-a]pyrimidine hydroperchlorate

The preparation was carried out according to a method described in the literature (M. Künstlinger, E. Breitmaier, Synthesis 1983 (2), 161-162). Deviating from this, the product was isolated as benzimidazo[1,2-a]pyrimidine hydroperchlorate by adding perchloric

35

acid.

Mp. 245°C

¹H-NMR (500 MHz, DMSO-d₆) [ppm]:

5 9.98 (dd, 1H); 9.26 (dd, 1H); 8.60 (d, 1H); 7.95 (d, 1H); 7.86-7.81 (m, 2H); 7.73 (t, 1H)

2. 1,2,3,4-Tetrahydro-benzimidazo[1,2-a]pyrimidine

10 0.602 g of benzimidazo[1,2-a]pyrimidine hydroperchlorate was heated in hydrochloric acid solution (2 M HCl) with palladium on activated charcoal for 9 hours under a hydrogen atmosphere. Subsequent filtration, removal of the solvent, and addition of diethyl ether yielded 1,2,3,4-tetrahydro-benzimidazo[1,2-
15 a]pyrimidine hydrochloride as colorless crystals, which were recrystallized from ethanol.

Yield: 0.18 g

Mp. 212°C

20 ¹H-NMR (500 MHz, DMSO-d₆) [ppm]:

12.62 (s, 1H); 9.18 (s, 1H); 7.47 (m, 1H); 7.38 (m, 1H); 7.27 (m, 1H); 4.08 (t, 2H); 3.48 (m, 2H); 2.14 (quint., 2H)

MS: m/z = 174 [M]⁺

25 The release of 1,2,3,4-tetrahydro-benzimidazo[1,2-a]pyrimidine was achieved in alkaline ethanol solution.

Mp. 190°C

¹H-NMR (500 MHz, DMSO-d₆) [ppm]:

30 7.13-7.07 (m, 3H); 6.92 (m, 1H); 6.85 (m, 1H); 3.96 (t, 2H); 3.31 (t, 2H); 2.03 (quint., 2H)

MS: m/z = 173 [M]⁺

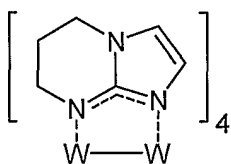
35 General synthesis of complexes of type M₂L₄

MCl₄ (WCl₄, 1.00 g, 3.07 mmol), at least 2 equivalents of the

respective ligand (9.21 mmol), and potassium in excess (approximately 1 g) are heated to reflux in 50 mL THF. The mixture is then allowed to cool, and the mother liquor is filtered off. The filtrate is evaporated to dryness and extracted with toluene.
 5 The product is precipitated as a brown solid with hexane, isolated by filtration, and dried in high vacuum. Yields are around 30%.

Example 4:

10 Tetrakis[tetrahydro-imidazo[1,2-a]pyrimidinato]diwolfram(II)



Synthesis as described above with 1.13 g of the ligand 5,6,7,8-tetrahydro-imidazo[1,2-a]pyrimidine.

¹H-NMR (500 MHz, C₆D₆) [ppm]:

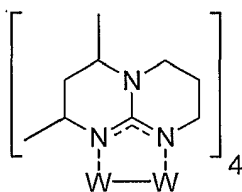
15

6.7-6.2 (br, 2H); 3.8-3.3 (br, 4H); 1.9-1.3 (br, 2H).

Example 5:

20

Tetrakis[dimethyl-1,3,4,6,7,8-hexahydro-2H-pyrimido-1,2-a]pyrimidinato]diwolfram(II)



Synthesis as described above with 1.54 g of the ligand 2,4-dimethyl-1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidine.
 25

¹H-NMR (500 MHz, C₆D₆) [ppm] :

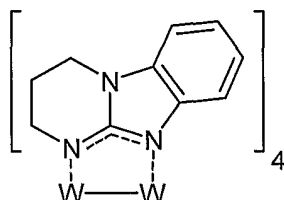
3.5-2.6 (br, 4H); 2.0-1.3 (br, 4H); 1.3-0.9 (br, 6H).

ESI-MS: m/z = 184 [M⁺ + 3 OH].

30

Example 6:

Tetrakis[tetrahydro-
benzo[4,5]imidazo[1,2-a]pyrimidinato]diwolfram(II)



Synthesis as described above with 1.54 g of the ligand 1,2,3,4-tetrahydro-benzimidazo[1,2-a]pyrimidine.

Deviating from the general synthesis procedure, this product is precipitated from the mother liquor with hexane. The isolated solid is insoluble in toluene.

¹H-NMR (500 MHz, THF-d₈) [ppm]:

6.60 (m, br, 1H); 6.55 (m, br, 1H); 6.40 (m, br, 1H); 6.34 (m, br, 1H); 3.72 (br, 2H); 3.42 (br, 2H); 1.77 (br, 2H).

Carbenes

For the synthesis of N-heterocyclic carbenes (NHC), several standard procedures are known in the literature: the imidazole method, the thioketone method, and the silver oxide method (metal transfer method). See, for example: W. A. Herrmann, Angew. Chem., Int. Ed. Engl. 41 (2002) 1290-1309; W. A. Herrmann, C. Kocher, Angew. Chem., Int. Ed. Engl. 36 (1997) 2162-87; A. H. Cowley, J. Organomet. Chem. 617-8 (2001) 105-9; T. Westkamp, V. P. W. Böhm, W. A. Herrmann, J. Organomet. Chem. 600 (2000) 12-22.

The thioketone method is essentially based on the principle also applied for silylenes and germylenes. However, instead of GeCl₂ or SiCl₄, thiophosgene is used and then reduced with potassium, sodium amalgam, or KC₈ (N. Kuhn, T. Kratz, Synthesis (1993) 561; F. E. Hahn, L. Wittenbecher, R. Boese, D. Bläser, Chem. Eur. J. 5 (1999) 1931-5). In the imidazole method, the N-substituted imidazole core

is first synthesized. The second nitrogen atom is then usually quaternized with an alkyl halide, and in the final step, the imidazolium salt is converted to the carbene with a suitable base (KOBut, Cs₂CO₃, BuLi, etc.) (see, for example: A. J. Arduengo III, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 113 (1991) 361-3; M. R. Grimmet, Adv. Heterocyclic Chemistry 12 (1970) 105 and 134).

The silver oxide method is a variant of the imidazole method, where silver oxide is used as the base. This results in a silver complex of the carbene, which can transfer the carbene to another metal (metal transfer) (Q.-X. Liu, F.-B. Xu, Q.-S. Li, X.-S. Zeng, X.-B. Leng, Y. L. Chou, Z.-Z. Zhang, Organometallics 22 (2003) 309-14; T. Ramnial, C. D. Abernethy, M. D. Spicer, I. D. McKenzie, I. D. Gay, J. A. C. Clyburne, Inorg. Chem. 42 (2003) 1391-3).

Silylenes

The synthesis of N-heterocyclic silylenes is carried out analogously to the corresponding germylenes. However, silicon(IV) chloride is used, which must then be reduced (see, for example: M. Denk, R. Lennon, R. Hayshi, R. West, A. V. Belyakov, H. P. Verne, A. Haaland, M. Wagner, N. Metzler, J. Am. Chem. Soc. 116 (1994) 2691-2; B. Gehrhus, M. F. Lappert, J. Organomet. Chem. 617-8 (2001) 209-23).

Germylenes

Heterocyclic germylenes (N, S) can usually be prepared by metallation of the corresponding diimines, diamines, aminothiols, or dithiols and subsequent reaction with germanium(II) chloride according to known methods (J. Pfeiffer, M. Noltemeyer, A. Meller, Z. Anorg. Allg. Chem. 572 (1989) 145-50; A. Meller, C.-P. Gräbe, Chem. Ber. 118 (1985) 2020-9; J. Pfeiffer, W. Maringgele, M. Noltemeyer, A. Meller, Chem. Ber. 122 (1989) 245-52; O. Köhl, P. Lönnecke, J. Heinicke, Polyhedron 20 (2001) 2215-22).

The synthesis of metal complexes is described, for example, in: O. Köhl, P. Lönnecke, J. Heinicke, Inorg. Chem. 42 (2003) 2836-8; W.

A. Herrmann, M. Denk, J. Behm, W. Scherer, F.-R. Klingan, H. Bock, B. Solouki, M. Wagner, *Angew. Chem., Int. Ed. Engl.* 31 (1992) 1485.

Pi-perimeter

5 There are many compounds of pi-perimeter ligands and their metal complexes, leading to a variety of synthesis routes. Examples include:

Cyclopentadienyl: C. Janiak, H. Schumann, *Adv. Organomet. Chem.* 33
10 (1991) 331; J. Okuda, *Top. Curr. Chem.* 160 (1991) 99; N. J. Coville, K. E. du Plooy, W. Pickl, *Coord. Chem. Rev.* 116 (1992) 1; R. L. Halterman, *Chem. Rev.* 92 (1992) 965; M. L. Hays, T. P. Hanusa, *Adv. Organomet. Chem.* 40 (1996) 117; S. Brydges, L. E. Harrington, M. J. McGlinchey, *Coord. Chem. Rev.* 233-4 (2002) 75; T. Cuenca, P.
15 Royo, *Coord. Chem. Rev.* 193-5 (1999) 447-98.

Arene: A. S. Abd-El-Aziz, *Coord. Chem. Rev.* 233-4 (2002) 177; A. S. Abd-El-Aziz, *Coord. Chem. Rev.* 203 (2000) 219; R. D. Pike, D. A. Sweigart, *Coord. Chem. Rev.* 187 (1999) 183.

