Coordination Chemistry of Functional Phosphanes, VI[◇]

Rhodium and Iridium Complexes with 2-(Diphenylphosphanyl)phenylamido Ligands

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Treatment of *trans*-[MCl(CO)(PPh$_3$)$_2$] (M = Rh, Ir) with the lithium salts of the bidentate hybride ligands 2-Ph$_2$PC$_6$H$_4$N(R)H ['PN(R)H'; R = H, Me] produced the chelate complexes [M(CO)(PPh$_3$)('PNR')] [M/NR = Rh/NH (**1a**), Ir/NH (**2a**), Rh/NMe (**1b**), Ir/NMe (**2b**)] containing the CO ligand and the NR substituent in mutual *trans*-arrangement. **2b** was shown by single-crystal X-ray diffraction to possess an amido-nitrogen atom in a trigonal-planar environment. Oxidative addition of H$_2$ to **2b** reversibly formed *cis*-[IrH$_2$(CO)(PPh$_3$)('PNMe')] (**3**), in which H$_2$ has added perpendicular to the N–Ir–CO axis. While both **1a,b** and **2a,b** proved to be completely unreactive toward CO$_2$ at ambient temperature and pressure, reactions of **1a** and **2a/b** with sulfur dioxide reversibly formed pentacoordinate SO$_2$ adducts, [M(SO$_2$)(CO)(PPh$_3$)('PNR')] [M/NR = Rh/NH (**4a**), Ir/NH (**5a**), Ir/NMe (**5b**)] with M–S-bonded pyramidal MSO$_2$ units as established by an X-ray structure analysis of **5a**. Complex **5b** reacted with dioxygen to form the sulfato compound [Ir(O$_2$SO$_2$)(CO)(PPh$_3$)('PNMe')] (**6**). Combination of **2a** with HCl in CHCl$_3$ at −60°C resulted in protonation of both the iridium and the nitrogen atom to give an ionic chelate complex, [IrHCl(CO)(PPh$_3$)('PNH$_2$')]Cl (**7**), containing one of its NH groups hydrogen-bonded to Ir–Cl. Ring opening of the chelate structure with formation of [IrHCl$_2$(CO)(PPh$_3$)(PPh$_2$C$_6$H$_4$N(Me)H-*o*)] (**8**) was observed in the analogous reaction of **2b** with hydrogen chloride. NMR spectroscopy showed **8** to exist in CDCl$_3$ solution as a mixture of three Ir–PPh$_2$C$_6$H$_4$N(Me)H-*o* rotamers, stabilized by intramolecular –N(Me)H···ClIr hydrogen bonding.

Recently we have been investigating some aspects of the chelation of bidentate *P,O* and *P,S* hybrid ligands 2-Ph$_2$PC$_6$H$_4$EH (EH = OH, SH), both in their neutral ('PEH') and deprotonated ('PE$^-$') forms, in particular with regard to their reactivity towards Brønsted and Lewis acids[1][2]. In this context, the ring-opened compound [IrHCl$_2$(CO)(PPh$_3$)(POH)], resulting from combination of the phenolato chelate complex [Ir(CO)(PPh$_3$)('PO')] with HCl in chloroform at low temperature, has been shown by NMR spectroscopy (^{1}H, ^{31}P) to exist as two Ir–'POH' rotamers. As evidenced from an X-ray structure analysis, one of these possesses an intramolecular hydrogen bond between the OH group and the chloro ligand *trans* to Ir–H, while the other one appears to exhibit a "bifurcated"[4] hydrogen bonding interaction Cl···H(O)···H involving both the chloro and the hydrido ligand of the fragment *cis*-Cl–Ir–H with distances, in the solid state, of 2.3(2) Å for the IrCl···HO hydrogen bond and 2.1(2) Å for the IrH···HO interaction[1]. These observations and the growing interest in iridium complexes displaying intramolecular M–H···H–Y and M–X···H–Y hydrogen bonds[4][5][6][7][8] prompted us to extend our studies studies to rhodium and iridium complexes derived from the *P,N*-ligands 2-(diphenylphosphanyl)aniline, 2-Ph$_2$PC$_6$H$_4$NH$_2$[9][10] ('PNH$_2$'), and 2-(diphenylphosphanyl)-*N*-methylaniline, 2-Ph$_2$PC$_6$H$_4$N(Me)H[10][11] ('PN(Me)H'), as it has been demonstrated recently that N–H bonds have a distinct propensity to behave as the Y$^{\delta-}$–H$^{\delta+}$ donor component both toward Ir–X and Ir–H bonds as the weak base components[4][6][7][8]. A further aspect of the work reported in this communication was to elucidate the Lewis base and/or Lewis acid behavior of the Vaska-type amido(phosphane) complexes [M(CO)(PPh$_3$)('PNR')] (M = Rh, Ir; R = H, Me) toward small molecules, which themselves can act both as Lewis acids and Lewis bases, e.g. CO$_2$ or SO$_2$, or can be activated at M$^{\delta+}$–X$^{\delta-}$ centers heterolytically, such as H$_2$.

Results and Discussion

The 16e chelate complexes [M(CO)(PPh$_3$)('PNR')] [M/NR = Rh/NH (**1a**), Ir/NH (**2a**), Rh/NMe (**1b**), Ir/NMe (**2b**)] were obtained in smooth substitution reactions by the addition at room temperature of equimolar amounts of the *N*-lithio derivatives 'PN(H)Li' and 'PN(Me)Li' to the requisite rhodium or iridium precursor *trans*-[MCl(CO)(PPh$_3$)$_2$] in THF solution. In the infrared, the new yellow to orange colored complexes are primarily characterized by a single carbonyl stretch band in the

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[◇] Parts III–V: Refs.[1][2][3].

