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A new tripodal ligand system based on the iminophosphorane functional group. Part 1: Synthesis and characterization

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Abstract—Two tripodal alcohols, viz., 1,1,1-tris(hydroxymethyl)ethane and α,α,α-tris(hydroxymethyl)toluene were converted by an efficient multi-step pathway involving azide formation into the corresponding tris(iminophosphorane) scaffolds bearing cyclopentyl (Cp) or phenyl groups on their phosphorus atoms, R–C(CH_2–N=PR'_3)$_3$ (R=Me or Ph, R′=Cp or Ph). The synthesis of some representative transition-metal complexes of Cu(I), Cu(II), Ni(II), and Pd(II) bearing these new tridentate ligands is also reported.

1. Introduction

The search for well-defined transition-metal-based catalysts for the polymerization of ethylene and α-olefins is an area of current intense activity, both in academic and industrial research laboratories. Compared to relatively ill-defined Ziegler–Natta systems, a key advantage of single-site catalysts is the possibility for rational ligand-oriented catalyst design, allowing a better control over polymer parameters, such as molecular weight, polydispersity, and tacticity. Whereas many of the well-defined systems developed over the past 40 years were based on early transition metals, recent advances have resulted in highly active late transition-metal catalysts.[1–4] The possibility of predetermining the structure of a coordination compound has been the main driving force in the development of increasingly sophisticated systems.[5] In particular, bidentate ligands containing sp^2-hybridized nitrogen donor atoms have attracted much attention in recent years for the tailoring of transition-metal catalysts.[6–8] An important development in this field was reported by Brookhart et al. who showed that α-diimines were efficient ligands for the iron- or cobalt-catalyzed polymerization of ethylene.[9]

Simple iminophosphoranes of general formula RN=PR'_3 are neutral monodentate ligands capable of metal complexation via the lone pair present on their nitrogen atom.[10–13] They have also been referred to as phosphinimines, iminophosphines, phosphinimides, phosphazo compounds, λ^5-phosphazenes, and (mono)phosphazenes. Since the P=N bond is highly polarized, they act predominantly as two-electron σ-donors with only minor π-acceptor properties. Indeed, there is some evidence from charge-density studies against hypervalency of the phosphorus atom and, accordingly, the formal P=N double bond is better regarded as a polar P^+–N^- single bond.[14]

Iminophosphoranes offer a steric environment similar to some extent to that of imines, but with clearly different electronic properties. Yet, they have seldom been used as ligands in olefin oligomerization or polymerization[15,16] and tripodal versions of this class of ligands have not been prepared to date, although Sundermeyer et al. reported the synthesis of a related tripodal bis(2,6-iminophosphoranyl)pyridine and its use in iron- or cobalt-catalyzed ethylene polymerization.[17] Since the RN=PR'_3 unit is readily assembled by combining primary amines RNH_2 or the corresponding azides RN_3 with phosphines PR'_3, we envisioned a simple route to tripodal chelating tris(iminophosphorane) scaffolds and their possible use as ligands in transition-metal catalyzed reactions. In this report, we describe the first applications of this concept, i.e., the synthesis of four new tripodal ligands and their use for the preparation of some representative transition-metal complexes.

2. Results and discussion

The generic tripodal iminophosphorane structure depicted in Scheme 1 is somewhat reminiscent of the well-known scorpionate scaffold[18] or of Gade's tripodal amido ligands[19]

