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Functionalized phosphorus analogues of the β-diketiminato ligand systems: bis(*N*-arylphosphinimino)acetonitrile-derived complexes of rhodium and iridium†

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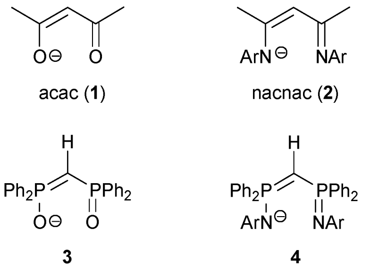
Staudinger reaction of dppm-CN (**5**) gave the corresponding bis(*N*-phenylphosphinimino)acetonitrile system (**6**). Deprotonation with LDA furnished the corresponding anionic ligand **9**. Its reaction with [(CO)$_2$RhCl]$_2$ gave the corresponding $\kappa^2 N,N'$-chelate complex **11**. X-Ray diffraction revealed a non-planar boat-like conformation of the six-membered chelate ring in the crystal. Treatment of **9** with [(nbd)RhCl]$_2$ gave the six-membered chelate complex **12** which features a different twist-like structure in the solid state, as does **13**, which was formed by reacting **9** with [(cod)IrCl]$_2$.

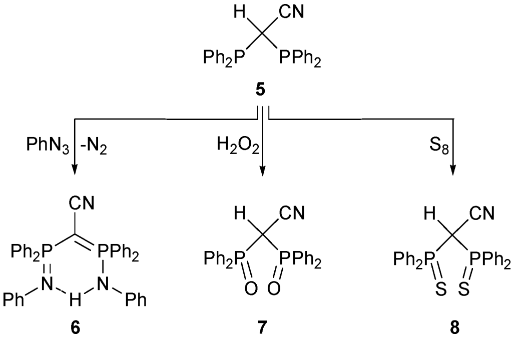
Introduction

Acetylacetonate (acac, **1**) is a frequently used very versatile ligand in transition metal chemistry.[1] A variety of derivatives and analogues have been developed, among them cyclic annulated systems and other heteroatom derivatives.[2] The *N*-arylimino derivatives, the β-diketiminato or "nacnac" ligands (**2**), have found some specific use and interest recently.[3–5] The anions of the P-oxides, P-sulfides and P-imines[6–10] of bis(diphenylphosphino)methane (dppm)[11] might be regarded as heavy relatives of the acac and the nacnac ligand family, respectively (see Scheme 1). We have prepared a series of cyano-functionalized derivatives of these systems.[12] The neutral ligands are probably even more acidic than the parent dppm systems. We have now used the bis(*N*-arylimino)dppm-CN monoanion as a nacnac analogous ligand in transition metal chemistry. We here report about the preparation of first Group 9 metal complexes and describe their structural and conformational features in the solid state.



Scheme 1

This chemistry was initiated with the observation that acetonitrile could readily be converted in a one pot procedure to the neutral chelate ligand bis(diphenylphosphino)acetonitrile (dppm-CN) (**5**) by treatment with base (*n*-BuLi) followed by chlorodiphenylphosphine.[13] We prepared a number of dppm-CN derivatives[14] and dppm-CN metal complexes. The Pd-systems turned out to be very active catalysts *e.g.* in Suzuki–Miyaura coupling reactions.[13] The corresponding P-oxides and P-sulfides (**7**, **8**) were prepared (Scheme 2) and their corresponding mono-lithium derivatives structurally investigated.[15]



Scheme 2

The Staudinger reaction[16] of dppm-CN with phenyl azide gave the corresponding bis-phosphinimine (**6**). It was shown to feature an NH tautomeric form in the crystal and in solution.[15] We have now generated the corresponding mono-anion of **6** and used it for the preparation of the respective Rh and Ir complexes.

Results and discussion

The ligand system (**6**) was prepared by treatment of dppm-CN (**5**) with phenyl azide as previously described by us.[15] Its treatment with LDA in THF gave the corresponding anionic ligand system as its lithium salt (**9**) (Scheme 3). The product was isolated as a very pale yellow solid that contained a little less than one equiv. of THF. The ^{1}H NMR spectrum of **9** (in d$_6$-DMSO) features well resolved and separated sets of signals of the phenyl groups at phosphorus [δ 7.60 (*o*), 7.22 (*p*), 7.09 (*m*)] and at nitrogen [δ 7.05 (*m*), 6.85 (*o*), 6.53 (*p*)]. The ^{13}C NMR resonance of the central