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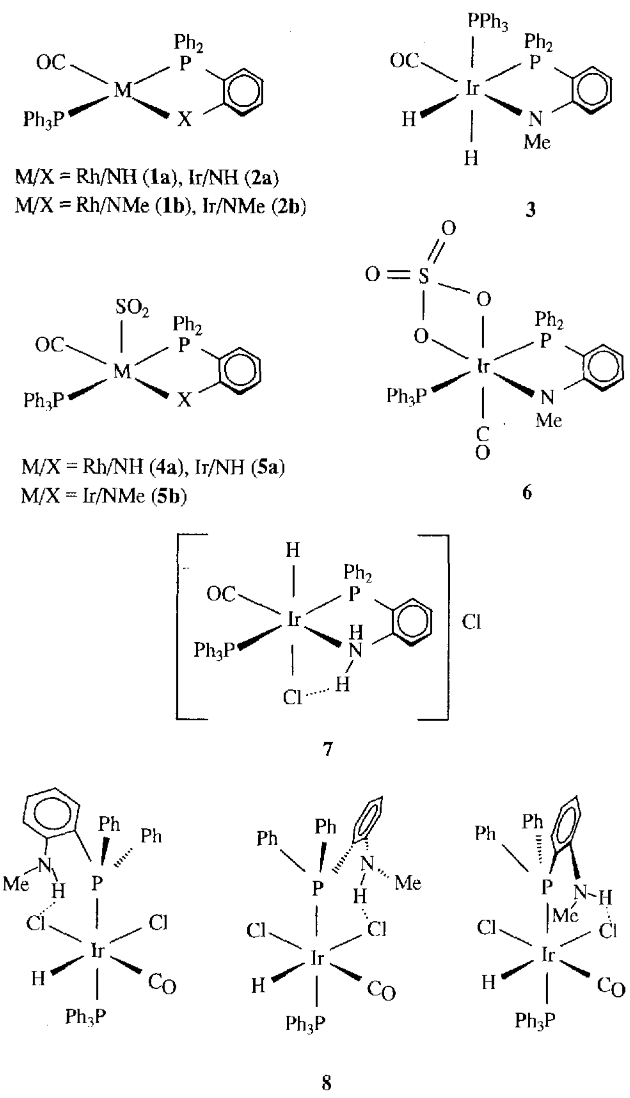
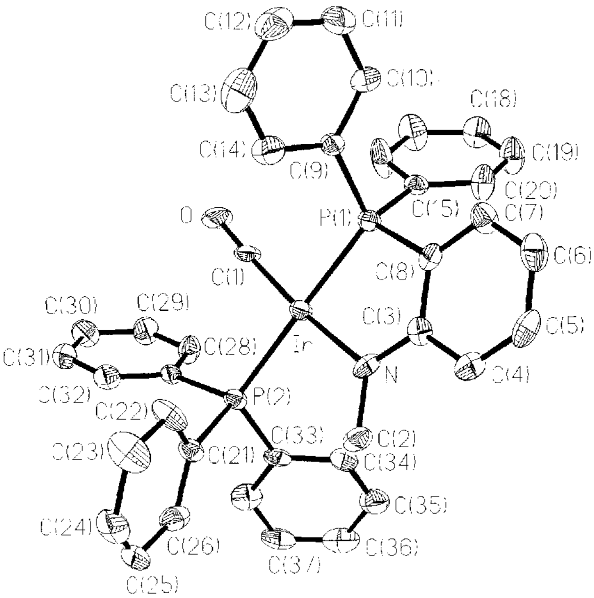
Scheme 1



1930–1950 cm^{-1} region, each positioned at slightly lower wavenumbers than those of the starting chloro compounds. *P,N*-chelation in **1** and **2** is evident from the pronounced downfield ring shifts[12] of their 'PNR' ^{31}P resonances (δ ca. 49 for M = Rh; δ ca. 38 for M = Ir), as compared to those of the free 'PN(R)H' ligands (δ ca. −22). Coupling constants ^{2}J(P,P) of approximately 300 Hz indicate the two phosphane ligands to be coordinated in mutual *trans* positions[13]. These structural assignments were confirmed by a single-crystal X-ray diffraction study of iridium complex **2b**. The molecule displays a four-coordinate planar coordination geometry about the central metal (Figure 1) as evidenced inter alia from the sum of the four interligand *cis* angles, 360.3°. Remarkably, the total of the three angles Ir−N−C(2), Ir−N−C(3), and C(2)−N−C(3) at the amido function, 359.5°, also is as required for a planar surrounding of the nitrogen atom. The five-membered chelate ring itself exhibits a slight bend along the N···P(1) line of 3.7°, i.e., it adopts a very flat "envelope" conformation with the metal atom deviating by only 0.11 Å from the least-squares mean plane through the atoms P(1), N(1), C(3), and C(8). The phenylene ring anellated to the chelate system adopts an orientation almost parallel to the coordination plane, the angle between the normals to both planes being 6.1°. The Ir−NH bond length, 2.100(6) Å, is close to the metalamide distances of 2.09(4) to 2.10(6) Å observed for the tris(chelate) iridium(III) complex [Ir('PNH')$_3$][14].

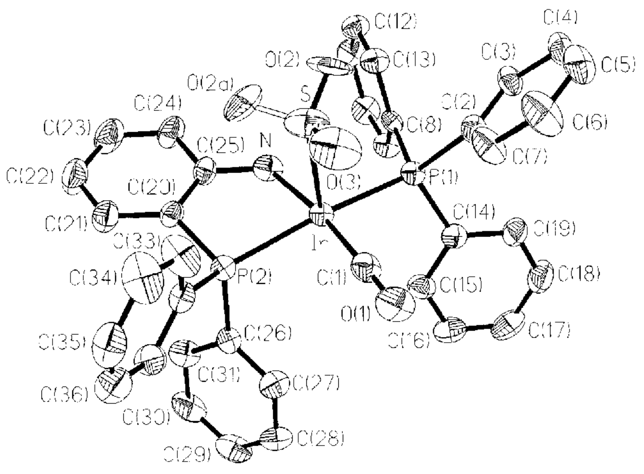
Figure 1. Molecular structure of [Ir(CO)(PPh$_3$)('PNMe')] (**2b**)[a]



[a] Selected bond lengths [Å] and angles [°]: Ir−P(1), 2.277(3); Ir−P(2), 2.339(3); Ir−N, 2.100(6); Ir−C(1), 1.839(8); C(1)−O, 1.147(9); N−C(2), 1.438(10), N−C(3), 1.370(10). P(1)−Ir−P(2), 177.59(11); P(1)−Ir−N, 82.4(2); P(1)−Ir−C(1), 91.0(3); P(2)−Ir−N(1), 97.5(2); P(2)−Ir−C(1), 89.4(3); N−Ir−C(1), 171.8(3); Ir−C(1)−O, 177.3(7); Ir−N−C(2), 124.3(5); Ir−N−C(3), 119.2(6); C(2)−Ir−C(3), 116.0(6).