Keywords: Azide; Cu complexes; Ni complexes; Pd complexes; Staudinger reaction.
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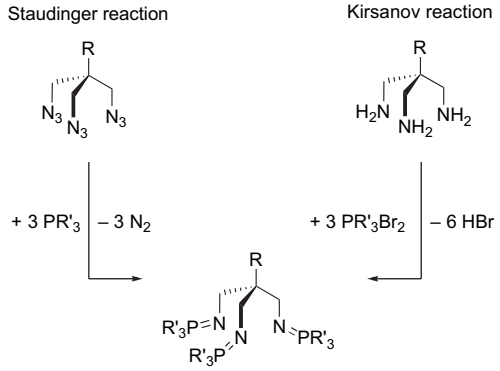
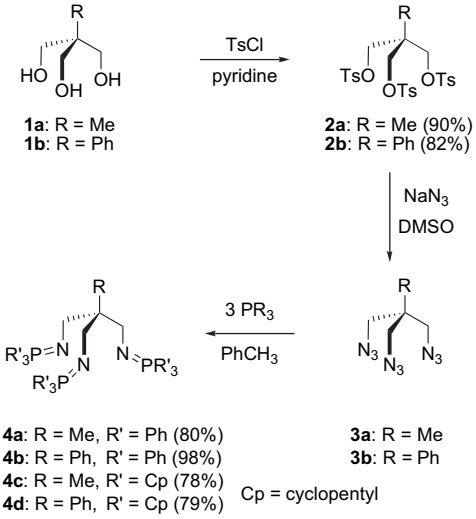
and Stalke's phosphane and phosphorane Janus Head ligands,[20] but has never been reported in the literature. Compared to these earlier tripodal systems, such a new type of ligand, besides an expected greater flexibility, presents the major advantage of being easily amenable to structural variations. Indeed, a wide range of phosphine moieties PR'_3 can be coupled with nitrogen-containing partners, thereby allowing the introduction of R′ substituents that include alkyl, cycloalkyl, or aryl groups. Further diversity can be generated by using phosphines bearing non-identical substituents R′, R″, and R‴. Moreover, the bridgehead R groups can also be subjected to ample modification.



Scheme 1. Synthetic routes for the preparation of triiminophosphoranes.

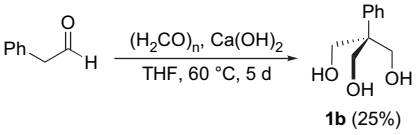
The preparation of *N*-substituted iminophosphoranes can be achieved by the union of suitable nitrogen and phosphorus fragments or via substitution on a more simple phosphazene compound, such as $Ph_3P{=}NH$, using electrophilic reagents.[21] Two major synthetic pathways were devised for the junction of the P=N bond: the Staudinger reaction of tertiary phosphines with organoazides accompanied by elimination of dinitrogen[22] and the Kirsanov reaction[†] of dihalophosphines (R_3PX_2, X=Cl or Br) with primary amines carried out in the presence of an auxiliary base (Scheme 1).[24–27] A few other direct methods were also reported, but they suffer from a lack of generality.[28–30]

Since the reaction of azides with tertiary phosphines usually proceeds smoothly and almost quantitatively without noticeable formation of any side products apart from dinitrogen, the Staudinger reaction has been extensively employed for the high-yield synthesis of a wide variety of iminophosphoranes.[31–33] Thus, we have adopted this method for the imination of two tripodal azides bearing a bridgehead methyl or phenyl R group. These precursors were combined with two representative phosphines possessing different stereo-electronic properties, namely triphenylphosphine (PPh_3) and tricyclopentylphosphine (PCp_3). The whole synthesis was performed through an original multi-step pathway starting from the corresponding triols (Scheme 2).



Scheme 2. Multi-step synthesis of triiminophosphoranes used in this work.

1,1,1-Tris(hydroxymethyl)ethane, the synthetic precursor bearing a methyl group at the bridgehead carbon, was commercially available whereas its phenyl-substituted equivalent had to be synthesized through a Tollens condensation from phenylacetaldehyde and paraformaldehyde in the presence of calcium hydroxide (Eq. 1).[34] This type of condensation is a demanding and poor-yielding reaction, which required refluxing and stirring in THF for five days. Filtration and removal of the solvent, followed by a distillation under reduced pressure (190 °C, 0.05 Torr), afforded the crude triol **1b** as a yellow oil, which solidified at room temperature. Pure α,α,α-tris(hydroxymethyl)toluene was isolated as a white solid after recrystallization from ethyl acetate. To compensate for the low yield (25%), the reaction was carried out on a rather large scale in order to get a sufficient quantity of starting material for the next synthetic steps.