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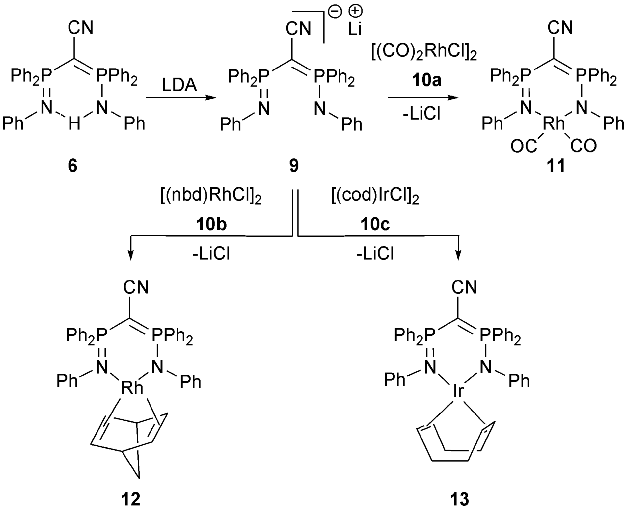
‡ X-Ray crystal structure analyses.



Scheme 3

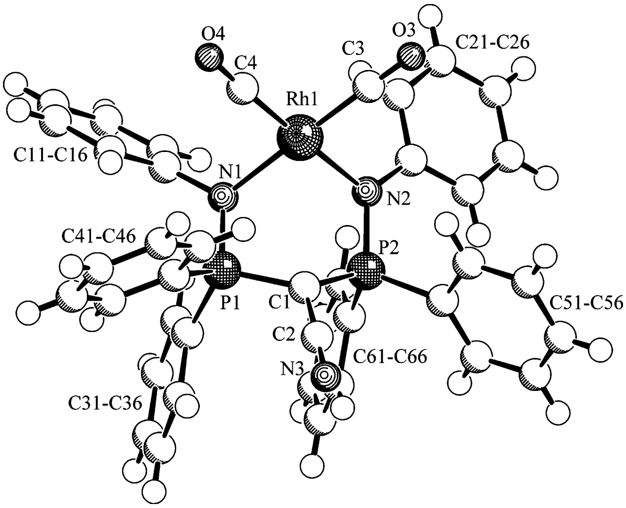


Fig. 1 Molecular structure of complex **11**.

carbon atom C1 is found at δ 18.0 (t, $^1J_{PC}$ = 97.8 Hz). The –CN ^{13}C NMR resonance occurs at δ 128.3. Compound **9** features a prominent ν(CN) IR band at 2159 cm^{-1}. It shows a single ^{31}P NMR resonance at a typical chemical shift of δ +4.8 (in d$_6$-DMSO).[17]

The ligand system **9** was then reacted with the di(carbonyl)-rhodium(I) chloride dimer [(CO)$_2$RhCl]$_2$ (**10a**) in toluene at room temperature. After 12 h the reaction was worked up to give the Rh-chelate complex **11** in 64% yield. The rhodium complex features a ^{31}P NMR signal at δ 29.3 (in CD$_2$Cl$_2$).[18] It shows a single ^{13}C NMR [Rh]-CO resonance at δ 185.1 with a coupling constant of $^1J_{RhC}$ = 69.9 Hz. Carbon atom C1 features a ^{13}C NMR resonance at δ 21.6 with a coupling constant $^1J_{PC}$ = 145.6 Hz, which is markedly larger than observed for the precursor **9** (see above). The cyano (C2) ^{13}C NMR resonance occurs at δ 123.1 with $^2J_{PC}$ = 9.3 Hz. Again the PPh$_2$ and NPh ^{1}H/^{13}C phenyl NMR resonances are nicely separated. They feature a single set of signals for the pairs of phenyl groups at phosphorus indicating rapid conformational equilibration of the framework in solution at ambient temperature (for details see the Experimental section). The Rh-carbonyl complex (**11**) shows a pair of prominent IR *ν*(CO) stretching bands at 2061 cm^{-1} and 1989 cm^{-1}, respectively, which is some 20 wavenumbers lower than was observed for the "classical" [(acac)Rh(CO)$_2$] reference system.[19] Complex **11** features an IR *ν*(CN) band at 2165 cm^{-1}.