20

Cycloheptatrienyl: M. L. H. Green, D. P. K. Ng, *Chem. Rev.* 95 (1995) 439; M. Tamm, B. Dreßel, R. Fröhlich, *J. Org. Chem.* 65 (2000) 6795; M. Tamm, T. Bannenberg, R. Dreßel, R. Fröhlich, D. Kunz, *Organometallics* 20 (2001) 900; M. Tamm, T. Bannenberg, R.
25 Fröhlich, S. Grimme, M. Gerenkamp, *Dalton Trans.* (2004) 482-91; M. Tamm, B. Dreßel, T. Lügger, R. Fröhlich, S. Grimme, *Eur. J. Inorg. Chem.* (2003) 1088.

Cyclooctatetraendiyl: F. T. Edelmann, D. M. M. Freckmann, H. Schumann, *Chem. Rev.* 102 (2002) 1851; P. W. Roesky, *Eur. J. Inorg. Chem.* (2001) 1653.

ArenFeCp: The synthesis is either from ferrocene by arene substitution and subsequent reduction or by reaction of
35 Cp^RFe(CO)₂Br with the arene and subsequent reduction: J.-R. Hamon, D. Astruc, P. Michaud, *J. Am. Chem. Soc.* 103 (1981) 758-66.

Correspondingly, other arene-transition-metal-metal Cp complexes can be synthesized, for example, with metal atoms such as Mn, Co, Ni, Cu, Zn, or even Cr, Mo, W.

5 Borates

In particular, borates according to compounds 11 to 14 and 16 can be synthesized through the following methods, although other suitable synthesis routes may also be possible. It is understood that other tripod ligands can also be obtained through similar
10 synthesis routes:

Construction of pyrazole:

The synthesis is generally carried out by reacting a β -diketone with hydrazine: M. B. Smith, J. March, March's Advanced Organic
15 Chemistry, Wiley, New York, 5th edition, 1193.

Construction of the Chelate ligand:

According to one variant, the synthesis can be carried out by reacting pyrazole with KBH_4 , as described by S. Trofimenko, J. Am.
20 Chem. Soc. 89 (1967) 3170

Alternatively, a multi-step synthesis involving the reaction of trimethyl borate and a Grignard reagent to form isoboronic acid, followed by reaction with pyrazole and pyrazolate, can yield the
25 chelate ligand: F. R. Bean, J. R. Johnson, J. Am. Chem. Soc. 54 (1932) 4415; E. Khotinsky, M. Melamed, Chem. Ber. 42 (1909) 3090; H. R. Snyder, J. A. Kuck, J. R. Johnson, J. Am Chem. Soc. 60 (1938) 105; D. L. Reger, M. E. Tarquini, Inorg. Chem. 21 (1982) 840..

30 The construction of the metal complex used in this invention is described, for example, in: S. Trofimenko, J. Am. Chem. Soc. 88 (1966) 1842; C. A. Kilner, E. J. L. McInnes, M. A. Leech, G. S. Beddard, J. A. K. Howard, F. E. Mabbs, D. Collison, A. J. Bridgeman, M. A. Halcrow, Dalton Trans. (2004) 236-43; S. Trofimenko:
35 Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands, Imperial College Press, London 1999; S. Trofimenko, Chem.

Rev. 93 (1993) 943; S. Trofimenko, Chem. Rev. 72 (1972) 497; S. Trofimenko, J. Am. Chem. Soc. 89 (1967) 3170; S. Trofimenko, J. Am. Chem. Soc. 89 (1967) 6288; A. Paulo, J. D. G. Correia, M. P. C. Campello, I. Santos, Polyhedron 23 (2004) 331-60; S. Trofimenko, Polyhedron 23 (2004) 197-203.

Corresponding ligands with a carbon bridging atom instead of boron are available according to C. Pettinari, A. Cingolani, G. G. Lobbia, F. Marchetti, D. Martini, M. Pellei, R. Pettinari, C. Santini, Polyhedron 23 (2004) 451-69.

Ligands and complexes based on 2-imidazolidinethione can be obtained according to J. K. Voo, C. D. Incarvito, G. P. A. Yap, A. L. Rheingold, C. G. Riordan, Polyhedron 23 (2004) 405-12; H. M. Alvarez, J. M. Tanski, D. Rabinovich, Polyhedron 23 (2004) 395-403; C. A. Dodds, M. Jagoda, J. Reglinski, M. D. Spicer, Polyhedron 23 (2004) 445-50.

Carboranes

The construction of the carborane system generally requires special conditions. Some representatives are commercially available.

Corresponding syntheses are described, for example, by R. A. Wiersboeck, M. F. Hawthorne, J. Am. Chem. Soc. 86 (1964) 1642-3; J. A. Dupont, M. F. Hawthorne, J. Am. Chem. Soc. 86 (1964) 1643; L. J. Todd, A. R. Burke, A. R. Garber, H. T. Silverstein, B. N. Storhoff, Inorg. Chem. 9 (1970) 2175-9.

The synthesis of the corresponding metal complexes was described by J. Bould, John D. Kennedy, G. Ferguson, F. T. Deeney, G. M. O'Riordan, T. R. Spalding, Dalton Trans. (2003) 4557-64.

Triazacycloalkanes

The substituents on the nitrogen atom can be introduced by alkylation or arylation of the trisammonium bromide of the parent compound. This is followed by a reaction with metal precursors.

See, for example: R. Zhou, C. Wang, Y. Hu, T. C. Flood, Organometallics 16 (1997) 434; L. Wang, C. Wang, R. Bau, T. C. Flood, Organometallics 15 (1996) 491; L. Wang, J. R. Sowa Jr., C. Wang, R. S. Lu, P. G. Gasman, T. C. Flood, Organometallics 15 (1996) 4240; S. M. Yang, M. C. W. Chan, K. K. Cheung, C. M. Che, S. M. Peng, Organometallics 16 (1997) 2819; S. M. Yang, W. C. Cheng, S. M. Peng, K. K. Cheung, C. M. Che, Dalton Trans (1995) 2955; A. L. Gott, P. C. McGowan, T. J. Podesta, C. W. Tate, Inorg. Chim. Acta 357 (2004) 689-98.

Tripod ligands

The class of tripod ligands also exhibits great diversity. Some synthesis routes for compounds used in this invention were described by:

Ligands based on carbenes, in particular with a carbene donor atom: H. Nakai, Y. Tang, P. Gantzel, K. Meyer, Chem. Comm. (2003) 24-5; X. Hu, I. Castro-Rodriguez, K. Meyer, J. Am. Chem. Soc. 125 (2003) 12237-45; U. Kernbach, M. Ramm, P. Luger, W. P. Fehlhammer, Angew. Chem., Int. Ed. Engl. 35 (1996) 310-2;

Ligands based on nitrogen, in particular with an N donor atom: T. R  ther, N. Braussaud, K. J. Cavell, Organometallics 20 (2001) 1247-50; L. Peters, N. Burzlaff, Polyhedron 23 (2004) 245-51; V. V. Karambelkar, R. C. diTargiani, C. D. Incarvito, L. N. Zakharov, A. L. Rheingold, C. L. Stern, D. P. Goldberg, Polyhedron 23 (2004) 471-80; D. L. Reger, J. R. Gardiner, M. D. Smith, Polyhedron 23 (2004) 291-9; M. Scarpellini, J. C. Toledo Jr., A. Neves, J. Ellena, E. E. Castellano, D. W. Franco, Inorg. Chim Acta 357 (2004) 707-15;

Ligands based on phosphorus, in particular with a P donor atom: H. A. Mayer, W. C. Kaska, Chem. Rev. 94 (1994) 1239; B. C. Janssen, A. Asam, G. Huttner, V. Sernau, L. Zsolnai, Chem. Ber. 127 (1994) 501; H. Heidel, J. Scherer, A. Asam, G. Huttner, O. Walter, L. Zsolnai, Chem. Ber. 128 (1995) 293; S. Beyreuther, J. Hunger, G.

Huttner, S. Mann, L. Zsolnai, Chem. Ber. 129 (1996) 745; J. C. Thomas, J. C. Peters, Polyhedron 23 (2004) 489-97.

Ligands based on sulfur, in particular with an S donor atom: H. M. Alvarez, J. M. Tanski, D. Rabinovich, Polyhedron 23 (2004) 395-403.

The preparation of metal-triphos ligands suitable for use in this invention was described by: O. Köhl, S. Blaurock, J. Sieler, E. Hey-Hawkins, Polyhedron 20 (2001) 2171-7; G. S. Ferguson, P. T. Wolczanski, L. Parkanyi, M. C. Zonneville, Organometallics 7 (1988) 1967; S. M. Baxter, G. S. Ferguson, P. T. Wolczanski, J. Am. Chem. Soc. 110 (1988) 4231.

Fullerenes

In general, the approach is similar to that used with cyclopentadienyl ligands, but not limited to it. The metallated species can be reacted with a metal precursor. See, for example: L.A. Rivera-Rivera, G. Crespo-Roman, D. Acevedo-Acevedo, Y. Ocasio-Delgado, J. E. Cortes-Figueroa, Inorg. Chim. Acta 357 (2004) 881-7.

Pincer ligands

For the synthesis of pincer ligands that can be used in metal complexes according to the invention, see, for example: A. M. Magill, D. S. McGuinness, K. J. Cavell, G. J. P. Britovsek, V. C. Gibson, A. J. P. White, D. J. Williams, A. H. White, B. W. Skelton, J. Organomet. Chem. 617-8 (2001) 546-60.