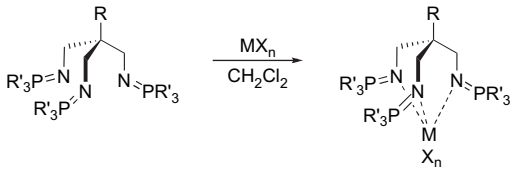
(1)

After this preliminary step, the two triols **1a** and **1b** were converted into the corresponding tritosylates by a nucleophilic substitution reaction with tosyl chloride in pyridine (Scheme 2). Intermediate tritosylates **2a** and **2b** were isolated in high yields as white crystalline solids. Their identity and purity were established by various analytical techniques. They were further reacted with sodium azide in DMSO for 4 h at 90 °C to afford the corresponding triazides **3a** and **3b**. The crude azides were obtained as slightly yellow oils and used immediately after work-up to avoid explosion risks (see Caution in Section 4). Thus, they were not fully characterized. The presence of the azide function in these molecules was, however, ascertained by the presence of a strong absorption band at ca. 2100 cm^{-1} in their IR spectra.[35]

In a final step, the desired iminophosphorane tripodes were obtained via the Staudinger coupling of intermediates **3a**

[†] When studying the reaction of sulfamic acid with phosphorus pentachloride, Kirsanov obtained the first representative of trichlorophosphazosulfanils.[23] The appellation 'Kirsanov reaction' was subsequently employed to designate any reaction between compounds containing a NH_2 group with phosphorus pentachloride or its organic derivatives.

Table 1. Preparation of transition-metal complexes bearing triiminophosphorane ligands



Ligand	Metal source	Complex color	Yield (%)
4a: R=Me, R′=Ph	$NiBr_2$	Blue	71
4a: R=Me, R′=Ph	CuBr	Green	92
4a: R=Me, R′=Ph	$PdCl_2$	Yellow	89
4b: R=Ph, R′=Ph	$NiBr_2$	Blue	96
4b: R=Ph, R′=Ph	CuBr	Yellow	80
4b: R=Ph, R′=Ph	$PdCl_2$	Yellow-green	94
4c: R=Me, R′=Cp	$NiBr_2$	Grey-blue	94
4c: R=Me, R′=Cp	$Cu(OTf)_2$	Green	82
4d: R=Ph, R′=Cp	$NiBr_2$	Blue	97
4d: R=Ph, R′=Cp	$Cu(OTf)_2$	Light green	83

and **3b** with triphenyl- or tricyclopentylphosphine. The latter pyrophoric trialkylphosphine came as a 50 wt % solution in toluene. Both PPh_3 and PCp_3 were further diluted with this solvent before the methyl- and phenyl-capped triazides were added with a cannula. Evolution of dinitrogen was observed as soon as the two reaction partners came into contact, as evidenced from the instantaneous formation of bubbles in solution when the first drops of azides were added to the phosphines. After work-up triiminophosphoranes **4a–d** were obtained in yields comprised between 78 and 98% (see Scheme 2). Compounds **4a** and **4b** prepared from triphenylphosphine were isolated as white powders, whereas tricyclopentylphosphine yielded thick orange oily products **4c** and **4d**. In all cases, overall yields for the three-step synthesis were more than satisfactory.

The four tripodal derivatives **4a–d** were used to prepare some representative transition-metal complexes incorporating the iminophosphorane functionality. These coordination compounds were obtained by reacting an appropriate metal salt with a slight excess of tris(iminophosphorane) ligand in dichloromethane at room temperature. Nickel(II) bromide, copper(II) triflate, copper(I) bromide, and palladium(II) chloride served as metal sources in these experiments. The yields were generally very good, between 80 and 95% (Table 1). The nickel triiminophosphorane complexes were isolated as blue powders, whereas copper and palladium species afforded yellow or yellow-green powders. No crystals suitable for X-ray diffraction analysis could be obtained so far. However, the good solubility of the complexes in organic media, together with the simplicity and symmetry observed in the IR and NMR spectra strongly supports a tridentate mode of coordination and does not suggest formation of either oligomeric or polymeric aggregates.

3. Conclusion and perspectives

Four new tripodal ligands based on the iminophosphorane functionality and several representative transition-metal complexes derived thereof were successfully prepared using a multi-step synthetic pathway based on the Staudinger reaction. Because the methodology adopted is general and affords good overall yields, it could be easily extended to the synthesis of a wide variety of tris(iminophosphorane) ligands bearing different alkyl or aryl substituents.

The catalytic activity of the transition-metal complexes described in this work has been investigated. We recently reported on the use of copper(II) tris(iminophosphorane) species as catalysts for olefin cyclopropanation with ethyl diazoacetate.[36] Nickel, palladium, and iron complexes were screened in ethylene polymerization reactions using high throughput techniques. The results of these experiments will be reported in a forthcoming article.