Complex **11** was characterized by an X-ray crystal structure analysis (single crystals were obtained from a toluene–pentane mixture at −35 °C). The structure (see Fig. 1) shows that both nitrogen atoms of the monoanionic chelate ligand are bonded to Rh (Rh1–N2: 2.125(2) Å, Rh1–N1: 2.117(2) Å, angle N1–Rh1–N2: 87.6(1)°). The Rh atom features a square-planar coordination environment. It has a pair of *cis*-CO ligands bonded to it (Rh1–C3: 1.846(3) Å, Rh1–C4: 1.846(3) Å, angles C3–Rh1–C4: 88.5(1)°, C4–Rh1–N1: 93.4(1)°, C3–Rh1–N2: 90.5(1)°). The angles at the carbonyl carbon atoms amount to 177.6(3)° (Rh1–C4–O4) and 178.4(4)° (Rh1–C3–O3) (corresponding bond lengths C4–O4: 1.133(4) Å, C3–O3: 1.130(4) Å). The chelate ligand is delocalized but non-planar. It exhibits similar bond lengths for the pair of N–P bonds (N1–P1: 1.617(2) Å, N2–P2: 1.620(2) Å) and also for the pair of adjacent P1/P2–C1 linkages (P1–C1: 1.752(3) Å, P2–C1: 1.746(3) Å).

The overall conformation of the chelate complex six-membered framework is strongly deviating from planarity. It exhibits a pronounced boat-shaped conformation (dihedral angles: Rh1–N2–P2–C1: 3.3(2)°, Rh1–N1–P1–C1: −32.0(2)°, P1–N1 · · · N2–P2: 14.9°, P1–C1–P2–N2: 63.0(2)°, P2–C1–P1–N1: −44.9(2)°, N1–Rh1–N2–P2: −57.9(1)° N2–Rh1–N1–P1: 77.5(1)°). The sums of bond angles at N1 (353.8°) and N2 (359.9°) are close to a trigonal-planar situation. The phosphorus atoms in complex **11** are pseudo-tetrahedrally coordinated (angles N1–P1–C1: 104.8(1)°, C41–P1–C31: 105.4(1)°, N2–P2–C1: 108.3(1)°, C61–P2–C51: 108.8(1)°). The P–N as well as the adjacent P–C bonds inside the non-planar six-membered ring structure are rather short (see above). The coordination geometry of carbon atom C1 deviates only marginally from trigonal-planar (angles P1–C1–P2: 119.5(2)°, P1–C1–C2: 117.6(2)°, P2–C1–C2: 117.9(2)°, Σ 355.0°). The C1–C≡N unit is linear (C1–C2: 1.405(4) Å, C2–N3: 1.140(4) Å, angle C1–C2–N3: 178.1(4)°).

The pronounced boat-shaped conformation of **11** in the solid state places the phenyl groups at each phosphorus atom in markedly different environments. The C41–C46 Ph substituent at P1 (and C51–C56 at P2) is oriented in a pseudo-equatorial position at the framework, whereas the C31–C36 Ph group at P1 and the C61–C66 Ph substituent at P2 are oriented pseudoaxially. We note that the planes of the latter are arranged almost parallel to each other (see Fig. 1).

The reaction of the mono-anionic ligand **9** with [(nbd)RhCl]$_2$ (**10b**) under similar conditions gave the corresponding (κ^2*N*,*N′*-chelate ligand)Rh(I)(nbd) complex **12** (74% isolated). Single crystals of **12** suited for the X-ray crystal structure analysis were obtained from a toluene–pentane mixture at −35 °C. Complex **12** features a six-membered chelate complex framework. The ligand system is κ^2*N*,*N′*-bonded to the Rh center. The Rh atom is pseudo square-planar coordinated by the π-bonds of the norbornadiene ligand and the pair of chelate ligand nitrogen atoms (N1A–Rh1A: 2.124(5) Å [corresponding values of the second independent molecule B are given in square brackets, N1B-Rh1B: 2.132(5) Å], N2A–Rh1A: 2.135(5) Å [2.106(5) Å], angle N1A–Rh1A–N2A: 92.2(2)° [91.9(2)°]). The chelate ligand is delocalized (N1A–P1A: 1.603(5) Å [1.624(5) Å], N2A–P2A: 1.599(5) Å [1.612(5) Å], P1A–C1A 1.741(6) Å [1.740(6) Å], P2A–C1A: 1.749(6) Å [1.742(6) Å]) but it is not planar. In complex **12** the six-membered P_2N_2CRh ring system exhibits a twist conformation (see Fig. 2 and Fig. 3). This orients the phenyl groups of the trigonally-planar P=N nitrogen atoms toward opposite sides of the framework. Carbon atom C1 is also planar-tricoordinate (bond angles P1A–C1A–P2A: 115.8(3)° [115.0(3)°], P1A–C1A–C2A: 122.4(4)° [123.0(5)°], P2A–C1A–C2A: 121.8(4)° [121.9(5)°]). It has the linear CN substituent attached to it (C1A–C2A: 1.402(9) Å [1.394(9) Å], C2A–N3A: 1.144(8) Å [1.168(8) Å], angle C1A–C2A–N3A: 178.0(7)° [179.4(9)°]). The phosphorus atoms in **12** feature a pseudotetrahedral coordination geometry (angles C1A–P2A–N2A: 110.9(3)° [113.0(3)°], C1A–P1A–N1A: 111.6(3)° [109.9(3)°]).