The trigonal-planar environment of the amido-nitrogen in **2b** points to an involvement of its lone-pair of electrons in π-bonding to the central metal with consequent $sp^3 \rightarrow sp^2$ rehybridization and decreased basicity at the nitrogen atom. It was therefore not surprising to see that the reaction of **2b** with dihydrogen (50 bar) in CDCl$_3$ only led to *cis*-[IrH$_2$(CO)(PPh$_3$)('PNMe')] (**3**) without any evidence for the formation of the tautomeric heterolytic activation product [IrH(CO)(PPh$_3$)('PN(Me)H')], originally hoped for as a possible *P,P,N*-coordinated analogue of the well-known tris(phosphane) complex [IrH(CO)(PPh$_3$)$_3$]. Similar to the H$_2$ adducts *cis*-[IrH$_2$(CO)(PPh$_3$)('PE')] (E = O, S) reported earlier[1], dihydride **3** is only stable under H$_2$ atmosphere, to the effect that attempts at its isolation in crystalline form rapidly restored **2b** as the H$_2$-loss product. In the formation of **3**, the H$_2$ molecule has added "perpendicular" to the N−Ir−CO axis (P atoms *cis*) in a kinetically controlled fashion[15], in contrast to the (thermodynamically favored) "parallel"[15] H$_2$ adducts (P atoms *trans*) derived from [Ir(CO)(PPh$_3$)('PO')] and [Ir(CO)(PPh$_3$)('PS')], respectively[1]. The stereochemistry of **3** is clearly defined by its ^{1}H- and ^{31}P-NMR spectra. The hydrido ligands resonate with unit intensity as two pairs of doublets at $\delta = -9.48$ [*trans*-^2J(P,H) = 156.7, *cis*-^2J(P,H) = 16.1 Hz] and $\delta = -7.60$ [*trans*-^2J(P,H) = 127.9, *cis*-^2J(P,H) = 16.7 Hz]. Consistently, the two *P*-donors give rise to an AX pattern characterized by $^2J(P_A,P_X)$ = 18.7 Hz, typical of phosphanes occupying *cis* positions in octahedral platinum metal complexes[13]. In the model suggested for the stereoelectronic origin of the directing effect on H_2 addition to square-planar d^8 complexes by Crabtree[15], the formation of the "perpendicular" adduct **3** requires a trigonal-bipyramidal intermediate with the σ-donating and π-accepting H_2 ligand and the two strongly σ-donating phosphanes in equatorial positions, the π-donating amido-nitrogen and the π-accepting carbonyl group occupying axial sites. Conceivably, such a transient η^2-H_2 appears to be favored over its isomer leading to the "parallel" adduct (H_2, N, and CO equatorial, phosphanes axial) as the strongly π-donating and π-accepting NMe and CO ligands should have a strong tendency for remaining mutually *trans*.

Figure 2. Molecular structure of [Ir(SO$_2$)(CO)(PPh$_3$)('PNH')] (**5a**)[a]



[a] Selected bond lengths [Å] and angles [°]: Ir−S, 2.456(3); Ir−P(1), 2.349(2); Ir−P(2), 2.316(2); Ir−N, 2.027(8); Ir−C(1), 1.838(11); S−O(2), 1.35(2); S−O(2a), 1.32(2); S−O(3), 1.478(9); C(1)−O(1), 1.148(12); S−Ir−P(1), 96.38(11); S−Ir−P(2), 98.55(11); S−Ir−N, 91.7(2); S−Ir−C(1), 91.6(3); P(1)−Ir−P(2), 162.68(7); P(1)−Ir−N, 91.4(3); P(1)−Ir−C(1), 94.3(3); P(2)−Ir−N, 79.5(3); P(2)−Ir−C(1), 94.0(3); N−Ir−C(1), 173.0(4); Ir−S−O(2), 106.9(8); Ir−S−O(2a), 107.9(6); Ir−S−O(3), 105.7(3); O(2)−S−O(2a), 93.9(12); O(2)−S−O(3), 122.7(12); O(2a)−S−O(3), 118.7(9); Ir−C(1)−O(1), 178.1(8).