4. Experimental section

4.1. General information

All manipulations were carried out under an atmosphere of argon using standard Schlenk and cannula techniques. Argon was purified by passage through columns of BASF R3-11 catalyst and 4 Å molecular sieve. Solvents were refluxed over appropriate drying agents and kept under argon. ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX 400 spectrometer operating at 400.13 and 100.62 MHz, respectively, with TMS as internal standard. FTIR spectra were recorded on a Perkin–Elmer FTIR 1720X instrument. Melting points (mp) were determined with an Electrothermal 9100 apparatus and are not corrected. Elemental analyses were performed by Solvay S.A., Brussels. Tricyclopentylphosphine (50 wt % solution in toluene) was a gift from Cytec. All the other chemicals were purchased from Aldrich.

4.2. Ligand synthesis

4.2.1. Synthesis of α,α,α-tris(hydroxymethyl)toluene (1b). A suspension of phenylacetaldehyde (107 g, 0.90 mol), paraformaldehyde (168 g, 5.60 mol) and calcium hydroxide (52 g, 0.70 mol) in THF (600 mL) was stirred at 60–65 °C for 5 days. After cooling to room temperature, the reaction mixture was filtered through Celite and the solvent was removed on a rotary evaporator. Vacuum distillation (180–190 °C, 0.05 Torr) yielded a yellow oil, which crystallized after a weekend at room temperature. Pure α,α,α-tris(hydroxymethyl)toluene was obtained as a white solid after recrystallization from ethyl acetate. Yield: 25%, mp: 81–82 °C, lit. 80–81 °C.[34] ^1H NMR (CD_2Cl_2): δ=2.25 (s, 3H, OH), 4.04 (d, 6H, CH_2), 7.30–7.40 (m, 5H, phenyl) ppm. ^{13}C NMR (CD_2Cl_2): δ=66.6 (CH_2), 126.9 (phenyl), 127.0 (phenyl), 128.7 (phenyl), 139.8 (phenyl) ppm. FTIR (KBr): $\bar{\nu}$ = 3245 (br), 2948, 1600, 1579, 1445, 1240, 1154, 1123, 1039, 881, 840, 766, 702, 572 cm^{-1}.

4.2.2. Synthesis of α,α,α-tris[(4-tolylsulfonyl)methyl]ethane (2a). α,α,α-Tris(hydroxymethyl)ethane (6 g, 0.05 mol) was dissolved in pyridine (100 mL). The solution was cooled in an ice-water bath and tosyl chloride (46 g, 0.225 mol) was added portionwise in 30 min. The solution became yellow and a precipitate of pyridinium chloride appeared progressively. The mixture was stirred for 2 h at 0 °C, then for one night at room temperature. It was slowly poured into a mixture

of water (250 mL), methanol (500 mL), and concentrated hydrochloric acid (200 mL) with stirring. The resulting suspension was filtered on a Büchner funnel and the precipitate was washed with water and methanol (a few mL). It was dried under vacuum. After recrystallization from *n*-propanol, the pure product was isolated as a white solid. Yield: 90%, mp: 101–103 °C. ^{1}H NMR (CD_2Cl_2): δ=0.86 (s, 3H, CH_3 head of the bridge), 2.46 (s, 9H, CH_3 tosyl), 3.75 (s, 6H, CH_2), 7.38 (d, 6H, phenyl), 7.70 (d, 6H, phenyl) ppm. ^{13}C NMR (CD_2Cl_2): δ=15.8 (CH_3 bridgehead), 21.3 (CH_3 tosyl), 39.3 (C), 69.8 (CH_2), 128.8 (aryl), 129.9 (aryl), 132 (aryl), 145 (aryl) ppm. FTIR (KBr): $\overline{\nu}$ = 3050, 2963, 2922, 1926, 1657, 1600, 1495, 1458, 1358, 1307, 1293, 1178, 1098, 1039, 1007, 986, 963, 868, 838, 814, 790, 705, 669, 601, 557, 532, 494 cm^{-1}.