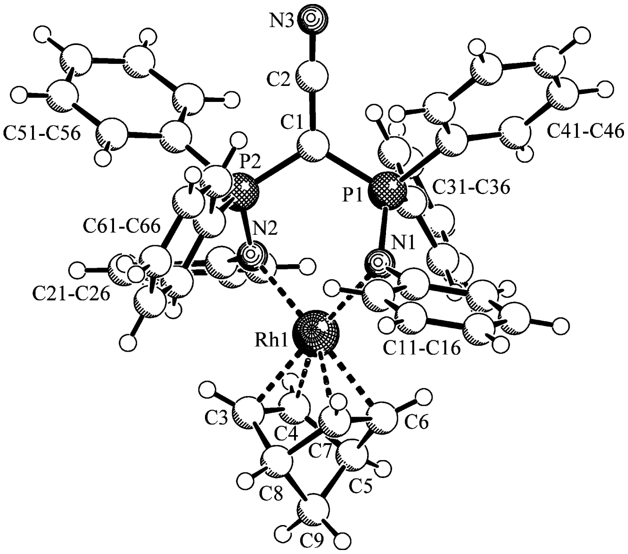


Fig. 2 Molecular geometry of complex **12**.

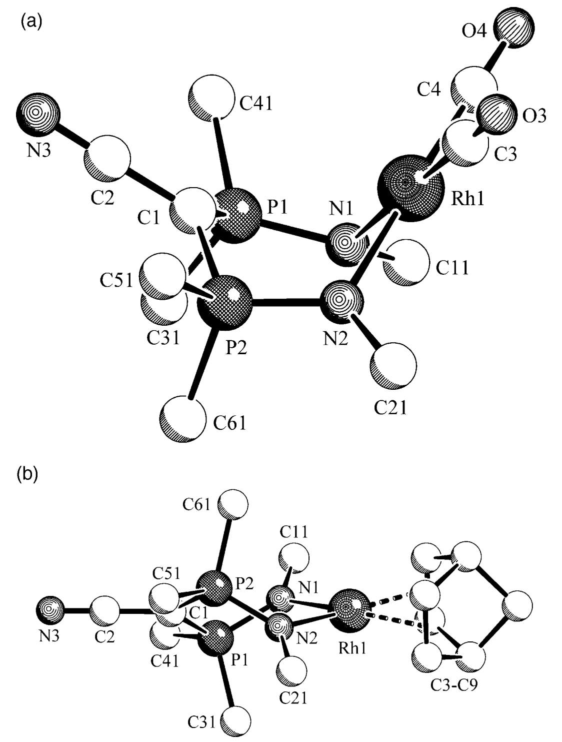


Fig. 3 A comparison of the different conformational frameworks of the κ^2*N*,*N*′-chelate Rh complexes **11** (boat, top) and **12** (twist, bottom).

In solution at room temperature complex **12** features NMR spectra of a rapidly conformationally equilibrating ring system. Consequently we observe a single set of ^{1}H NMR resonances of the two pairs of phenyl substituents at phosphorus and a separate set of signals of the pair of N–Ph groups (for details see the Experimental section). The ^{31}P NMR resonance of complex **12** is at δ 29.4. Complex **12** features a ν(CN) IR band at 2148 cm^{-1}.

We have also reacted an iridium(I) complex with the reagent **9**. Treatment of the (cyclooctadiene)iridium chloride dimer [(cod)IrCl]$_2$ (**10c**) with the lithium salt **9** of the ligand system under the usual conditions gave complex **13** as a yellow solid in 66% yield. Complex **13** was characterized by X-ray diffraction. Single crystals were obtained from a toluene–pentane mixture at −35 °C. The κ^2*N*,*N*′-ligand core of **13** is almost isostructural to that of **12**. It features *cis*-coordination of the pair of nitrogen ligands to iridium (N1–Ir: 2.122(2) Å, N2–Ir: 2.136(2) Å, angle N1–Ir–N2: 90.2(1)°). The metal center features a pseudo square-planar coordination environment. The chelate ligand is electronically degenerate; it features similar bond lengths for the pairs of P–N and P–C1 vectors (P1–N1: 1.626(2) Å/P2–N2: 1.618(2) Å; P1–C1: 1.744(3) Å/P2–C1: 1.738(3) Å). The six-membered chelate complex framework exhibits a twist conformation (see Fig. 4).