None of the four d^8 complexes **1a**,**b** and **2a**,**b** underwent any noticable transformation when stirred in THF under CO_2 at ambient temperature and pressure for 18 h, indicating that neither the metal nor the nitrogen basicity suffices for an interaction of the weakly Lewis-acidic CO_2 molecule with either atomic site. In contrast, analogous treatment with gaseous SO_2 of **1a**, **2a**, and **2b** in toluene solution resulted in the immediate formation the M−SO$_2$ adducts [M(SO$_2$)(CO)(PPh$_3$)('PNR')] [M/R = Rh/H (**4a**), Ir/H (**5a**), Ir/Me (**5b**)], which like many other five-coordinate sulfur dioxide-containing complexes of rhodium(I) and iridium(I) possess reversibly bound SO_2. The SO stretching frequencies ν_s and ν_{as} of adducts **4a** and **5a**,**b** are observed in the ranges 1040−1050 cm^{-1} and 1180−1210 cm^{-1}, respectively. Exposure of **5b** in toluene solution to the air cleanly produced the sulfato derivative [Ir(O$_2$SO$_2$)(CO)(PPh$_3$)('PNMe')] (**6**). In line with geometry-dependent properties of transition metal−SO$_2$ complexes previously discussed by Kubas[16], the reversibility of SO_2 bonding, the location of ν(SO), and the propensity of **5b** to undergo the sulfato reaction can be taken as structural indicators for pyramidal L$_n$M−SO$_2$ bonding with the L$_n$M fragment acting as a σ base. Correspondingly, an X-ray crystal structure analysis of **5a** showed the presence of a square-pyramidal molecule, in which the SO_2 ligand occupies the apical position (Figure 2). The sulfur atom has the expected pyramidal geometry, the S−O(3) bond, 1.478(9) Å, being approximately collinear with the Ir−CO linkage. Large thermal oscillation of the second SO_2 oxygen atom resulted in its two-fold disorder about the S−O(3) axis with concomitant librational shortening of the distances S−O(2), 1.35(2) Å, and S−O(2a), 1.32(2) Å. Similar artificially short S−O distances resulting from large thermal motions of this group have been reported recently for the SO_2 ligand of [Ir(SO$_2$){OS(O)OH}(CO)(PCy$_3$)$_2$][17]. The relatively long Ir−S distance, 2.456(3) Å, is typical of SO_2-containing complexes with pyramidal M−SO$_2$ building blocks (M−S, 2.35−2.50 Å)[16].

Iridium complex **2a** reacted with gaseous HCl in CHCl$_3$ or toluene solution at −60°C by oxidative addition to the central metal and protonation at nitrogen to form the ionic chelate complex [IrHCl(CO)(PPh$_3$)('PNH$_2$')]Cl (**7**). In agreement with the assignment of the complex as a 1:1 electrolyte, the conductivity of a 10^{-3} M solution of **7** in acetonitrile was measured as $\Lambda = 52$ cm^2 Ω^{-1} mol^{-1}. The overall geometry of the cation shown in Scheme 1 was confirmed by spectral data. In particular, the ^{31}P-NMR spectrum of **7** consists of two doublets at $\delta = 5.4$ and 27.6, each split by 315 Hz, and the proton NMR contains an IrH triplet at $\delta = -15.18$ showing equal *cis* coupling (10.8 Hz) to the two P nuclei. The amino group gives rise to two doublets of unit intensity at $\delta = 4.19$ and 11.35 [*gem*-^2J(H,H) = 11.7 Hz]. The significant low-field shift of the latter N−H proton resonance is characteristic of intramolecular hydrogen bonding between the ligating amino NH group and either the electronegative *cis* chloro ligand or the polarized *cis* Ir$^{\delta+}$−H$^{\delta-}$ bond[8c]. A COSY study of **7** showed that the NH proton is *not* coupled to the IrH hydrogen. An NOE difference experiment also ruled out the possibility of a short IrH···HN contact in **7**; irradiation at the hydride resonance resulted only in a less than 1% enhancement for the NH peak, in contrast to the more than 10% NOE enhancement reported for the NH resonances of iridium complexes featuring unequivocal IrH···HN bonding[4][7]. Hence, the ^{1}H NMR data are most easily accomodated if the NH proton resonating at low field is hydrogen-bonded to Ir−Cl rather than Ir−H.

Treatment of the 'PNMe' complex **2b** with hydrogen chloride under the conditions chosen for the HCl reaction of the 'PNH' analogue **2a** also resulted in oxidative addition to iridium and protonation at nitrogen. However, different from the conversion of **2a** into stable cationic **7**$^+$, the protonation of the methylamido ligand in **2b** was followed by dissociation of the N(Me)H group from the metal, allowing the chloride ion to coordinate with formation of covalent [IrHCl$_2$(CO)(PPh$_3$)(PPh$_2$C$_6$H$_4$N(Me)H-*o*)] (**8**) (Λ ca. 3 cm^2 Ω^{-1} mol^{-1}). Three isomers with overlapping methyl proton signals (δ = 2.70) and partially overlapping NH resonances (δ = 5.43 and 5.70; both broad) are seen for CDCl$_3$ solutions of **8**: **8A** [δ(IrH) = $-$15.52 (t, *cis*-^2J(P,H) = 10.8 Hz); δ(^{31}P) = $-$0.37, $-$2.85 (AB pattern, *trans*-^2J(P$_A$,P$_B$) = 382.7 Hz)], **8B** [δ(IrH) = $-$15.49 (t, *cis*-^2J(P,H) = 11.1 Hz); δ(^{31}P) = $-$2.71 (apparent A$_2$ singlet, i.e., $\Delta\nu \ll J$)], and **8C** [d(IrH) = $-$15.41 (t, *cis*-^2J(P,H) = 11.2 Hz); δ(^{31}P) = $-$2.85 (apparent A$_2$ singlet)]; isomer ratio at equilibrium, **8A/8B/8C** ca. 5:9:2. The closely resembling triplet splittings of ca. 11 Hz of the hydride resonances, in addition to the very similar values of both δ(IrH) and δ(^{31}P) observed for the three isomers, indicate a common coordination geometry with the Ir$-$H bond *cis* to two near-equivalent *trans*-located phosphane ligands. Moreover, the ν(CO) and ν(IrH) wavenumbers, coinciding for the mixture of isomers at 2038 and 2231 cm^{-1}, respectively, are consistent with the presence of *trans*-Cl$-$Ir$-$CO and *trans*-H$-$Ir$-$Cl units[18] in each isomeric form **8A**, **8B**, and **8C** and preclude the existence of geometric isomers with the hydride and the carbonyl ligand in mutual *trans* coordination. The evidence suggests complex **8** exists as three Ir$-$PPh$_2$C$_6$H$_4$N(Me)H-*o* rotamers differing by three energetically favored orientations of the *ortho*-substituted ring with respect to the *trans*-Cl$-$Ir$-$CO and *trans*-H$-$Ir$-$Cl bonds in the coordination plane perpendicular to the Ir$-$P linkage. Conceivable contributions to the preference for these rotamers could arise from the involvement of the dangling methylamino group in hydrogen bonding to the *cis*-Ir$-$H bond and the two stereochemically different *cis* chloro ligands. As with **7**, however, the existence of **8** as an isomer containing the amino hydrogen and the metal-bound hydride in close proximity had to be eliminated because no measureable enhancement was observed for the NH (or, vice versa, IrH) resonance, when the hydride (or NH$_2$) region was selectively irradiated in an NOE study of the isomeric mixture. Hence, the rotamers are assigned structures in which the ring bearing the N(Me)H group is sterically locked in three preferred orientations exclusively by IrCl$\cdots$HN hydrogen bonding (Scheme 1).