4.2.3. Synthesis of α,α,α-tris[(4-tolylsulfonyl)methyl]-toluene (2b). α,α,α-Tris(hydroxymethyl)toluene (9.1 g, 0.05 mol) was dissolved in pyridine (100 mL). The solution was cooled in an ice-water bath and tosyl chloride (34.4 g, 0.18 mol) was added portionwise in 30 min. A precipitate of pyridinium chloride appeared progressively. The suspension was stirred overnight at 4 °C. It was then heated for 1 h at 30 °C and poured into cold water (500 mL) with stirring. The mixture was filtered on a Büchner funnel and the solid was washed with diethyl ether (3×30 mL). It was dissolved in chloroform (300 mL). The resulting solution was dried over Na_2SO_4 and filtered. Upon addition of ethanol (700 mL) a white solid precipitated overnight. It was filtered and dried under vacuum to afford the title compound. Yield: 82%, mp: 140–141 °C. ^{1}H NMR (CD_2Cl_2): δ=2.45 (s, 9H, CH_3), 4.18 (s, 6H, CH_2), 6.95 (d, 2H, phenyl), 7.20 (m, 3H, phenyl), 7.25 (m, 1H, phenyl), 7.32 (d, 6H, tosyl), 7.62 (d, 6H, tosyl) ppm. ^{13}C NMR (CD_2Cl_2): δ=21.4 (CH_3), 46.0 (C), 68.8 (CH_2), 126.1 (phenyl), 127.8 (tosyl), 128.0 (phenyl), 128.8 (phenyl), 130.0 (tosyl), 131.7 (tosyl), 134.9 (phenyl), 145.5 (tosyl) ppm. FTIR (KBr): $\overline{\nu}$ = 3062, 2924, 1598, 1494, 1472, 1402, 1362, 1295, 1191, 1177, 1097, 987, 959, 875, 850, 814, 788, 761, 732, 694, 671, 617, 590, 552, 531 cm^{-1}.

4.2.4. Synthesis of α,α,α-tris(azidomethyl)ethane (3a). A solution of α,α,α-tris[(4-tolylsulfonyl)methyl]ethane (1.16 g, 2 mmol) and sodium azide (1.17 g, 18 mmol) in DMSO (20 mL) was stirred at 90 °C for 4 h. After cooling to room temperature, the reaction mixture was poured into cold water (100 mL). The aqueous solution was extracted with diethyl ether (3×100 mL). The combined organic phases were washed with water (2×100 mL), dried over $MgSO_4$, and concentrated on a rotary evaporator. The residual oil was used without further purification for the next step. A strong absorption band at 2104 cm^{-1} in the infrared spectrum confirmed the presence of an azide. Caution: While most azides can be handled without incident, some members of this class of compounds are explosive. Hence, prudent practice should be scrupulously adhered to in the laboratory.

4.2.5. Synthesis of α,α,α-tris(azidomethyl)toluene (3b). The procedure described above was followed starting from α,α,α-tris[(4-tolylsulfonyl)methyl]toluene (1.29 g, 2 mmol) and sodium azide (1.17 g, 18 mmol). The residual oil was used without further purification for the next step. A strong absorption band at 2104 cm^{-1} in the infrared spectrum confirmed the presence of an azide. Yield: 0.69 g (86%). FTIR (NaCl): $\overline{\nu}$ = 3020, 2104, 1598, 1447, 1365, 1216, 1174, 757, 669 cm^{-1}.

4.2.6. Synthesis of α,α,α-tris(triphenylphosphine-iminophosphorane)ethane (4a). Triphenylphosphine (2.93 g, 11.1 mmol) was dissolved in dry toluene (15 mL) and heated to 60 °C in an oil bath. To this solution, α,α,α-tris(azidomethyl)ethane (0.66 g, 3.381 mmol) in dry toluene (15 mL) was added dropwise in 30 min with a cannula. Gas emission occurred as soon as the azide was added. The mixture was stirred overnight at 60 °C and then cooled to room temperature. The solution turned slightly yellow. After removal of the solvent under vacuum, a white solid was obtained. It was washed with pentane (3×10 mL) and dried under vacuum. This crude product was recrystallized from benzene–hexane, filtered under an inert atmosphere, and washed again with dry pentane (3×5 mL) to afford the title compound as a white solid. Yield: 80%, mp: 140 °C. ^{1}H NMR ($CDCl_3$): δ=0.82 (s, 3H, CH_3), 2.9–3.2 (m, 6H, CH_2), 7.36–7.66 (m, 45H, phenyl) ppm. ^{13}C NMR (C_6D_6): δ=22.4 (CH_3), 51.2 (CH_2), 51.7 (CH_2), 52.3 (CH_2), 131–137 (phenyl) ppm. ^{31}P NMR (CD_2Cl_2): δ=28.1 ppm. FTIR (KBr): $\overline{\nu}$ = 3064, 3045, 2949, 2911, 2834, 2795, 1476, 1431, 1226, 1104, 1027, 989, 874, 752, 694, 515 cm^{-1}. Elemental analysis (%) calcd for $C_{59}H_{54}N_3P_3$ (898.02): C 78.91, H 6.06, N 4.68; found C 79.2, H 5.8, N 5.1.