Pincer ligands based on carbenes: The synthesis of the ligand system can be achieved through high-temperature synthesis from 2,6-dibromopyridine and N-substituted imidazole: R. S. Simons, P. Custer, C. A. Tessier, W. J. Youngs, Organometallics 22 (2003) 1979-82; J. A. Loch, M. Albrecht, E. Peris, J. Mata, J. W. Faller, R. H. Crabtree, Organometallics 21 (2002) 700; M. Poyatos, J. A. Mata, E. Falomir, R. H. Crabtree, E. Peris, Organometallics 22

(2003) 1110-4; A. A. D. Tulloch, A. A. Danopoulos, S. Winston, S. Kleinhenz, G. Eastham, Dalton Trans (2000) 4499; A. A. Danopoulos, A. A. D. Tulloch, S. Winston, G. Eastham, M. B. Hursthouse, Dalton Trans (2003) 1009-15.

5

Pincer ligands based on phosphorus, in particular with a P donor atom, can be synthesized from an alpha,alpha'-xylyl or lutidine dihalide by salt metathesis with a secondary phosphane, as described in W. V. Dahlhoff, S. M. Nelson, J. Chem. Soc (A) (1971) 2184; L. Barloy, S. Y. Ku, J. A. Osborn, A. DeCian, J. Fisher, Polyhedron 16 (1997) 291; B. D. Steffey, A. Miedamer, M. L. Maciejewski-Farmer, P. R. Bernatis, A. M. Herring, V. S. Allured, V. Caperos, D. L. DuBois, Organometallics 13 (1994) 4844; C. Hahn, A. Vitagliano, F. Giordano, R. Taube, Organometallics 17 (1998) 2060; G. Vasapollo, C. F. Nobile, A. Sacco, J. Organomet. Chem. 296 (1985) 435-41; G. Jin, H. M. Lee, I. D. William, J. Organomet. Chem. 534 (1997) 173; G. Jin, H. M. Lee, H. P. Xin, I. D. William, Organometallics 15 (1996) 5453; T. Karlen, P. Dani, D. M. Grove, P. Steenwinkel, G. Van Koten, Organometallics 15 (1996) 5687;

Bidentate ligands

Biscarenes with carbene donor atoms, suitable for the invention, can be provided as described by M. Poyatos, M. Sanau, E. Paris, Inorg. Chem. 42 (2003) 2572-6. The synthesis follows the previously mentioned literature references.

Monodentate ligands

The synthesis can follow the previously mentioned literature references. Such ligands are also partially commercially available.

Matrix materials

The present invention describes suitable n-dopants for organic semiconducting materials such as electron transport materials commonly used in electronic devices, including optoelectronic

devices such as OLEDs, field-effect transistors, or organic solar cells. The semiconducting materials are preferably intrinsically electron-conductive.

5 The matrix material can consist partially (> 10 or > 25 wt%) or essentially (> 50 wt% or > 75 wt%) or entirely of a metal phthalocyanine complex, a Buckminster fullerene, possibly also a porphyrin complex, in particular a metal porphyrin complex, an oligothiophene, oligophenyl, oligophenylene vinylene, or
10 oligofluorene compound, with the oligomers preferably comprising 2-500 or more, preferably 2-100 or 2-50 or 2-10 monomeric units. The oligomer can also comprise > 4, > 6, or > 10 or more monomeric units, in particular for the ranges indicated above, such as 4 or 6-10 monomeric units, 6 or 10-100 monomeric units, or 10-500
15 monomeric units. The monomers or oligomers can be substituted or unsubstituted, and block or mixed polymers of the mentioned oligomers can also be present. The matrix can also be a mixture of oligomers with different chain lengths, as is typical for conventional polymer layers.

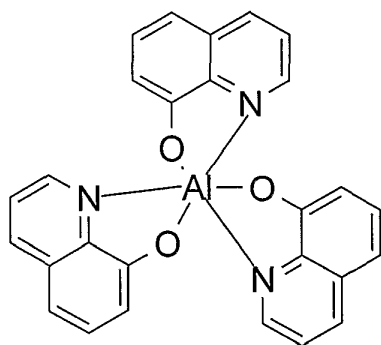
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The matrix material can also be a compound with a triarylamine unit or a spirobifluorene compound. The mentioned matrix materials can also be present in combination with each other, possibly also in combination with other matrix materials. The matrix materials
25 can have electron-donating substituents such as alkyl or alkoxy groups that have reduced ionization energy or reduce the ionization energy of the matrix material.

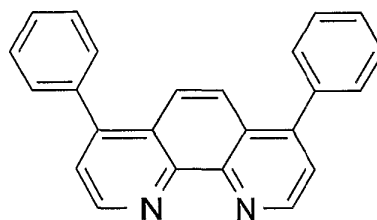
The metal phthalocyanine complexes or porphyrin complexes used as
30 matrix materials can have a main group or transition metal atom. The metal atom Me can be 4-, 5-, or 6-fold coordinated, for example in the form of oxo (Me=O), dioxo (O=Me=O), imino, diimino, hydroxo, dihydroxo, amino, or diamino complexes, without being limited to these. The phthalocyanine or porphyrin complex can be partially
35 hydrogenated, but the mesomeric ring system is preferably not disturbed. The phthalocyanine complexes can have, for example,

magnesium, zinc, iron, nickel, cobalt, magnesium, copper, or vanadyl (VO) as the central atom. The same or different metal or oxo-metal atoms can be present in the case of porphyrin complexes.

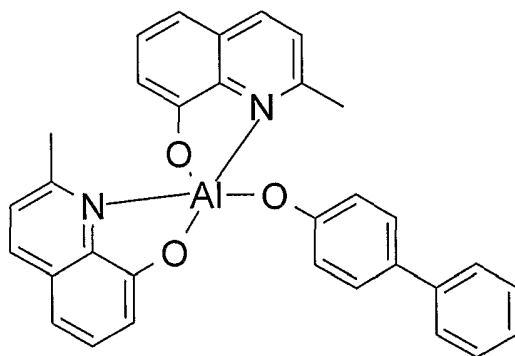
- 5 Quinolinato complexes, such as aluminum or other main group metal complexes, can also be used as n-dopable matrix materials, with the quinolinato ligand possibly being substituted. In particular, the matrix material can be tris(8-hydroxyquinolinato)aluminum. Other aluminum complexes with O and/or N donor atoms can also be used if necessary.
- 10



tris(8-hydroxyquinolinato)aluminum



BPhen = bathophenanthroline
(4,7-Diphenyl-1,10-phenanthroline)
C₂₄H₁₆N₂



- 15 Bis(2-methyl-8-quinolinolato)-4-(phenylphenolato)-aluminum(III)

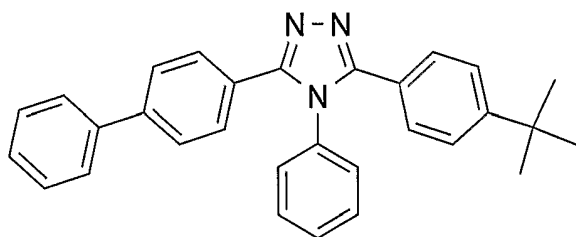
The quinolinato complexes can contain one, two, or three quinolinato ligands, with the other ligands preferably complexing to the central atom with O and/or N donor atoms, as in the above

20

Al complex.

Phenanthrolines, which can be substituted or unsubstituted, in particular aryl-substituted, such as phenyl or naphthyl-substituted, can also be used as matrix materials. In particular, Bphen can be used as a matrix material.

Heteroaromatics, in particular triazoles, can also be used as matrix materials, possibly also pyrroles, imidazoles, triazoles, pyridines, pyrimidines, pyridazines, and the like. The heteroaromatics are preferably substituted, in particular aryl-substituted, such as phenyl or naphthyl-substituted. In particular, the following triazole can be used as a matrix material.



3-(4-Biphenyl)-4-phenyl-5-tert-butylphenyl-1,2,4-triazoles

C₃₀H₂₇N₃

The matrix material preferably consists entirely of a metal phthalocyanine complex, in particular ZnPc, a porphyrin complex, or a Buckminster fullerene, in particular fullerene C₆₀.

It is understood that the mentioned matrix materials can also be mixed with each other or with other materials within the scope of the invention. It is also understood that other suitable organic matrix materials with semiconducting properties can also be used.

Doping concentration

The invention also relates to an organic semiconducting material containing a metal complex according to the invention as an n-dopant. Preferably, the dopant is present in a doping concentration of $\leq 1:1$ to the matrix molecule or the monomeric unit of a polymeric matrix molecule, preferably in a doping concentration of 1:2 or smaller, particularly preferably 1:5 or smaller, or 1:10 or smaller. The doping concentration can range from 1:1 to 1:100,000 or smaller, in particular in the range of 1:5 to 10,000 or 1:10 to 1,000, for example in the range of 1:10 to 1:100 or 1:25 to 1:50, without being limited to these ranges.

Implementation of doping

The doping of the respective matrix material with the n-dopants according to the invention can be carried out by one or a combination of the following methods:

- a) Co-evaporation in vacuum with a source for the matrix material and one for the dopant
- b) Sequential deposition of the matrix material and the n-dopant on a substrate with subsequent diffusion of the dopant, in particular through thermal treatment
- c) Doping a matrix layer by a solution of n-dopants followed by evaporation of the solvent, in particular through thermal treatment
- d) Surface doping of a matrix material layer by a surface-applied layer of dopants
- e) Preparation of a solution of matrix molecules and dopants and subsequent formation of a layer from this solution by conventional methods such as solvent evaporation or spin-coating

Doping can also be carried out by evaporating the dopant from a precursor compound, which releases the dopant upon heating and/or irradiation. Examples of precursor compounds include carbonyl compounds, dinitrogen compounds, or the like, which release the dopant by splitting off CO, nitrogen, or the like. Other suitable

precursors such as salts, e.g., halides, can also be used. Irradiation can be performed using electromagnetic radiation, in particular visible light, UV light, or IR light, for example laser light, or other types of radiation. The irradiation can essentially provide the heat necessary for evaporation; it can also be specifically directed into certain bands of the compounds to be evaporated or their precursors or complex compounds, such as charge-transfer complexes, to facilitate the evaporation of the compounds by dissociation of the complexes through excitation into excited states. The complex can also be stable enough to evaporate or be applied to the substrate under given conditions without dissociating. It should be understood that other suitable methods for doping can also be used.