It has been argued that "non-classical" IrH$\cdots$HN hydrogen bonding may be as strong as, or even stronger than, an analogous conventional IrCl$\cdots$HN bond in the same system, provided (i) a favorable geometry allows the close approach of the N$^{\delta-}-$H$^{\delta+}$ group to the Ir$^{\delta+}-$H$^{\delta-}$ linkage and (ii) a ligand exerting a high *trans* influence on the polarized Ir$^{\delta+}-$H$^{\delta-}$ bond contributes to an increase in the δ^- charge on the hydride ligand[8c]. That IrCl$\cdots$HN hydrogen bonding appears to be favored over IrH$\cdots$HN hydrogen bonding in **8** may therefore be ascribed to (i) an unsuitable geometry resulting from shielding of the Ir$-$H bond by the methylamino CH$_3$ group and/or the relatively low *trans* influence of chloride in the *trans*-H$-$Ir$-$Cl unit as opposed to, e. g., hydride in *mer*-[IrH$_3$(NC$_5$H$_4$NH$_2$-2)(PPh$_3$)$_2$][8c].

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Experimental Section

General: All preparations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were distilled from the appropriate drying agents prior to use. – IR: Perkin Elmer 580 B or Mattson Polaris-trade mark sign (KBr pellets, unless stated otherwise). – NMR: Jeol FT-JNM-EX 270 and Jeol FT-JNM-GX 270 (269.6 MHz for ^{1}H, 67.7 MHz for ^{13}C, 109.4 MHz for ^{31}P) or Bruker DPX 300 (300.1 MHz for ^{1}H; 75.5 MHz for ^{13}C, 121.5 MHz for ^{31}P); CDCl$_3$ solution with TMS as internal or with H$_3$PO$_4$ as external standard. – *trans*-[RhCl(CO)(PPh$_3$)$_2$][19], *trans*-[IrCl(CO)(PPh$_3$)$_2$][20], and 2-PhP$_2$C$_6$H$_4$NH$_2$[10] were prepared by literature methods; 2-Ph$_2$PC$_6$H$_4$N(Me)H was obtained by analogy to a procedure described for 2,6-(Ph$_2$P)$_2$C$_6$H$_3$N(Me)H[11].

[Rh(CO)(PPh$_3$)('PNH')] (**1a**), *[Rh(CO)(PPh$_3$)('PNMe')]* (**1b**), *[Ir(CO)(PPh$_3$)('PNH')]* (**2a**), *and [Ir(CO)(PPh$_3$)('PNMe')]* (**2b**): To a solution of 277 mg (1.0 mmol) of 2-Ph$_2$PC$_6$H$_4$NH$_2$ or 291 mg (1.0 mmol) of 2-Ph$_2$PC$_6$H$_4$NHMe in 20 ml of THF cooled to -60°C, 0.625 ml of a 1.6 M solution of *n*-butyllithium in hexane was added dropwise. The reaction mixture was allowed to warm to room temperature within 20 min and then added to a solution containing 691 mg (1.0 mmol) of *trans*-[RhCl(CO)(PPh$_3$)$_2$] or 780 mg (1.0 mmol) of *trans*-[IrCl(CO)(PPh$_3$)$_2$] in 30 ml of THF. After stirring for 3 h at ambient conditions, solvent was removed in vacuo to leave an orange oil which was taken up in 15 ml of hot DMF. Careful addition of 50 ml of methanol caused the precipitation of the product complexes as golden (**1a**), orange-yellow (**1b**), yellow (**2a**), or orange (**2b**) crystals. – **1a**: Yield 616 mg (92%). – IR: $\tilde{\nu}$ = 1950 (CO), 3360 (NH) cm^{-1}. – ^{1}H NMR (269.6 MHz): δ = 3.52 (br, 1 H, NH), 6.03 (dd, J = 4.1, 8.2 Hz, 1 H, C$_6$H$_4$), 6.24 (t, J = 7.2 Hz, 1 H, C$_6$H$_4$), 6.86 (t, J = 7.5 Hz, 1 H, C$_6$H$_4$), 7.06 (t, J = 8.2 Hz, 1 H, C$_6$H$_4$), 7.4 (m, 15 H, C$_6$H$_5$), 7.7 (m, 6 H, C$_6$H$_5$), 7.8 (m, 4 H, C$_6$H$_5$). – ^{13}C{^{1}H} NMR (75.5 MHz): δ = 169.3 [d, ^2J(P,C) = 31.4 Hz, NC$_{ar}$], 194.8 [dt, ^1J(Rh,C) = 60.6, *cis*-^2J(P,C) = 13.3 Hz, CO]. – ^{31}P{^{1}H} NMR (109.4 MHz): δ = 37.0 [dd, ^1J(Rh,P) = 130.7, *trans*-^2J(P,P) = 286.9 Hz, PPh$_3$], 48.9 [dd, ^1J(Rh,P) = 136.6 Hz, 'PNH']. – C$_{37}$H$_{30}$NOP$_2$Rh (669.51): calcd. C 66.38, H 4.52, N 2.09; found C 66.38, H, 4.63, N 1.91. – **1b**: Yield 608 mg (89%). – IR: $\tilde{\nu}$ = 1954 (CO) cm^{-1}. – ^{1}H NMR (269.6 MHz): δ = 2.77 (s, 3 H, CH$_3$), 6.3 (m, 2 H, C$_6$H$_4$), 7.1 (m, 2 H, C$_6$H$_4$), 7.4 (m, 15 H, C$_6$H$_5$), 7.8 (m, 10 H, C$_6$H$_5$). – ^{13}C{^{1}H} NMR (75.5 MHz): δ = 47.1 (s, CH$_3$), 169.6 [dd, ^2J(P,C) = 30.6, ^3J(P,C) = 2.4 Hz, NC$_{ar}$], 193.5 [dt, ^1J(Rh,C) = 60.4, *cis*-^2J(P,C) = 16.2 Hz, CO]. – ^{31}P{^{1}H} NMR (121.5 MHz): δ = 33.5 [dd, ^1J(Rh,P) = 136.2, *trans*-^2J(P,P) = 289.6 Hz, PPh$_3$], 49.1 [dd, ^1J(Rh,P) = 134.0 Hz, 'PNMe']. – C$_{38}$H$_{32}$NOP$_2$Rh (683.54): calcd. C 66.77, H 4.72, N 2.05; found C 66.78, H 4.65, N 1.62. – **2a**: Yield 660 mg (87%). – IR: $\tilde{\nu}$ = 1931 (CO), 3368 (NH) cm^{-1}. – ^{1}H NMR (269.6 MHz): δ = 4.35 (br, 1 H, NH), 6.01 (dd, J = 5.1, 8.1 Hz, 1 H, C$_6$H$_4$), 6.24 (t, J = 7.3 Hz, 1 H, C$_6$H$_4$), 6.83 (t, J = 7.6 Hz, 1 H, C$_6$H$_4$), 7.08 (t, J = 8.1 Hz, 1 H, C$_6$H$_4$), 7.4 (m, 15 H, C$_6$H$_5$), 7.7 (m, 6 H, C$_6$H$_5$), 7.8 (m, 4 H, C$_6$H$_5$). – ^{13}C{^{1}H} NMR (67.7 MHz): δ = 170.4 [dd, ^2J(P,C) = 27.2, ^3J(P,C) = 5.9 Hz, NC$_{ar}$], 185.7 [t, *cis*-^2J(P,C) =