4.2.7. Synthesis of α,α,α-tris(triphenylphosphine-iminophosphorane)toluene (4b). This product was obtained as a white solid according to the procedure described above starting from triphenylphosphine (2.33 g, 8.85 mmol) and α,α,α-tris(azidomethyl)toluene (0.69 g, 2.682 mmol). It was kept under an inert atmosphere. Yield: 98%, mp: 92 °C. ^{1}H NMR ($CDCl_3$): δ=3.25–3.65 (m, 6H, CH_2), 7.04–7.58 (m, 50H, phenyl) ppm. ^{31}P NMR (CD_2Cl_2): δ=27.7 ppm. FTIR (KBr): $\overline{\nu}$ = 3051, 2840, 2802, 1585, 1482, 1431, 1232, 1181, 694, 521 cm^{-1}. Elemental analysis (%) calcd for $C_{64}H_{56}N_3P_3$ (960.09): C 80.07, H 5.88, N 4.38; found C 80.9, H 5.5, N 4.4.

4.2.8. Synthesis of α,α,α-tris(tricyclopentylphosphine-iminophosphorane)ethane (4c). A 50 wt % solution of tricyclopentylphosphine in toluene (4.4 g, 9.29 mmol) was diluted with dry toluene (15 mL) and heated to 60 °C in an oil bath. To this solution, α,α,α-tris(azidomethyl)ethane (0.55 g, 2.817 mmol) in dry toluene (15 mL) was added dropwise in 30 min with a cannula. Gas emission occurred as soon as the azide was added. The mixture was stirred overnight at 60 °C and then cooled to room temperature. The solution turned slightly yellow. A small portion of charcoal was added and the mixture was heated to 60 °C for 4 h. It was then filtered through Celite at room temperature under an inert atmosphere. Removal of the solvent under vacuum afforded an orange oil that was further dried under vacuum. Yield: 78%. ^{1}H NMR (C_6D_6): δ=0.33 (s, 3H, CH_3), 1.5–2.03 (m, 81H, cyclopentyl), 3.56 (d, 6H, CH_2) ppm. FTIR (NaCl): 2949, 2866, 2789, 1655, 1450, 1256, 1155, 1123, 1046, 899, 861, 790, 720 cm^{-1}. Elemental analysis (%) calcd for $C_{50}H_{90}N_3P_3$ (826.20): C 72.69, H 10.98, N 5.09; found C 73.1, H 11.7, N 4.8.

4.2.9. Synthesis of α,α,α-tris(tricyclopentylphosphine-iminophosphorane)toluene (4d). This product was

obtained as an orange oil according to the procedure described above starting from 50 wt % solution of tricyclopentylphosphine in toluene (4.35 g, 9.11 mmol) and α,α,α-tris(azidomethyl)toluene (0.71 g, 2.76 mmol). Yield: 1.94 g (79%). ^{1}H NMR (CD_2Cl_2): δ=1.60–2.48 (m, 81H, cyclopentyl), 3.55 (d, 6H, CH_2), 7.24 (t, 1H, *para*-CH phenyl), 7.35 (t, 2H, *meta*-CH phenyl), 7.76 (d, 2H, *ortho*-CH phenyl) ppm. ^{13}C NMR (CD_2Cl_2): δ=27.1 (C3 cyclopentyl), 28.2 (C2 cyclopentyl), 34.6 (C1 cyclopentyl), 37.8 (CH_2), 38.4 (CH_2), 47.8 (CH_2), 50.0 (C), 127.8 (phenyl), 128.8 (phenyl), 130.2 (phenyl), 141.3 (phenyl) ppm. FTIR (NaCl): $\overline{\nu}$ = 3043, 2951, 2865, 1658, 1595, 1493, 1448, 1262, 1227, 1176, 1121, 1057, 1030, 906, 761, 729, 697 cm^{-1}.