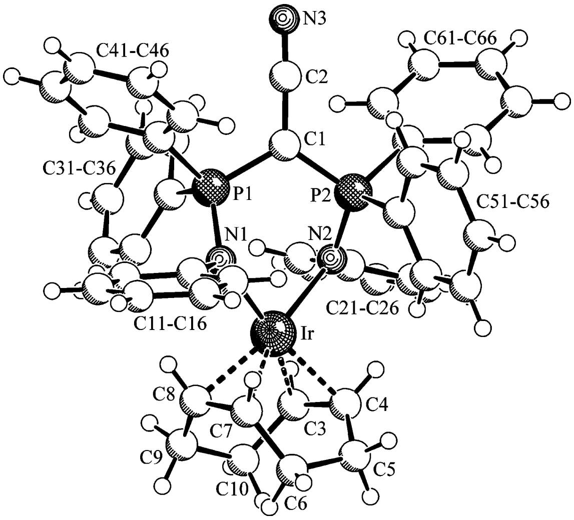


Fig. 4 A view of the molecular structure of the iridium complex **13**. Selected bond lengths (Å) and angles (°): Ir–N1 2.122(2), Ir–N2 2.136(2), Ir–C3 2.124(3), Ir–C4 2.119(3), Ir–C7 2.125(3), Ir–C8 2.126(3), N1–P1 1.626(2), N2–P2 1.618(2), P1–C1 1.744(3), P2–C1 1.738(3), C1–C2 1.398(4), C2–N3 1.158(4), N1–C11 1.429(3), N2–C21 1.439(3), P1–C31 1.819(3), P1–C41 1.805(3), P2–C51 1.808(3), P2–C61 1.814(3), C3–C4 1.411(4), C4–C5 1.511(4), C5–C6 1.512(4), C6–C7 1.513(4), C7–C8 1.400(4), C8–C9 1.509(4), C9–C10 1.519(5), C10–C3 1.518(5); N1–Ir–N2 90.2(1), Ir–N1–P1 119.7(1), Ir–N1–C11 121.9(2), C11–N1–P1 118.3(2), N1–P1–C1 112.4(1), N1–P1–C31 110.5(1), N1–P1–C41 111.1(1), C1–P1–C31 109.9(1), C1–P1–C41 106.1(1), P1–C1–P2 115.9(2), P1–C1–C2 119.9(2), P2–C1–C2 124.0(2), C1–C2–N3 178.1(3), C1–P2–N2 111.0(1), C1–P2–C51 110.4(1), C1–P2–C61 107.2(1), N2–P2–C51 110.4(1), N2–P2–C61 112.7(1), P2–N2–Ir 122.2(1), P2–N2–C21 118.3(2), Ir–N2–C21 119.3(2), for additional values see the text.

At room temperature in solution (CD$_2$Cl$_2$) complex **13** shows NMR spectra of a conformationally equilibrating system (for details see the Experimental section). The ^{1}H NMR spectrum of the cod ligand thus features only a set of three resonances at δ 2.95 (m, 4H, -CH=CH-) and δ 2.00/1.24 (each m, Σ 8H, -CH$_2$–CH$_2$-). The ^{13}C NMR C1 resonance was located at δ 24.6 (t) with a coupling constant of $^{1}J_{PC}$ = 130.7 Hz. The corresponding C2 (*i.e.* –CN) carbon NMR signal occurs at δ 124.1 (t, $^{2}J_{PC}$ = 7.9 Hz).[15] Complex **13** features a prominent ν(CN) IR stretching band at 2154 cm^{-1}.