In this way, n-doped layers of organic semiconductors can be produced according to the invention, which can be used in various applications.

Semiconducting layer

The metal complexes used according to the invention can produce semiconducting layers that can also be configured in lines, such as conductivity paths, contacts, or the like. The metal complexes can be used as n-dopants along with another compound that can function as a matrix material, with a doping ratio of 1:1 or smaller. The metal complex used according to the invention can also be present in higher proportions relative to the other compound or component, so that the metal complex to compound ratio is $> 1:1$, for example $\geq 2:1$, $\geq 5:1$, $\geq 10:1$, or $\geq 20:1$ or higher. The other component can be one that is used as a matrix material for the production of doped layers but is not limited to this. The metal complex used according to the invention can also be present in essentially pure form, for example as a pure layer.

The area containing a metal complex according to the invention or consisting essentially or entirely of it can be electrically conductively contacted with an organic semiconducting material

and/or an inorganic semiconducting material, for example, arranged on such a substrate.

Preferably, the mentioned metal complexes are used according to the invention as n-dopants, e.g., in a ratio of $\leq 1:1$ or $\leq 1:2$, or as detailed above. Using the metal complexes as n-dopants according to the invention, semiconducting layers with conductivities at room temperature in the range of 10^{-5} S/cm or higher can be achieved when using fullerene C_{60} as the matrix, for example, 10^{-3} S/cm or higher, or 10^{-1} S/cm. When using phthalocyanine-zinc as the matrix, a conductivity of higher than 10^{-8} S/cm, for example 10^{-6} S/cm, was achieved. It was previously not possible to dope this matrix with organic donors due to the low reduction potential of the matrix. The conductivity of undoped phthalocyanine zinc, however, is at most 10^{-10} S/cm.

It is understood that the layer or structure with the metal complex according to the invention can contain one or more different such complexes.

Electronic device

Using the organic compounds according to the invention to produce n-doped organic semiconducting materials, which can be arranged in particular in the form of layers or electrical conduction paths, a variety of electronic devices or devices containing such with an n-doped organic semiconducting layer can be produced, which are thus included in the invention. In the sense of the invention, the term "electronic devices" also includes optoelectronic devices. The invention's compounds can beneficially alter the electronic properties of an electronically functionally effective area of the device, such as its electrical conductivity, light-emitting properties, or the like. For example, using the metal complexes as n-dopants according to the invention can improve the conductivity of the doped layers and/or the charge carrier injection from contacts into the doped layer.

The invention in particular includes organic light-emitting diodes

(OLEDs), organic solar cells, organic diodes, in particular those with high rectification ratios like 10^3 - 10^7 , preferably 10^4 - 10^7 , or 10^5 - 10^7 , and organic field-effect transistors manufactured using the neutral metal complexes according to the invention.

5

In the electronic device, an n-doped layer based on an organic matrix material according to the invention can be present in the following layer structures, preferably with the base materials or matrix materials of the individual layers being organic:

10

M-i-n: Metal-insulator-n-doped semiconductor, where the layer M forms the metal base contact and can be, for example, ITO, Au, Ag, Al, etc. The top contact forms an ohmic contact with the n-doped layer and can be, for example, Al. The layer "i" stands for an undoped layer.

15

n-i-M: The same applies to the M-i-n structure, but the ohmic contact is provided on the substrate.

20

p-i-n: p-doped semiconductor-insulator-n-doped semiconductor, n-i-p: n-doped semiconductor-insulator-p-doped semiconductor, "i" again being an undoped layer, "p" a p-doped layer. The contact materials here inject holes, with a layer or contact of ITO or Au provided on the p-side, or inject electrons, with a layer or contact of ITO, Al, or Ag provided on the n-side.

25

If necessary, the i-layer can also be omitted in the above structures, resulting in layer sequences with p-n or n-p junctions.

30

The use of the dopants according to the invention is not limited to the above examples; in particular, the layer structures can be supplemented or modified by introducing additional suitable layers. In particular, OLEDs with such layer sequences, especially with pin or an inverse structure, can be constructed using the n-dopants according to the invention.

35

With the help of the n-dopants according to the invention, organic

diodes of the metal-insulator-n-doped semiconductor (min) type or possibly also of the pin type can be produced, for example based on phthalocyanine-zinc. These diodes show a rectification ratio of 10^5 and higher. Furthermore, using the dopants according to the invention, electronic devices with p-n junctions can be produced, using the same semiconductor material for both the p- and n-doped sides (homo-p-n junction), with the n-doped semiconductor material using a metal complex according to the invention. Such devices are thus included in the invention.

The metal complexes can also be used in the electronic devices according to the invention in layers, conductivity paths, point contacts, or the like, if these predominate over another component, for example as an injection layer in pure or essentially pure form.

Application examples

An electron-rich neutral metal complex according to the invention is provided, where the metal complex can be, for example:

M-bis-(terpyridine) with M equal to Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W; M_2hpp_4 with M equal to Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W; $M_2(AlkylCOO)_4$ F with M equal to Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W and with each alkyl, identical or different, having C1 to C10; $M_2(Guanidinate)_4$ with M equal to Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W; $M_2(Formamidinate)_4$ with M equal to Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W; $M_2(Carboxylate)_4$ with M equal to Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W; $M_2(Halide)_4$ with M equal to Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W; Bis(η^5 -cyclopentadienyl) -M with M equal to Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W; Benzene-M-(η^5 -cyclopentadienyl) with M equal to Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W; $Fe(Ligand)_2$, where the ligand can be one of compounds 20 to 37 with E = -C-, -Ge-, or -Si-, where at least one R, some or all Rs are preferably each hydrogen or methyl or ethyl. Instead of Fe, the central atom can in particular be Cr, Mn, Co, Ni, Cu, Zn, Mo, or W. Moreover, compounds 21, 22, 23, and 24 can in particular be used, where R is hydrogen or methyl. E can in particular be -C- or -Ge-, resulting in the corresponding biscarbene ligands or

bisgermylene ligands. It is understood that one or more of the hydrogen atoms of the ligands may be replaced by other substituents, including alkyl groups.

- 5 A metal complex according to one of compounds 11 to 14, 16 can also be provided, where R and R'' are each methyl and E is each S. The central atom is Fe. Alternatively, the central atom can be Cr, Mn, Co, Ni, Cu, Zn, Mo, or W.
- 10 The provided metal complex is evaporated simultaneously with the matrix material. According to the example, the matrix material is phthalocyanine-zinc or fullerene C₆₀. The n-dopant and matrix material can be evaporated in such a way that the layer deposited on a substrate in a vacuum evaporation system has a doping ratio
- 15 of n-dopant to matrix material of 1:10.

The layer of organic semiconductor material doped with the n-dopant according to the invention is applied to an ITO layer (indium tin oxide) arranged on a glass substrate. After applying the n-doped

20 organic semiconductor layer according to the invention, a metal cathode is applied, for example, by vapor deposition of a suitable metal to produce an organic light-emitting diode. It is understood that the organic light-emitting diode can also have an inverted layer structure, where the layer sequence is: glass substrate -

25 metal cathode - n-doped organic layer - transparent conductive top layer (for example ITO). It is understood that additional layers may be provided between the individual layers mentioned depending on the application.

30 Example 1:

The neutral cobalt complex cobalt-bis(phenylene-1-yl-2,6 dipyridyl) (ligand: compound 29) was produced by conventional methods.

- 35 The neutral complex was sealed under protective gas in ampoules. Under exclusion of oxygen, this material was used to fill an

evaporator source. Doped layers with a doping ratio of dopant:matrix material of 1:10 were produced by co-evaporation of matrix and dopant with ZnPc as the matrix material. In thin-film field-effect transistors with such a doped ZnPc layer, an increase in the source-drain current for positive gate voltage was found. This demonstrates the presence of electrons as majority charge carriers in the ZnPc layer. This showed that it is indeed an n-doped semiconductor material.

The same applies to the ruthenium complex Ru-bis-(pyridine-2,6-di-(1H2H-N-imidazolyl-)) (ligand: compound 23 with E = -C).

Example 2:

A layer of zinc-phthalocyanine (ZnPc) was doped with the metal complex [Cr2(hpp)4]. The doped layer was produced by co-evaporation of the ZnPc matrix and the dopant Cr2(hpp)4 in high vacuum. The concentration of the dopant in the matrix was 1.9 mol%. The sublimation temperature of the dopant was 160°C. The doped layer showed high conductivity of $4 \cdot 10^{-6}$ S/cm. By heating the layer at 70°C, the conductivity could be increased to $6 \cdot 10^{-5}$ S/cm. The activation energy of the conductivity was 0.27 eV.