4.3. Representative examples for the synthesis of metal complexes

4.3.1. Synthesis of CH_3–C(CH_2–N=PCp_3)$_3$–$NiBr_2$. A solution of α,α,α-tris(tricyclopentylphosphine-iminophosphorane)ethane (0.512 g, 0.6 mmol) in dry CH_2Cl_2 (10 mL) was added with a cannula under an inert atmosphere to a suspension of dimethoxyethane nickel bromide complex (0.16 g, 0.5 mmol) in dry CH_2Cl_2 (20 mL) and the reaction mixture was stirred for 16 h at room temperature. The initially orange suspension turned brown and then to green. The solvent was evaporated under vacuum and the remaining blue-grey solid was washed with dry diethyl ether (3×10 mL) and dried under vacuum. Yield: 0.5 g (94%). ^{1}H NMR (CD_2Cl_2): δ=1.13 (s, 3H, CH_3), 1.39–3.1 (m, 72H, CH_2 cyclopentyl), 3.28 (s, 9H, CH cyclopentyl), 4.00 (s, 6H, CH_2) ppm. ^{13}C NMR (CD_2Cl_2): δ=17.8 (CH_3), 27.2 (C3 and C4 cyclopentyl), 28.5 (C2 and C5 cyclopentyl), 30.2 (CH_2), 33.1 (CH_2), 34.5 (CH_2), 38.4 (d, C1 cyclopentyl) ppm. ^{31}P NMR (CD_2Cl_2): δ=64.9 ppm. FTIR (KBr): $\overline{\nu}$ = 3090, 2949, 2866, 1623, 1450, 1380, 1296, 1258, 1091, 1002, 944, 912, 598, 521 cm^{-1}. Elemental analysis (%) calcd for $C_{50}H_{90}Br_2N_3NiP_3$ (1044.70): C 57.42, H 8.68, N 4.02; found C 56.4, H 8.4, N 3.8.

4.3.2. Synthesis of Ph–C(CH_2–N=PCp_3)$_3$–$Cu(OTf)_2$. A solution of α,α,α-tris(tricyclopentylphosphine-iminophosphorane)toluene (0.422 g, 0.56 mmol) in dry CH_2Cl_2 (15 mL) was added to a solution of copper(II) triflate (0.143 g, 0.47 mmol) in dry CH_2Cl_2 (10 mL). The solution became green instantaneously. The reaction mixture was stirred for 18 h at room temperature, during that period of time the copper salt had completely disappeared. The solvent was evaporated under vacuum and the resulting solid was washed with diethyl ether (5×10 mL) and dried under vacuum to afford a light green powder. Yield: 0.41 g (83%). ^{1}H NMR (CD_2Cl_2): δ=1.65–1.91 (m, 72H, CH_2 cyclopentyl), 2.39 (s, 9H, CH cyclopentyl), 3.50 (s, 6H, CH_2), 7.36–7.52 (m, 5H, CH phenyl) ppm. ^{13}C NMR (CD_2Cl_2): δ=27.2 (C3 cyclopentyl), 28.6 (C4 cyclopentyl), 35.1 (C2 cyclopentyl), 35.7 (C5 cyclopentyl), 37.9 (CH_2), 38.6 (CH_2), 48.6 (CH_2), 52.76 (C1 cyclopentyl), 123.5 (C5 aromatic), 128.5 (C2 aromatic), 129.2 (C3 aromatic), 129.5 (C3 aromatic), 142.1 (C1 aromatic) ppm. FTIR (KBr): $\overline{\nu}$ = 3056, 2959, 2871, 1451, 1384, 1260, 1222, 1151, 1099, 1030, 911, 703, 637, 572, 516 cm^{-1}. Elemental analysis (%) calcd for $C_{57}H_{92}CuF_6N_3O_6P_3S_2$ (1249.96): C 54.77, H 7.42, N 3.36; found C 53.9, H 6.9, N 3.0.