Conclusions

We conclude that the mono-anionic ligand system **9** readily forms κ^2N,N'-chelate complexes of the Group 9 metals Rh and Ir. The resulting complexes are thermally very stable. Some of them can even be handled for short periods of time in air without appreciable decomposition. Thus, the new ligand system seems to be similarly versatile and potentially useful as its acac or nacnac congeners. Moreover, the ligand system **9** is readily available due to the simple one-pot procedure of the formation of the precursor dppm-CN (**5**). The metal complexes of the parent bis(phosphinimino)methanide ligand (**4**, see Scheme 1) show a variety of complex modes, ranging from κ^2N,N' through κ^2C,N to κ^3C,N,N' coordination. It seems that the new mono-anionic dppm-CN ligand in **9** is less C-nucleophilic as compared to the parent **4**, which is probably due to the carbanion stabilization by the attached CN substituent. Consequently, in all three complexes studied here, the metal to C1 separations are rather large (**11**: Rh$\cdots$C1 3.032 Å, **12**: Rh$\cdots$C1 3.772 Å [3.793 Å], **13**: Ir$\cdots$C1 3.843 Å) and probably outside of a range of any strong direct interaction. The frameworks of the newly prepared six-membered chelate complexes (**11** to **13**) are distinctively non-planar which is similar to the κ^2N,N' metal complexes of **4**.[7–10,20] They may adopt a pronounced boat conformation (as observed for **11**) or favour twist-like conformational arrangements, as was observed for **12** or **13**. We shall see in the future what advantages this new functionalized chelate ligand might have in applications in organometallic chemistry and catalysis.

Experimental

General

All reactions were carried out in an inert atmosphere (argon) in Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under argon prior use. Bis(*N*-phenyphosphinimino)acetonitrile (**6**) was prepared using the known procedure.[15] The following instruments were used for the physical characterization of the compounds. NMR: Bruker AC 200 P-FT (^{31}P: 81.0 MHz), Varian Inova 500 (^{1}H: 499.8 MHz, ^{13}C: 125.7 MHz), Unity Plus 600 (^{1}H: 599.9 MHz, ^{13}C: 150.8 MHz). Most NMR assignments were supported by additional 2D experiments. Melting points: DSC 2010 (TA-Instrument). IR: Varian 3100 FT-IR spectrometer. Elemental analysis: Elementar Vario El III.

Deprotonation reaction of compound 6, formation of 9

A solution of **6** (568 mg, 960 mmol) and lithium diisopropylamide (97 mg, 960 mmol) in tetrahydrofuran (60 ml) was stirred overnight at room temperature. The solvent was removed *in vacuo* and the residue washed with pentane (three times, 30 ml each). The solid light-yellow product was dried *in vacuo* (485 mg, 77%). Mp: 129 °C (DSC); Found: C, 74.79; H, 5.65; N, 6.23. Calc. for $C_{38}H_{30}LiN_3P_2\cdot3/4thf$: C, 75.57; H, 5.57; N, 6.45%); ν_{max}(KBr)/cm^{-1} 3054, 3006, 2972, 2873, 2159, 1590, 1483, 1436, 1288, 1262, 1205, 1179, 1106, 1036, 1012, 746, 717 and 693; δ_H(499.8 MHz; d$_6$-DMSO; 298 K) 7.60 (m, 8H, *o*-Ph^P), 7.22 (m, 4H, *p*-Ph^P), 7.09 (m, 8H, *m*-Ph^P), 7.05 (m, 4H, *m*-Ph^N), 6.85 (m, 4H, *o*-Ph^N), 6.53 (m, 2H, *p*-Ph^N), 3.59 (m, 3H, α-THF) and 1.75 (m, 3H, β-THF); δ_C(125.7 MHz; d$_6$-DMSO; 298 K) 153.6 (s, *i*-Ph^N), 135.3 (pd, $^{1}J_{PC}$ + $^{3}J_{PC}$ = 117.9 Hz, *i*-Ph^P), 132.3 (m, *o*-Ph^P), 129.5 (s, *p*-Ph^P), 128.3 (br. m, C2), 128.1 (s, *m*-Ph^N), 127.0 (m, *m*-Ph^P), 123.6 (m, *o*-Ph^N), 114.4 (s, *p*-Ph^N), 67.0 (s, α-THF), 25.1 (s, β-THF) and 18.0 (t, $^{1}J_{PC}$= 97.8 Hz, C1); $\delta_{P\{1H\}}$(81.0 MHz; d$_6$-DMSO; 298 K) 4.8 (s, $\nu_{1/2}$ = 11.9 Hz).

General procedure for the synthesis of the complexes 11, 12, and 13

Either [(CO)$_2$RhCl]$_2$ (**10a**) or [(nbd)RhCl]$_2$ (**10b**) or [(cod)IrCl]$_2$ (**10c**) (93.3 μmol, 0.5 equiv.) was added to a suspension of compound **9** (186.6 μmol, 1.0 equiv.) in toluene (15 ml). This reaction mixture was stirred for 12 hours at room temperature. Subsequently the insoluble LiCl was filtered off, the solvent removed *in vacuo* and the solid washed with pentane (three times, 6 ml each). The resulting yellow solid was dried *in vacuo*.