Example 3:

A layer of fullerene C60 was doped with the metal complex cobaltocene. First, a pure layer of the fullerene was produced by sublimation in high vacuum. This layer had a low conductivity of $1 \cdot 10^{-7}$ S/cm. The doped layer was then placed in a container containing an evaporator filled with cobaltocene. The container was filled with nitrogen. The cobaltocene was thermally sublimated in this container. The cobaltocene deposited on the surface of the fullerene layer formed a thin highly doped layer there. The transverse current measured in the layer increased by 3 orders of magnitude. The conductivity of the highly doped layer was thus at least $1 \cdot 10^{-4}$ S/cm. The doped fullerene layer was subsequently transferred back to the vacuum chamber. High conductivities of at least $2 \cdot 10^{-5}$ S/cm were still measured there. This demonstrated that

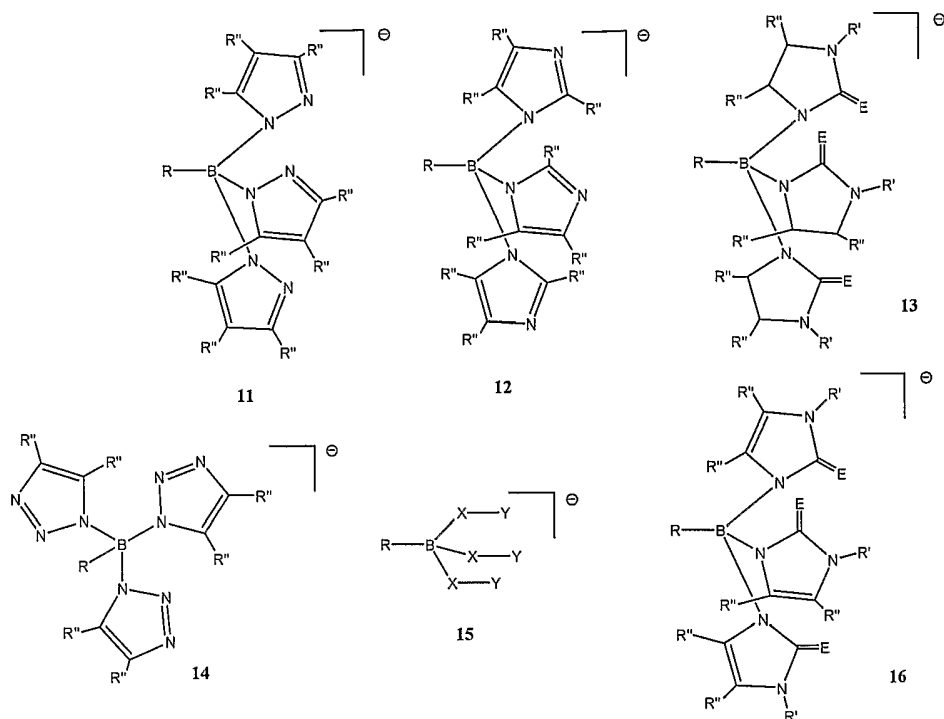
the observed increase in conductivity was indeed due to the doping of the fullerene, as any formed layers of pure, neutral cobaltocene are not stable in high vacuum due to their vapor pressure.

Patent claims

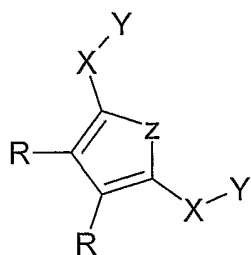
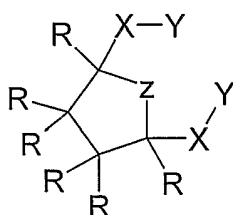
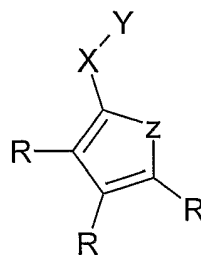
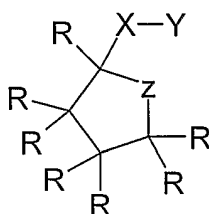
1. Use of a metal complex as a dopant for doping an organic
semiconducting matrix material to alter its electrical
properties, wherein the metal complex represents an n-dopant
with respect to the matrix material, or use of a metal complex
for the production of an electronic device with an
electronically functional area containing the metal complex,
characterized in that the metal complex is a neutral
electron-rich metal complex.
2. Use according to claim 1, characterized in that the central
atom is a neutral or charged transition metal atom.
3. Use according to claim 1 or 2, characterized in that at least
one central atom of the complex has a formal valence electron
count of 16 or more and/or that the complex is multinuclear
and has at least one metal-metal bond between two central
metal atoms of the complex.
4. Use according to any one of claims 1 to 3, characterized in
that at least one donor atom binding to the central atom of
the ligand is different from an aromatic nitrogen atom as
part of a 6-membered ring.
5. Use according to any one of claims 1 to 4, characterized in
that at least one, several, or all donor atoms binding to the
central atom are selected from the group consisting of B, Al,
Ga, In, C, Si, Ge, Sn, Pb, P, As, Sb, Bi, S, Se, Te.
6. Use according to any one of claims 1 to 5, characterized in
that at least one ligand forms a pi-complex with the central
atom.
7. Use according to any one of claims 1 to 6, characterized in

that the metal complex is a multinuclear metal complex, in which at least one, several, or all ligands coordinate to at least two central metal atoms.

- 5 8. Use according to any one of claims 1 to 7, characterized in that at least one or all ligands of the complex are selected from the group consisting of halides, carboxylates, formamidinates, pyrimido-pyrimidines, hpp, and guanidines.
- 10 9. Use according to any one of claims 1 to 8, characterized in that at least one ligand belongs to the class of borates, carboranes, triazacycloalkanes, triazacycloalkenes, pyrroles, thiophenes, pyrazoles, imidazoles, thiazoles, oxazoles, or fullerenes.
- 15 10. Use according to claim 9, characterized in that at least one borate ligand is one of the following compounds 11, 12, 13, 14, 16, where R, R', and R'' are independently any substituent including hydrogen and R, R', and R'' can be identical or
- 20 different, and E is at least a divalent atom or atom group:

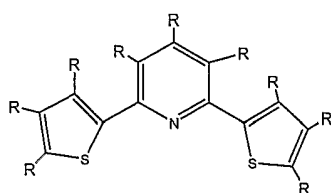


11. Use according to any one of claims 1 to 10, characterized in that at least one donor atom binding to at least one central metal atom is a carbanion carbon atom or, with respect to the ligand, a formally divalent atom selected from the group C (carbene), Si (silylene), Ge (germylene), Sn, Pb.
12. Use according to claim 11, characterized in that the ligand has at least one or two donor atoms binding to at least one central metal atom as a carbanion carbon atom or, with respect to the ligand, a formally divalent atom selected from the group C (carbene), Si (silylene), Ge (germylene), which are each part of an aromatic or non-aromatic ring, and the ring containing the donor atom has an additional heteroatom, which is N, P, As, S, Se, or Te.
13. Use according to any one of claims 1 to 12, characterized in that at least one ligand is a compound of formula 27, 27a, 28, 28a, 45, 45a, 46, or 46a,

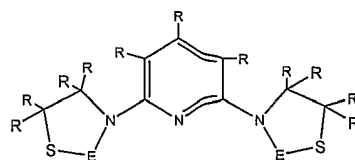
**27a****28a****45a****46a**

where R is independently any substituent, including hydrogen;
X is a donor-capable hetero- or carbon atom, X is at least a
divalent atom or atom group, where one or two X may be absent,
and Z and Y are each a donor-capable carbon or heteroatom,
where Z and Y, as well as two atoms Y, may each be identical
or different from each other.

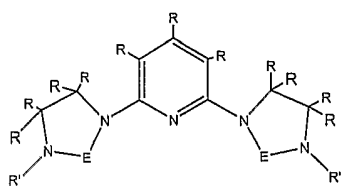
14. Use according to any one of claims 1 to 13, characterized in
that at least one ligand is one of the following compounds
20-26, 29-37, where R



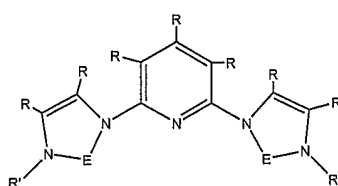
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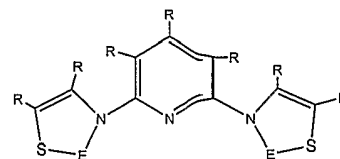
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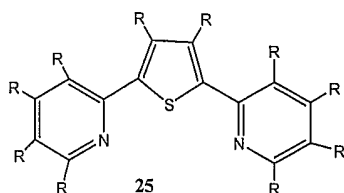
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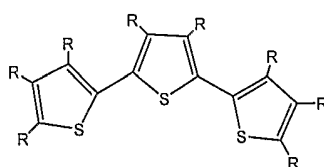
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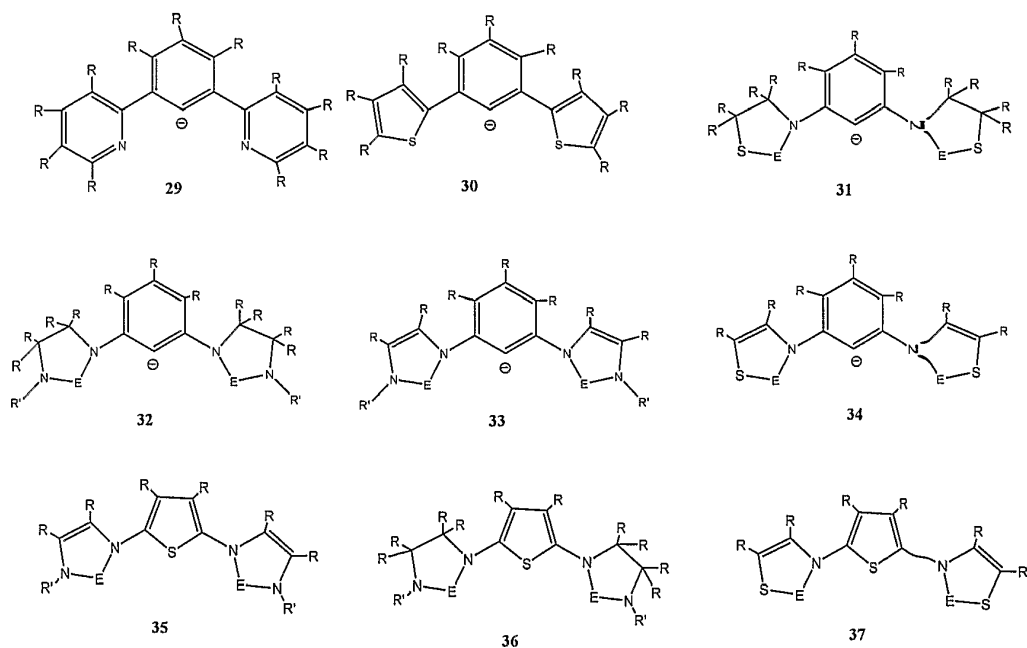