10.2 Hz, CO]. – ^{31}P{^{1}H} NMR (109.4 MHz): δ = 28.3 [d, *trans*-^{2}J(P,P) = 305.0 Hz, PPh$_3$]; 37.1 (d, 'PNH'). – $C_{37}H_{30}IrNOP_2$ (758.82): calcd. C 58.57, H 3.99, N 1.85; found C 58.32, H, 3.98, N, 1.65. – **2b**: Yield 703 mg (91%). – IR: $\tilde{\nu}$ = 1939 (CO) cm^{-1}. – ^{1}H NMR (269.6 MHz): δ = 2.87 (s, 3 H, CH$_3$), 6.39 (m, 2 H, C$_6$H$_4$), 7.1 (m, 2 H, C$_6$H$_4$), 7.4 (m, 15 H, C$_6$H$_5$), 7.8 (m, 10 H, C$_6$H$_5$). – ^{13}C{^{1}H} NMR (75.5 MHz): δ = 49.0 [d, ^{3}J(P,C) = 7.0 Hz, CH$_3$], 171.1 [d, ^{2}J(P,C) = 27.1 Hz, NC$_{ar}$], 182.5 [t, *cis*-^{2}J(P,C) = 10.8 Hz, CO]. – ^{31}P{^{1}H} NMR (109.4 MHz): δ = 30.9 [d, *trans*-^{2}J(P,P) = 308.0 Hz, PPh$_3$], 37.7 (d, 'PNMe'). – $C_{38}H_{32}IrNOP_2$ (772.85) calcd. C 59.06, H 4.17, N 1.81; found C 58.79, H 4.13, N 1.56.

[IrH$_2$(CO)(PPh$_3$)('PNMe')] (**3**): A solution of 40 mg (0.05 mmol) of **2b** in 1.5 ml of CDCl$_3$ was stirred under 50 bar of H$_2$ at room temperature for 20 h and subsequently characterized by IR and NMR spectroscopy. – IR (CDCl$_3$): $\tilde{\nu}$ = 2009 (CO), 2067 (IrH) cm^{-1}. – ^{1}H NMR (300.1 MHz): δ = −9.48 [dd, *trans*-^{2}J(P,H) = 156.7, *cis*-^{2}J(P,H) = 16.1 Hz, 1 H, IrH], −7.60 [dd, *trans*-^{2}J(P,H) = 127.9, *cis*-^{2}J(P,H) = 16.7 Hz, 1 H, IrH], 2.70 (s, 3 H, CH$_3$), 6.04 (t, J = 6.7, 1 H), 6.15 (t, J = 7.7 Hz, 1 H), 7.0 (m, 16 H), 7.3 (m, 7 H), 7.6 (m, 1 H); 7.8 (m, 2 H) (all C$_6$H$_4$ and C$_6$H$_5$). – ^{13}C{^{1}H} NMR (75.5 MHz): δ = 50.4 [d, ^{3}J(P,C) = 5.4 Hz, CH$_3$], 169.1 [d, ^{2}J(P,C) = 25.1 Hz, NC$_{ar}$], 172.4 [t, *cis*-^{2}J(P,C) = 5.2 Hz, CO]. – ^{31}P{^{1}H}NMR (109.4 MHz): δ = −6.0 [d, *cis*-^{2}J(P,P) = 18.7 Hz, PPh$_3$], 18.0 (d, 'PNMe').