Reaction of compound 9 with di(carbonyl)rhodium chloride dimer (10a), preparation of complex 11

A mixture of **9** (118 mg, 186 μmol) and [(CO)$_2$RhCl]$_2$ (**10a**) (36 mg, 93 μmol) in toluene (15 ml) yielded the yellow, air-stable product **11** (90 mg, 64%). Mp: >200 °C (DSC); Found: C, 63.30; H, 4.03; N, 5.13. Calc. for $C_{40}H_{30}N_3O_2P_2Rh$: C, 64.10; H, 4.03; N, 5.61%; ν_{max}(KBr)/cm^{-1} 3057, 2165, 2061, 1989, 1589, 1483, 1435, 1259, 1175, 1102, 1009, 989, 803, 721 and 690; δ_H(499.8 MHz; CD$_2$Cl$_2$; 298 K) 7.71 (m, 8H, *o*-Ph^P), 7.48 (m, 4H, *p*-Ph^P), 7.33 (m, 8H, *m*-Ph^P), 7.12 (m, 4H, *o*-Ph^N), 7.02 (m, 4H, *m*-Ph^N) and 6.84 (m, 2H, *p*-Ph^N); δ_C(125.7 MHz; CD$_2$Cl$_2$; 298 K) 185.1 (d, $^{1}J_{RhC}$ = 69.9 Hz, Rh-*C*O), 152.0 (s, *i*-Ph^N), 133.2 (m, *o*-Ph^P), 132.3 (m, *p*-Ph^P), 129.2 (pd, $^{1}J_{PC}$ + $^{3}J_{PC}$ = 95.1 Hz, *i*-Ph^P), 128.8 (m, *m*-Ph^P), 128.8 (s, *m*-Ph^N), 124.4 (m, *o*-Ph^N), 123.1 (t, $^{2}J_{PC}$ = 9.3 Hz, C2), 121.5 (s, *p*-Ph^N), and 21.6 (t, $^{1}J_{PC}$ = 145.6 Hz, C1); $\delta_{P\{1H\}}$(81.0 MHz; CD$_2$Cl$_2$; 298 K) 29.3 (s, $\nu_{1/2}$ = 2.3 Hz). Crystal data for $C_{40}H_{30}N_3O_2P_2Rh$, M = 749.52, monoclinic, space group $P2_1/c$ (No. 14), a = 9.8125(2), b = 20.4272(5), c = 17.5318(2) Å, β = 102.278(2)°, V = 3433.73(12) Å^3, D_c = 1.450 g cm^{-3}, μ = 0.631 mm^{-1}, Z = 4, λ = 0.71073 Å, T = 198(2) K, 22757 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.66 Å^{-1}, 8114 independent (R_{int} = 0.056), and 5740 observed reflections [$I \geq 2\sigma(I)$], 433 refined parameters, R = 0.044, wR^2 = 0.100. CCDC 676924.†

Reaction of compound 9 with (norbornadiene)rhodium chloride dimer (10b), preparation of complex 12

A mixture of the lithium salt **9** (118 mg, 186 μmol) and [(nbd)RhCl]$_2$ (**10b**) (43 mg, 93 μmol) in toluene (15 ml) formed the yellow, air-stable product **12** (109 mg, 74%). Mp: >200 °C (DSC); Found: C, 68.11; H, 5.11; N, 5.14. Calc. for $C_{45}H_{38}N_3P_2Rh$: C, 68.79; H, 4.88; N, 5.35%; ν_{max}(KBr)/cm^{-1} 3054, 3003, 2953, 2908, 2851, 2148, 1588, 1482, 1435, 1257, 1233, 1196, 1107, 1010, 986, 803, 745 and 668; δ_H(599.6 MHz; CD_2Cl_2; 298 K) 7.93 (m, 8H, *o*-Ph^P), 7.55 (m, 4H, *p*-Ph^P), 7.47 (m, 8H, *m*-Ph^P), 6.76 (m, 4H, *m*-Ph^N), 6.63 (m, 2H, *p*-Ph^N), 6.16 (m, 4H, *o*-Ph^N), 3.44 (m, 2H, 5,8-H), 2.78 (m, 4H, 3,4,6,7-H) and 0.94 (m, 2H, 9-H); δ_C(125.7 MHz; CD_2Cl_2; 298 K) 149.3 (s, *i*-Ph^N), 133.8 (m, *o*-Ph^P), 132.9 (pd, $^1J_{PC}$ + $^3J_{PC}$ = 102.4 Hz, *i*-Ph^P), 131.9 (s, *p*-Ph^P), 128.5 (m, *o*-Ph^N), 128.4 (m, *m*-Ph^P), 127.7 (s, *m*-Ph^N), 124.6 (t, $^2J_{PC}$ = 9.4 Hz, C2), 121.5 (s, *p*-Ph^N), 61.3 (d, $^3J_{RhC}$ = 7.0 Hz, C9), 52.5 (d, $^1J_{RhC}$ = 10.6 Hz, C3,4,6,7), 49.0 (d, $^2J_{RhC}$ = 2.8 Hz, C5,8) and 25.3 (t, $^1J_{PC}$ = 136.5 Hz, C1); $\delta_{P\{1H\}}$(81.0 MHz; CD_2Cl_2; 298 K) 29.4 (s, $\nu_{1/2}$ = 3.9 Hz). Crystal data for $C_{45}H_{38}N_3P_2Rh\cdot C_7H_8$, M = 877.77, monoclinic, space group $P2_1/c$ (No. 14), a = 9.9780(1), b = 20.7312(3), c = 41.3429(7) Å, β = 91.050(1)°, V = 8550.6(2) Å^3, D_c = 1.364 g cm^{-3}, μ = 4.237 mm^{-1}, Z = 8, λ = 1.54178 Å, T = 223(2) K, 78803 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.60 Å^{-1}, 15282 independent (R_{int} = 0.128), and 10879 observed reflections [$I \geq 2\sigma(I)$], 1018 refined parameters, R = 0.063, wR^2 = 0.165. CCDC 676925.