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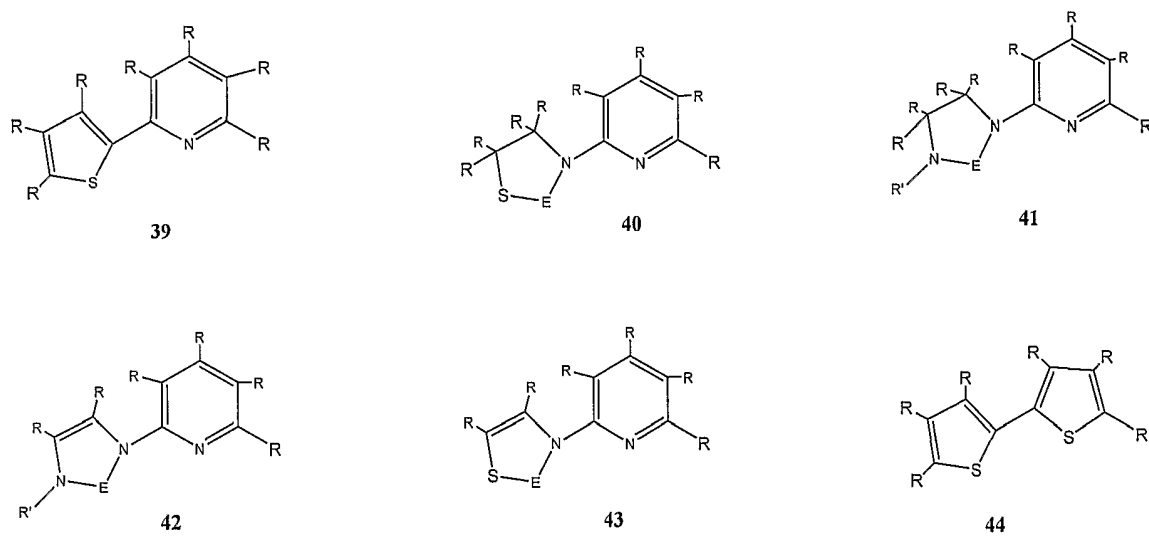
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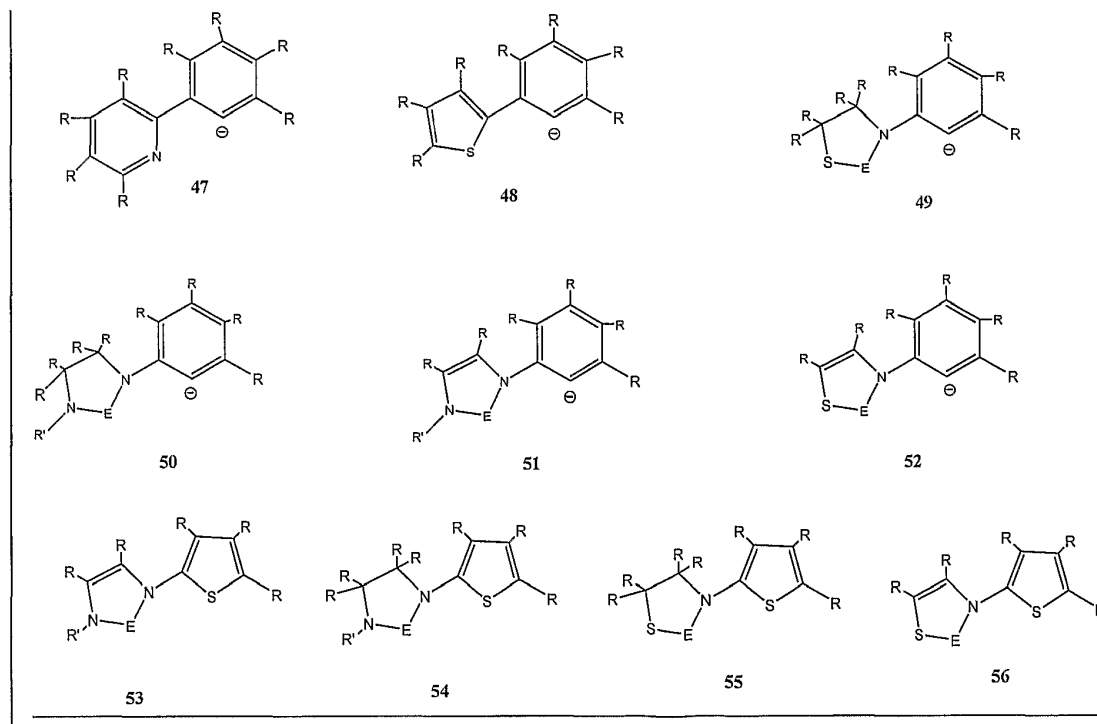


is independently any substituent, including hydrogen, E is an atom selected from the group C, Si, Ge, Sn, Pb, and independently P, As, or Sb can be present instead of N, and Se or Te can be independently present instead of S.

15. Use according to any one of claims 1 to 14, characterized in that at least one ligand is one of the following compounds 39-44, 47-56,



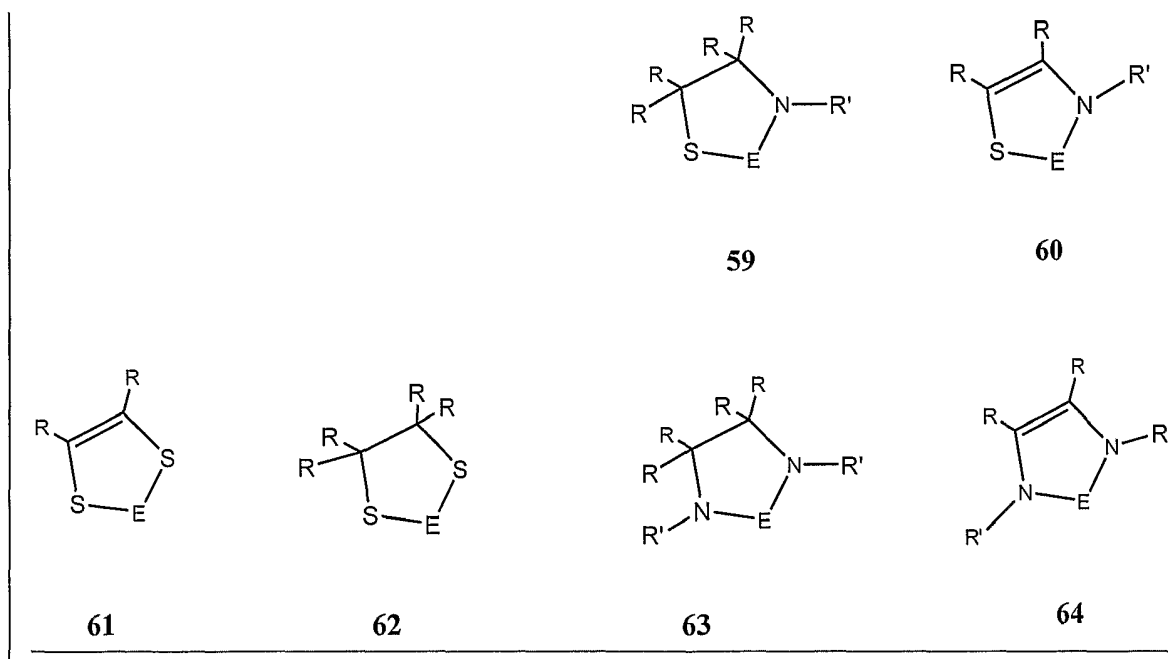
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where R is independently any substituent, including hydrogen,
 and R and R' can be identical or different, E is an atom
 selected from the group C, Si, Ge, Sn, Pb, and X is a donor-
 capable hetero- or carbon atom, and independently P, As, or
 Sb can be present instead of N, and Se or Te can be
 independently present instead of S.

16. Use according to claims 14 or 15, characterized in that E is
 selected from the group C (carbene), Si (silylene), Ge
 (germylene).

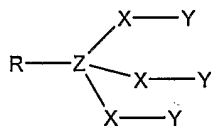
17. Use according to any one of claims 1 to 16, characterized in
 that at least one ligand is one of the following compounds
 59-64,



where R is independently any substituent, including hydrogen,
 E is an atom selected from the group C, Si, Ge, Sn, Pb, and
 X is a donor-capable hetero- or carbon atom, and
 independently P, As, or Sb can be present instead of N, and
 Se or Te can be independently present instead of S.

18. Use according to any one of claims 1 to 17, characterized in that at least one ligand is one of the above compounds 19, 38, 57, or 58, where R is independently any substituent, including hydrogen, X is a donor-capable hetero- or carbon atom, and independently P, As, or Sb can be used instead of N.
19. Use according to any one of claims 1 to 18, characterized in that at least one, several, or all rings carrying a donor atom have one or more substituted or unsubstituted alkyl substituents with C2-20.
20. Use according to any of claims 1 to 19, characterized in that at least one ligand is a tripod ligand of the general

structure:



18

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where R is any substituent, including H, where R can be identical to the structural sequence -X-Y, X represents at least a divalent atom or an atom group with or without heteroatoms, where X can be the same or different, Y is a donor-capable hetero- or carbon atom, where Y can be the same or different and part of a ring, and where Z as the central atom of the tripod ligand can be any atom, including a metal atom.

10

15 21. Use according to claim 20, characterized in that Y is an atom from the group C, N, P, S, Se, Ge, Sn.