[Rh(SO$_2$)(CO)(PPh$_3$)('PNH')] (**4a**), *[Ir(SO$_2$)(CO)(PPh$_3$)('PNH')]* (**5a**), *and [Ir(SO$_2$)(CO)(PPh$_3$)('PNMe')]* (**5b**): Solutions of 120 mg (0.18 mmol) of **1a**, 150 mg (0.20 mmol) of **2a**, or 140 mg (0.18 mmol) of **2b** in toluene (10 ml each) were saturated with SO$_2$ gas and stirred under sulfur dioxide atmosphere for 30 min. Pentane (50 ml) was then added to induce the deposition of the SO$_2$ adducts as raspberry-colored (**4a**), brick-red (**5a**), or grey-blue (**5b**) solids, which were dried in a stream of dry nitrogen. **4a**: Yield 125 mg (95%). – IR: $\tilde{\nu}$ = 1046 (SO$_2$, ν_s), 1189 m (SO$_2$, ν_{as}), 2017 (CO), 3369 (NH) cm^{-1}. – ^{1}H-NMR (269.6 MHz): δ = 3.57 (br, 1 H, NH), 6.10 (dd, J = 4.9, 8.3 Hz, 1 H, C$_6$H$_4$), 6.33 (t, J = 7.3 Hz, 1 H, C$_6$H$_4$), 6.92 (t, J = 7.6 Hz, 1 H, C$_6$H$_4$), 7.11 (t, J = 8.8 Hz, 1 H, C$_6$H$_4$), 7.5 (m, 15 H, C$_6$H$_5$), 7.6 (m, 6 H, C$_6$H$_5$), 7.7 (m, 4 H, C$_6$H$_5$). – ^{13}C{^{1}H} NMR (75.5 MHz): δ = 168.0 [d, ^{2}J(P,C) = 29.9 Hz, NC$_{ar}$]; 189.9 [dt, ^{1}J(Rh,C) = 61.4, *cis*-^{2}J(P,C) = 12.0 Hz, CO]. – ^{31}P{^{1}H} NMR (121.5 MHz): δ = 32.6 [dd, ^{1}J(Rh,P) = 126.3, *trans*-^{2}J(P,P) = 278.0 Hz, PPh$_3$]; 50.0 [dd, ^{1}J(Rh,P) = 128.2 Hz, 'PNH']. – $C_{37}H_{30}NO_3P_2RhS$ (733.57): calcd. C 60.58, H 4.12, N 1.91, S, 4.37; found C 59.84, H 3.92, N 2.03, S 4.31. – **5a**: Yield 151 mg (92%). – IR: $\tilde{\nu}$ = 1040 (SO$_2$, ν_s), 1188 (SO$_2$, ν_{as}), 1996 (CO), 3374 (NH) cm^{-1}. – ^{1}H NMR (269.6 MHz): δ = 4.45 (br, 1 H, NH); 6.19 (dd, J = 4.8, 8.1 Hz, 1 H, C$_6$H$_4$), 6.42 (dt, J = 7.3, 2.0 Hz, 1 H, C$_6$H$_4$), 6.98 (t, J = 7.6 Hz, 1 H, C$_6$H$_4$), 7.24 (t, J = 8.9 Hz, 1 H, C$_6$H$_4$), 7.4 (m, 15 H, C$_6$H$_5$), 7.7 (m, 10 H, C$_6$H$_5$). – ^{13}C{^{1}H} NMR (67.7 MHz): δ = 168.1 [dd, ^{2}J(P,C) = 26.2, ^{3}J(P,C) = 6.1 Hz, NC$_{ar}$], 175.3 [t, *cis*-^{2}J(P,C) = 9.2 Hz, CO]. – ^{31}P{^{1}H} NMR (121.5 MHz): δ = 19.3 [d, *trans*-^{2}J(P,P) = 284.5 Hz, PPh$_3$], 35.7 (d, 'PNH'). – $C_{37}H_{30}IrNO_3P_2S$ (822.82): calcd. C 54.01, H 3.67, N 1.70, S 3.90; found C 53.31, H 3.47, N 1.70, S 3.95. – **5b**: Yield 141 mg (94%). – IR: $\tilde{\nu}$ = 1044 (SO$_2$, ν_s), 1208 (SO$_2$, ν_{as}), 1996 (CO) cm^{-1}. – ^{1}H NMR (269.6 MHz): δ = 3.23 (s, 3 H, CH$_3$), 6.49 (dt, J = 7.2, 1.8 Hz, 1 H, C$_6$H$_4$), 6.60 (dd, J = 5.5, 8.3 Hz, 1 H, C$_6$H$_4$), 7.3 (m, 2 H, C$_6$H$_4$), 7.4 (m, 15 H, C$_6$H$_5$), 7.7 (m, 10 H, C$_6$H$_5$). – ^{13}C{^{1}H} NMR (75.5 MHz): δ = 48.6 [d, ^{3}J(P,C) = 7.9 Hz, CH$_3$], 169.1 [d, ^{2}J(P,C) = 24.7 Hz, NC$_{ar}$], 173.4 [t, *cis*-^{2}J(P,C) = 7.9 Hz, CO]. – ^{31}P{^{1}H} NMR (109.4 MHz): δ = 14.8 [d, *trans*-^{2}J(P,P) = 282.7 Hz, PPh$_3$], 33.7 (d, 'PNMe'). – $C_{38}H_{32}IrNO_3P_2S$ (836.89): calcd. C 54.54, H 3.85, N 1.67, S 3.83; found C 54.62, H 4.08, N 1.71, S 3.75.

[Ir(O$_2$SO$_2$)(CO)(PPh$_3$)('PNMe')] (**6**): A solution of 80 mg (0.1 mmol) of **5b** in 5 ml of toluene was stirred in air for 24 h to furnish sulfato complex **6** as a light brown precipitate. – IR: $\tilde{\nu}$ = 646, 885, 1154, 1294 (all SO$_4^{2-}$), 2052 (CO) cm^{-1}. – $C_{38}H_{32}IrNO_5P_2S$ (868.89): calcd. C 52.53, H 3.71, N 1.61, S 3.69; found C 53.12, H 3.59, N 1.70. S, 3.96.