Reaction of compound 9 with (cyclooctadiene)iridium chloride dimer (10c), preparation of complex 13

Reaction of the lithium salt **9** (120 mg, 186 μmol) and [(cod)IrCl]$_2$ (**10c**) (63 mg, 93 μmol) in toluene (15 ml) yielded the yellow, air-stable product **13** (110 mg, 66%). Mp: >200 °C (DSC); Found: C, 61.42; H, 4.92; N, 4.22. Calc. for $C_{46}H_{42}IrN_3P_2$: C, 62.01; H, 4.75; N, 4.72%; ν_{max}(KBr)/cm^{-1} 3052, 2911, 2878, 2830, 2154, 1588, 1482, 1436, 1231, 1206, 1108, 1012, 982, 808, 748 and 693; δ_H(499.8 MHz; CD_2Cl_2; 298 K) 7.84 (m, 8H, *o*-Ph^P), 7.55 (m, 4H, *p*-Ph^P), 7.44 (m, 8H, *m*-Ph^P), 6.75 (m, 4H, *m*-Ph^N), 6.68 (m, 2H, *p*-Ph^N), 6.12 (m, 4H, *o*-Ph^N), 2.95 (m, 4H, 3,4,7,8-H), 2.00 (m, 4H, 5,6,9,10-H) and 1.24 (m, 4H, 5′,6′,9′,10′-H); δ_C(125.7 MHz; CD_2Cl_2; 298 K) 148.4 (s, *i*-Ph^N), 134.2 (m, *o*-Ph^P), 132.9 (pd, $^1J_{PC}$ + $^3J_{PC}$ = 104.8 Hz, *i*-Ph^P), 132.2 (m, *p*-Ph^P), 129.9 (m, *o*-Ph^N), 128.5 (m, *m*-Ph^P), 127.5 (s, *m*-Ph^N), 124.1 (t, $^2J_{PC}$ = 7.9 Hz, C2), 122.5 (m, *p*-Ph^N), 60.4 (s, C3,4,7,8), 31.1 (s, C5,6,9,10) and 24.6 (t, $^1J_{PC}$ = 130.7 Hz, C1); $\delta_{P\{1H\}}$(81.0 MHz; CD_2Cl_2; 298 K) 32.0 (s, $\nu_{1/2}$ = 1.9 Hz). Crystal data for $C_{46}H_{42}IrN_3P_2\cdot C_7H_8$, M = 983.10, monoclinic, space group $P2_1/c$ (No. 14), a = 19.7081(2), b = 11.3012(1), c = 21.4893(2) Å, β = 111.446(1)°, V = 4454.82(7) Å^3, D_c = 1.466 g cm^{-3}, μ = 3.108 mm^{-1}, Z = 4, λ = 0.71073 Å, T = 223(2) K, 41726 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.66 Å^{-1}, 10575 independent (R_{int} = 0.053), and 8671 observed reflections [$I \geq 2\sigma(I)$], 533 refined parameters, R = 0.029, wR^2 = 0.072. CCDC 676926.

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