20

22. Use according to any of claims 1 to 21, characterized in that the complex is: M_2hpp_4 with M being Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W; $M_2(AlkylCOO)_4$ F with M being Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W and with each alkyl being identical or different, with C1 to C10; $M_2(Guanidinate)_4$ with M being Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W; $M_2(Formamidinate)_4$ with M being Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W; $M_2(Carboxylate)_4$ with M being Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W; $M_2(Halide)_4$ with M being Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W; $Bis(\eta^5\text{-cyclopentadienyl})M$ with M being Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W; $Benzene-M-(\eta^5\text{-cyclopentadienyl})$ with M being Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W, where one or more hydrogen atoms of the ligands can be replaced by other groups including alkyl groups.

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23. Use according to any of claims 1 to 22, characterized in that

the metal complex has an ionization potential in the gas phase of less than 6 eV or that the metal complex has an oxidation potential $E(1/2)_{ox}$ relative to ferrocene/ferrocenium (Fe/Fe⁺) of ≤ -0.09 V.

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24. Semiconducting material produced using a metal complex according to any of claims 1 to 23 in the form of an electrically contactable layer or an electrical conduction path arranged on a substrate.

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25. Organic semiconducting material containing at least one organic matrix compound and an n-dopant, characterized in that one or more neutral metal complexes according to any of claims 1 to 23 are used as the n-dopant.

15

26. Organic semiconducting material according to claim 25, characterized in that the molar doping ratio of dopant to matrix molecule or the doping ratio of dopant to monomer units of a polymeric matrix molecule is between 1:1 and 1:100,000.

20

27. Method for producing an organic semiconducting material containing an organic matrix molecule and an n-dopant, characterized in that at least one or more neutral metal complexes according to any of claims 1 to 23 are used as the n-dopant.

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28. Electronic device with an electronically functional area, characterized in that the electronically functional area is produced using at least one or more of the neutral metal complexes according to any of claims 1 to 23.

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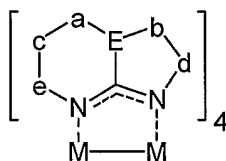
29. Electronic component according to claim 28, characterized in that the electronically functional area comprises an organic semiconducting matrix material, which is doped with at least one n-dopant to alter the electronic properties of the

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semiconducting matrix material using at least one or more of the neutral metal complexes according to any of claims 1 to 23.

30. Electronic device according to claim 29 or 30 in the form of an organic light-emitting diode (OLED), a photovoltaic cell, an organic solar cell, an organic diode, or an organic field-effect transistor, in which the semiconducting organic material doped with at least one or more neutral metal complexes according to any of claims 1 to 23 represents an electronically functional part of the electronic device.

31. Dopant for doping an organic semiconducting matrix material, having a structure selected from the group of:

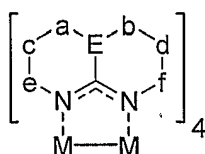


Type 65a

wherein

- the structural elements a-e can have the meanings: a = -CR₁R₂-, b = -CR₃R₄-, c = -CR₅R₆-, d = -CR₇R₈-, and e = -CR₉R₁₀-, where R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, and R₁₀ can simultaneously or independently be H, alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl, -NR₂, or -OR, preferably R₁, R₃, R₅, R₇, R₉ = H and R₂, R₄, R₆, R₈, R₁₀ = alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl, -NR₂ or -OR, or
- optionally, a or b or e or d can be NR with R = alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl, or
- at c, C is replaced by Si,

- wherein the bonds b-d and c-e or b-d and a-c can be unsaturated simultaneously or independently of each other,
- wherein the bonds b-d, a-c, and c-e can be part of a saturated or unsaturated ring system simultaneously or independently of each other, which can also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- wherein the bonds b-d, a-c, and c-e can be part of an aromatic or condensed aromatic ring system simultaneously or independently of each other, which can also contain the heteroelements O, S, Se, N,
- wherein the atom E is a main group element, preferably selected from the group N, P, As, Sb, without being limited to these,
- wherein the structural element a-E-b can optionally be part of a saturated or unsaturated ring system, which can also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- the structural element a-E-b can optionally be part of an aromatic ring system, which can also contain the heteroelements O, S, Se, N,
- wherein the metal M is a transition metal, preferably W or Mo;

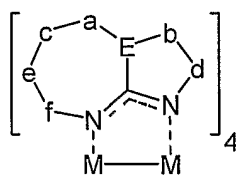


Type 65b

wherein

- the structural elements a-f can have the meanings: a = -CR₁R₂-, b = -CR₃R₄-, c = -CR₅R₆-, d = -CR₇R₈-, e = -CR₉R₁₀-, and f = CR₁₁R₁₂, where R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, R₁₀, R₁₁, and R₁₂ can be hydrogen, alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl,

- heteroaryl, - NR₂ or -OR, preferably R₁, R₃, R₅, R₇, R₉, R₁₁ = H and R₂, R₄, R₆, R₈, R₁₀, R₁₂ = alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl, - NR₂, or -OR, excluding the structure 65b with R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, R₁₀, R₁₁, and R₁₂ = H, or
- 5 - at the structural elements c and/or d, C can be replaced by Si, or
- optionally, a or b or e or f can be NR with R = alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl, or
- 10 - optionally, a and f or b and e can be NR with R = alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl,
- wherein the bonds a-c, b-d, c-e, and d-f, but not simultaneously a-c and c-e, and not simultaneously b-d and d-f, can be unsaturated,
- 15 - wherein the bonds a-c, b-d, c-e, and d-f can be part of a saturated or unsaturated ring system, which can also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- 20 - the bonds a-c, b-d, c-e, and d-f can be part of an aromatic or condensed aromatic ring system, which can also contain the heteroelements O, S, Se, N,
- wherein the atom E is a main group element, preferably selected from the group N, P, As, Sb, without being limited to these,
- 25 - wherein the structural element a-E-b can optionally be part of a saturated or unsaturated ring system, which can also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- 30 - the structural element a-E-b can optionally be part of an aromatic ring system, which can also contain the heteroelements O, S, Se, N,
- wherein the metal M is a transition metal, preferably W or Mo;
- 35



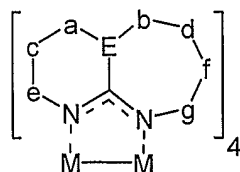
Type 65c

5 wherein

- the structural elements a-f can have the meanings: a = -CR₁R₂-, b = -CR₃R₄-, c = -CR₅R₆-, d = -CR₇R₈-, e = -CR₉R₁₀-, and f = CR₁₁R₁₂, where R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, R₁₀, R₁₁, and R₁₂ can simultaneously or independently be H, alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl, -NR₂ or -OR, preferably R₁, R₃, R₅, R₇, R₉, R₁₁ = H and R₂, R₄, R₆, R₈, R₁₀, R₁₂ = alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl, -NR₂ or -OR,
- or
- at c or e, C can be replaced by Si, or
- optionally, a or b or d or f can be NR with R = alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl, or
- optionally, a and d or b and f can be NR with R = alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl,
- wherein the bonds a-c, c-e, e-f, and b-d, but not simultaneously a-c, c-e, and e-f, and not simultaneously a-c and c-e, and not simultaneously c-e and e-f, can be unsaturated,
- wherein the bonds a-c, c-e, e-f, and b-d can be part of a saturated or unsaturated ring system, which can also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- the bonds a-c, c-e, e-f, and b-d can be part of an aromatic or condensed aromatic ring system, which can also contain the heteroelements O, S, Se, N,
- wherein the atom E is a main group element, preferably

selected from the group N, P, As, Sb, without being limited to these,

- wherein the structural element a-E-b can optionally be part of a saturated or unsaturated ring system, which can also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- the structural element a-E-b can optionally be part of an aromatic ring system, which can also contain the heteroelements O, S, Se, N,
- wherein the metal M is a transition metal, preferably W or Mo; or



Type 65d

- the structural elements a-g can have the meanings: a = -CR₁R₂-, b = -CR₃R₄-, c = -CR₅R₆-, d = -CR₇R₈-, e = -CR₉R₁₀-, f = CR₁₁R₁₂, and g = CR₁₃R₁₄, where R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, R₁₀, R₁₁, R₁₂, R₁₃, and R₁₄ can simultaneously or independently be H, alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl, -NR₂ or -OR, preferably R₁, R₃, R₅, R₇, R₉, R₁₁, R₁₃ = H and R₂, R₄, R₆, R₈, R₁₀, R₁₂, R₁₄ = alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl, -NR₂ or -OR, or
- at c, d, and f, but not d and f simultaneously, C can be replaced by Si, or
- optionally, a or b or e or g can be NR with R = alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl

with C₁-C₂₀, aryl, heteroaryl, or

- optionally, a and g or b and e can be NR with R = alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl,

- 5
- wherein the bonds a-c, c-e, b-d, d-f, and f-g, but not simultaneously a-c and c-e, and not simultaneously b-d, d-f, and f-g, and not simultaneously b-d and d-f, and not simultaneously d-f and f-g, can be unsaturated,

- 10
- wherein the bonds a-c, c-e, b-d, d-f, and f-g can be part of a saturated or unsaturated ring system, which can also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or

- the bonds a-c, c-e, b-d, d-f, and f-g can be part of an aromatic or condensed aromatic ring system, which can also contain the heteroelements O, S, Se, N,

- wherein the atom E is a main group element, preferably selected from the group N, P, As, Sb, without being limited to these,
- wherein the structural element a-E-b can optionally be part of a saturated or unsaturated ring system, which can also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- the structural element a-E-b can optionally be part of an aromatic ring system, which can also contain the heteroelements O, S, Se, N,
- wherein the metal M is a transition metal, preferably W or Mo.