4.3.3. Synthesis of CH_3–C(CH_2–N=PCp_3)$_3$–$Cu(OTf)_2$. This complex was synthesized as described above starting from α,α,α-tris(tricyclopentylphosphine-iminophosphorane)-ethane (0.50 g, 0.60 mmol) and copper(II) triflate (0.18 g, 0.50 mmol). It was isolated as an apple green solid. Yield: 0.49 g (82%). ^{1}H NMR (CD_2Cl_2): δ=1.07 (s, 3H, CH_3), 1.73–2.51 (m, 81H, cyclopentyl), 3.02 (s, 6H, CH_2) ppm. ^{13}C NMR (CD_2Cl_2): δ=20.0 (s, CH_3), 27.0 (C3 cyclopentyl), 28.6 (C4 cyclopentyl), 34.9 (C5 cyclopentyl), 35.5 (C2 cyclopentyl), 37.9 (CH_2), 38.6 (CH_2), 41.6 (CH_2) ppm. ^{31}P NMR (CD_2Cl_2): δ=53.0 ppm. FTIR (KBr): $\overline{\nu}$ = 2955, 2866, 1444, 1380, 1258, 1219, 1149, 1085, 1027, 906, 637, 515 cm^{-1}. Elemental analysis (%) calcd for $C_{52}H_{90}CuF_6N_3O_6P_3S_2$ (1073.90): C 52.58, H 7.64, N 3.54; found C 51.9, H 7.0, N 3.1.

4.3.4. Synthesis of Ph–C(CH_2–N=PPh_3)$_3$–CuBr. This complex was synthesized as described above from α,α,α-tris(triphenylphosphine-iminophosphorane)toluene (0.22 g, 0.23 mmol) and copper(I) bromide (0.03 g, 0.21 mmol). It was isolated as a yellow solid. Yield: 0.19 g (80%). ^{1}H NMR (CD_2Cl_2): δ=1.68 (s, 2H, CH_2), 1.91 (s, 2H, CH_2), 2.05 (s, 2H, CH_2), 7.46–7.65 (m, 50H, aromatic) ppm. ^{13}C NMR (CD_2Cl_2): δ=24.1 (CH_2), 27.38 (CH_2), 33.1 (CH_2), 126.0 (C4 phenyl), 129.5 (C3 and C5 phosphine), 130.8 (C3 and C5 phenyl), 132.8 (C2 and C6 phosphine), 133.4 (C2 and C6 phenyl), 134.4 (C4 phosphine), 136.1 (C1 phosphine) ppm. FTIR (KBr): $\overline{\nu}$ = 3051, 2956, 2920, 2847, 1674, 1588, 1481, 1436, 1259, 1182, 1108, 1027, 997, 919, 803, 747, 720, 694, 542, 523 cm^{-1}. Elemental analysis (%) calcd for $C_{64}H_{56}BrCuN_3P_3$ (1103.54): C 69.66, H 5.11, N 3.81; found C 69.0, H 4.8, N 3.81.

4.3.5. Synthesis of CH_3–C(CH_2–N=PPh_3)$_3$–CuBr. This compound was synthesized as described above from α,α,α-tris(triphenylphosphine-iminophosphorane)ethane (0.3 g, 0.33 mmol) and copper(I) bromide (0.04 g, 0.28 mmol). It was isolated as a paramagnetic green solid. Yield: 0.29 g (92%). ^{1}H NMR (CD_2Cl_2): δ=0.95 (s, 3H, CH_3), 2.55–3.11 (broad m, 6H, CH_2), 7.48–7.67 (m, 45H, phenyl) ppm. ^{31}P NMR (CD_2Cl_2): δ=27.0 ppm. FTIR (KBr): $\overline{\nu}$ = 3050, 2963, 2810, 1587, 1481, 1435, 1306, 1259, 1179, 1108, 1027, 997, 932, 862, 801, 747, 713, 693, 553, 522 cm^{-1}. Elemental analysis (%) calcd for $C_{59}H_{54}BrCuN_3P_3$ (1041.47): C 68.04, H 5.23, N 4.03; found C 67.5, H 4.8, N 4.4.

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