[IrHCl(CO)(PPh$_3$)('PNH$_2$')]Cl (**7**): A solution of 114 mg (0.15 mmol) of **2a** in 10 ml of CHCl$_3$ was cooled to −60°C and saturated with dry HCl gas, previously developped from NaCl and H$_2$SO$_4$. The clear colorless mixture was allowed to warm to room temperature within 1 h and evaporated to leave complex **7** as a white solid; yield 125 mg (quantitative). – IR: $\tilde{\nu}$ = 2042 (CO), 2207 (IrH), 3368 (NH) cm^{-1}. – ^{1}H NMR (300.1 MHz): δ = −15.18 [t, *cis*-^{2}J(P,H) = 10.8 Hz, 1 H, IrH], 4.19 [d, *gem*-^{2}J(H,H) = 11.7 Hz, 1 H, NH]; 7.1–7.9 (m, 29 H, C$_6$H$_4$ and C$_6$H$_5$), 11.35 (d, 1 H, NH). – ^{31}P{^{1}H} NMR (121.5 MHz): δ = 5.4 [d, *trans*-^{2}J(P,P) = 305.0 Hz, PPh$_3$]; 27.6 (d, 'PNH$_2$'). – $C_{37}H_{32}Cl_2IrNOP_2$ (831.73): calcd. C 53.43, H 3.88, N, 1.68; found C 53.04, H 3.75, N, 1.49.

[IrHCl$_2$(CO)(PPh$_3$)(PPh$_2$C$_6$H$_4$N(Me)H-o)] (**8**): The preparation was carried out as described for **7** by treating 130 mg (0.17 mmol) of **2b** with gaseous HCl in 10 ml of CHCl$_3$ at −60°C. After warming to room temperature, 100 mg (70%) of **8** were collected as an off-white precipitate. – IR: $\tilde{\nu}$ = 2038 (CO), 2231 (IrH), 3329 m (NH) cm^{-1}. – For relevant ^{1}H and ^{31}P NMR data of rotamers **8A**, **8B**, and **8 C**, see text. – $C_{38}H_{34}Cl_2IrNOP_2$ (845.75): calcd. C 53.97, H 4.05, N 1.66; found C 53.90, H 4.06, N 1.41.

X-ray Structure Determinations: Single-crystals of [Ir(CO)(PPh$_3$)('PNMe')] (**2b**) (size 0.2 × 0.3 × 0.4 mm) and [Ir(SO$_2$)(CO)(PPh$_3$)('PNH')] (**5a**) (size 0.08 × 0.35 × 0.55 mm) were grown from toluene/pentane, which furnished complex **2b** as an addition compound containing toluene of crystallization, **2b**·C$_7$H$_8$. The measurements were performed at −73±2°C on Siemens P4 (**2b**·C$_7$H$_8$) and at 20±2°C on Enraf-Nonius CAD4 (**5a**) diffractometers using graphite-monochromated Mo-K_α radiation (λ = 0.7107 Å): orientation matrices and unit cell parameters from the setting angles of >18 centered medium-angle reflections (**2b**·C$_7$H$_8$: $24 < 2\theta < 32°$; **5a**: $12 < 2\theta < 24°$); collection of the diffraction intensities of **2b**·C$_7$H$_8$ by ω scans (data uncorrected for absorption); intensity measurements of **5a** by the $\omega/2\theta$ scan technique (data corrected for absorption by π-scans; T_{min} = 0.53, T_{max} = 0.99). The structures were solved by direct and difference Fourier methods employing the SHELXTL-Plus[21] and SIR-92[22] program systems and subsequently refined by full-matrix least-squares procedures on F^2 (SHELXL-93[23]) with allowance for anisotropic thermal motion of all non-hydrogen atoms. The SO$_2$ ligand of **5a** displayed two-fold disorder of one of its SO groups about the other S=O bond, which was accounted for by assigning the particular oxygen positions, O(2) and O(2a), split occupancies of 0.45 and 0.55, respectively. H atoms were included in the final structural models assuming ideal geometry and using appropriate riding models. – **2b**·C$_7$H$_8$: $C_{45}H_{40}IrNOP_2$ (864.92); monoclinic, Cc, a = 10.686(2), b = 17.036(5), c = 20.480(4) Å, β = 93.04(1)°, V = 3723.1(15) Å^3, Z = 4, $d_{calcd.}$ = 1.543 g cm^{-3}, μ(Mo-K_α) = 3.71 mm^{-1}; $4.5 \le 2\theta \le 54.1°$, 6428 unique reflections ($-13 \le h \le 6$, $0 \le k \le 21$, $-26 \le l \le 26$); R_w2 = 0.072 for all data and 451 parameters ($w = \{\sigma^2(F_o^2) + [0.025(F_o^2 + 2 F_c^2)/3]^2\}^{-1}$), R = 0.031 for 5344 structure factors $F_o > 4\sigma(F_o)$. – **5a**: $C_{37}H_{30}IrNO_3P_2S$ (822.82): monoclinic, $P2_1/n$, a = 11.513(3), b = 22.442(5), c = 13.005(3) Å, β = 90.74(2)°, V = 3360(1) Å^3, Z = 4, $d_{calcd.}$ = 1.627 g cm^{-3}, μ(Mo-K_α) = 4.17 mm^{-1}; $4.7 \le 2\theta \le 48.0°$, 5248 unique reflections ($-2 \le h \le 13$, $-2 \le k \le 25$, $-14 \le l \le 14$); R_w2 = 0.126 for all data and 416 parameters ($w = \{\sigma^2(F_o^2) + [0.072(F_o^2 + 2\,F_o^2)/3]^2\}^{\ 1}$), R = 0.046 for 3878 structure factors $F_o > 4\sigma(F_o)$. – Further details of the crystal structure determinations may be obtained from the Fachinformationszentrum Karslruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-406918 (**2b**·C_7H_8) and CSD-406919 (**5a**).

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