32. Process for the preparation of a dopant according to claim 31, which comprises the steps of:

- (a) Reacting an inorganic metal salt of the central atom M with a free base of a ligand defined in claim 38 in an organic solvent in the presence of a reducing agent and heating to reflux,
- (b) Isolating and drying the obtained dopant product after the reaction.

33. Process according to claim 32, characterized in that the solvent is ether, an aromatic solvent, or a mixture thereof.

34. Process according to claim 33, characterized in that the ether is dialkyl ether, cyclic ether, cyclic and/or acyclic polyether.

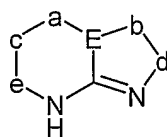
35. Process according to any one of claims 32 to 34, characterized in that the reducing agent is a base metal.

36. Process according to claim 35, characterized in that the base metal is sodium, potassium, and/or cesium.

37. Process according to any one of claims 32 to 36, characterized in that the isolation is carried out by crystallization, precipitation, and/or sublimation.

5

38. Ligand for a metal complex, selected from the group consisting of



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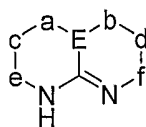
Type 65a'

wherein

- the structural elements a-e can have the meanings: a = -CR₁R₂-, b = -CR₃R₄-, c = -CR₅R₆-, d = -CR₇R₈-, and e = -CR₉R₁₀-, where R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, and R₁₀ can simultaneously or independently be H, alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl, -NR₂ or -OR, preferably R₁, R₃, R₅, R₇, R₉ = H and R₂, R₄, R₆, R₈, R₁₀ = alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl, -NR₂ or -OR, excluding structure 65a' with R₁ to R₁₀ = H, excluding structure 65a' with R₁ and R₂ = aryl, where in structure 65a' R₁ and R₁₀ are always H, or
- optionally, a or b or e or d can be NR with R = alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl, or

25

- optionally, a and d or b and e can be NR with R = alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl, or
- at c, C is replaced by Si,
- 5 - wherein the bonds b-d and c-e or b-d and a-c can simultaneously or independently be unsaturated, where the bonds b-d, a-c, and c-e can simultaneously or independently be part of a saturated or unsaturated ring system, which can also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, excluding the ligand with c-e = cyclohexyl and cyclohexenyl, or
- 10 - wherein the bonds b-d, a-c, and c-e can simultaneously or independently be part of an aromatic or condensed aromatic ring system, which can also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, excluding the ligand where b-d, a-c, and c-e are part of benzene,
- 15 - wherein the atom E is a main group element, preferably selected from the group N, P, As, Sb, without being limited to these,
- 20 - wherein the structural element a-E-b can optionally be part of a saturated or unsaturated ring system, which can also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- 25 - the structural element a-E-b can optionally be part of an aromatic ring system, which can also contain the heteroelements O, S, Se, N,
- wherein the metal M is a transition metal, preferably W or Mo;



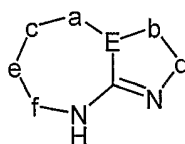
Type 65b'

wherein

- 5 - the structural elements a-f can have the meanings: a = -CR₁R₂-, b = -CR₃R₄-, c = -CR₅R₆-, d = -CR₇R₈-, e = -CR₉R₁₀-, and f = CR₁₁R₁₂, where R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, R₁₀, R₁₁, and R₁₂ can be hydrogen, alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl, -NR₂ or -OR, preferably R₁, R₃, R₅, R₇, R₉, R₁₁ = H and R₂, R₄, R₆, R₈, R₁₀, R₁₂ = alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl, -NR₂ or -OR, excluding structure 65b with R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, R₁₀, R₁₁, and R₁₂ = H, excluding the ligand with R₉, R₁₀, R₁₁, and R₁₂ = phenyl, methyl, allyl, RSCH₂- und ROCH₂-, excluding the ligand with R₉ = phenyl, R₁₀ = H, R₁₁ = phenyl, R₁₂ = H, excluding the ligand with R₁ = phenyl, excluding the ligand with R₅, R₆, R₇, R₈ = phenoxy, or
- 10 - at the structural elements c and/or d, C can be replaced by Si, or
- 15 - optionally, a or b or e or f can be NR with R = alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl, or
- 20 - optionally, a and f or b and e can be NR with R = alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl,
- 25 - wherein the bonds a-c, b-d, c-e, and d-f, but not simultaneously a-c and c-e, and not simultaneously b-d and d-f, can be unsaturated,
- 30 - wherein the bonds a-c, b-d, c-e, and d-f can be part of a saturated or unsaturated ring system, which can also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- the bonds a-c, b-d, c-e, and d-f can be part of an aromatic

or condensed aromatic ring system, which can also contain the heteroelements O, S, Se, N, excluding the ligand where a-c, b-d, c-e, and d-f are part of benzene,

- wherein the atom E is a main group element, preferably selected from the group N, P, As, Sb, without being limited to these,
- wherein the structural element a-E-b can optionally be part of a saturated or unsaturated ring system, which can also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, excluding the ligand with a-E-b = part of cyclopentyl and pyranyl with R₉ to R₁₂ = alkyl, or
- the structural element a-E-b can optionally be part of an aromatic ring system, which can also contain the heteroelements O, S, Se, N,
- wherein the metal M is a transition metal, preferably W or Mo;



Type 65c'

wherein

- the structural elements a-f can have the meanings: a = -CR₁R₂-, b = -CR₃R₄-, c = -CR₅R₆-, d = -CR₇R₈-, e = -CR₉R₁₀-, and f = CR₁₁R₁₂, where R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, R₁₀, R₁₁, and R₁₂ can simultaneously or independently be H, alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl, -NR₂ or -OR; preferably, R₁, R₃, R₅, R₇, R₉, R₁₁ = H and R₂, R₄, R₆, R₈, R₁₀, R₁₂ = alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl, -NR₂, or -OR, excluding the ligand with R₁ to R₁₂ = H, or
- at c or e, C can be replaced by Si, or
- optionally, a or b or d or f can be NR with R = alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl

with C₁-C₂₀, aryl, heteroaryl, or

- optionally, a and d or b and f can be NR with R = alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl,

- 5
- wherein the bonds a-c, c-e, e-f, and b-d, but not simultaneously a-c, c-e, and e-f, and not simultaneously a-c and c-e, and not simultaneously c-e and e-f, can be unsaturated,

- 10
- wherein the bonds a-c, c-e, e-f, and b-d can be part of a saturated or unsaturated ring system, which can also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or

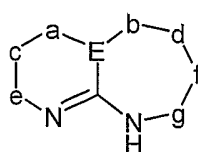
- the bonds a-c, c-e, e-f, and b-d can be part of an aromatic or condensed aromatic ring system, which can also contain the heteroelements O, S, Se, N, excluding the ligand with E=N and simultaneously e-f and/or b-d being part of benzene or naphthalene, excluding the ligand with E=N and simultaneously R₇ = R₈ = phenyl, excluding the ligand with E=N and R₃ = phenyl, benzyl,
- 15

- wherein the atom E is a main group element, preferably selected from the group N, P, As, Sb, without being limited to these, excluding the ligand with E=N and simultaneously the seven-membered ring with more than one unsaturated bond,
- 20

- wherein the structural element a-E-b can optionally be part of a saturated or unsaturated ring system, which can also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- 25

- the structural element a-E-b can optionally be part of an aromatic ring system, which can also contain the heteroelements O, S, Se, N,
- 30

- wherein the metal M is a transition metal, preferably W or Mo; or



Type 65d'

wherein

- the structural elements a-g can have the meanings: a = -CR₁R₂-, b = -CR₃R₄-, c = -CR₅R₆-, d = -CR₇R₈-, e = -CR₉R₁₀-, f = CR₁₁R₁₂, and g = CR₁₃R₁₄, where R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, R₁₀, R₁₁, R₁₂, R₁₃, and R₁₄ can simultaneously or independently be H, alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl, -NR₂, or -OR; preferably, R₁, R₃, R₅, R₇, R₉, R₁₁, R₁₃ = H and R₂, R₄, R₆, R₈, R₁₀, R₁₂, R₁₄ = alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl, -NR₂, or -OR, or
- at c, d, and f, but not d and f simultaneously, C can be replaced by Si, or
- optionally, a or b or e or g can be NR with R = alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl, or
- optionally, a and g or b and e can be NR with R = alkyl with C₁-C₂₀, cycloalkyl with C₁-C₂₀, alkenyl with C₁-C₂₀, alkynyl with C₁-C₂₀, aryl, heteroaryl,
- wherein the bonds a-c, c-e, b-d, d-f, and f-g, but not simultaneously a-c and c-e, and not simultaneously b-d, d-f, and f-g, and not simultaneously b-d and d-f, and not simultaneously d-f and f-g, can be unsaturated, excluding the ligand where b-d and f-g are simultaneously unsaturated,
- wherein the bonds a-c, c-e, b-d, d-f, and f-g can be part of a saturated or unsaturated ring system, which can also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- the bonds a-c, c-e, b-d, d-f, and f-g can be part of an aromatic or condensed aromatic ring system, which can also contain the heteroelements O, S, Se, N, excluding the ligand where c-e and f-g are simultaneously part of a benzene ring,
- wherein the atom E is a main group element, preferably selected from the group B, C, N, O, Si, P, S, As, Se, Sb, Te, particularly preferably selected from the group S, Se,

N, P, without being limited to these,

- wherein the structural element a-E-b can optionally be part of a saturated or unsaturated ring system, which can also contain the heteroelements O, S, Se, N, P, Si, Ge, Sn, or
- the structural element a-E-b can optionally be part of an aromatic ring system, which can also contain the heteroelements O, S, Se, N,
- wherein the metal M is a transition metal, preferably W or Mo.

39. Use of a ligand according to claim 38 in a process for preparing a dopant according to any one of claims 32-37.