Ligand vs. Metal Basicity: Reactions of 2-(Diphenylphosphanyl)anilido and 2-(Diphenylphosphanyl)phenolato Complexes of Rhodium(I) and Iridium(I) with HBF₄

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Dedicated to Professor Rolf W. Saalfrank on the occasion of his 70th birthday

Treatment of [M(CO)(PPh₃)(2-Ph₂PC₆H₄NH₂-κP)], where M/NR = Rh/NH (1), Rh/NCH₃ (2), Ir/NH (3), and Ir/NCH₃ (4), with Et₂O-HBF₄ in CH₂Cl₂ resulted in protonation at nitrogen with formation of [M(CO)(PPh₃)(2-Ph₂PC₆H₄NHR-κN,N,P)]BF₄ [M/NHR = Rh/NH₂ (7), Rh/NHCH₃ (8), Ir/NH₂ (9), Ir/NHCH₃ (10)]. Similar protonation of [Rh(CO)(PPh₃)(2-Ph₂PC₆H₄O-κO,P)] [5] in CH₂Cl₂ afforded [Rh(CO)(PPh₃)(2-Ph₂PC₆H₄OH-κO,P)]BF₄ (11), but furnished [Rh(CO)(PPh₃)-(NCH₃)(2-Ph₂PC₆H₄OH-κO,P)]BF₄ (12) if carried out in CH₃CN. [Ir(CO)(PPh₃)(2-Ph₂PC₆H₄O-κO,P)] (6) reacted with HBF₄ by protonation at the central metal atom and oxidative addition to give [IrH(FBF₄)(CO)(PPh₃)(2-Ph₂PC₆H₄O-κO,P)] (13), the substitutionally labile BF₄⁻ ligand of which underwent smooth exchange with neutral donors L producing [IrH(CO)(L)(PPh₃)(2-Ph₂PC₆H₄O-κO,P)]BF₄ with L = H₂O (14), CH₃CN (15) and PPh₃ (16). The structures of 6 and 15 were determined by single-crystal X-ray crystallography.

Key words: P,N Ligands, P,O Ligands, Rhodium Complexes, Iridium Complexes, Protonation

Introduction

In previous work we have been investigating several aspects of the coordination chemistry of bidentate 2-(diphenylphosphanyl)phenol, -thiophenol and -aniline ligands, both in their neutral 2-Ph₂PC₆H₄X⁻ (X = O, S, NH, NCH₃) and deprotonated 2-Ph₂PC₆H₄X⁻ forms [1 – 5], in particular with regard to the reactivity of their Ir(I) and Rh(I) complexes towards selected Brønsted and Lewis acids [1, 2]. In this context, the 2-(diphenylphosphanyl)anilido-substituted iridium(I) complex [Ir(CO)(PPh₃)(2-Ph₂PC₆H₄NH-κN,P)] was seen to react with HCl in CHCl₃ or toluene solution at −60 °C by oxidative addition to the central metal atom as well as protonation at nitrogen to form the ionic chelate complex [IrH(Cl)(CO)(PPh₃)(2-Ph₂PC₆H₄NH₂-κN,P)]Cl, containing one of its NH groups hydrogen-bonded to Ir-Cl [2]. Treatment of the N'-methyleneilido compound [Ir(CO)(PPh₃)(2-Ph₂PC₆H₄NCH₃-κN,P)] with hydrogen chloride under the conditions chosen for the reaction of its NH analog with HCl also resulted in oxidative addition to iridium and protonation at nitrogen. However, different from the conversion of [Ir(CO)(PPh₃)(2-Ph₂PC₆H₄NH-κN,P)] into the stable ionic product [IrH(Cl)(CO)(PPh₃)(2-Ph₂PC₆H₄NH₂-κN,P)]Cl, the protonation of the N'-methylenilido ligand was followed by dissociation of the NHCHR group from the metal, allowing the chloride ion to coordinate with formation of the covalent ring-opened product [IrHCl₂(CO)(PPh₃)(2-Ph₂PC₆H₄NHCH₃-κP)], stabilized by intramolecular -N(CH₃)H···Cl-Ir hydrogen bonding [2]. In contrast, the ring-opened compound [IrHCl₂(CO)(PPh₃)(2-Ph₂PC₆H₄POH-κP)], resulting from combination of the chelated phenolato complex [Ir(CO)(PPh₃)(2-Ph₂PC₆H₄O-κO,P)] with HCl in chloroform between −60 and +20 °C proved to be stable only in the presence of excess hydrogen chloride but otherwise was transformed by elimination of HCl and ring closure into [IrH(Cl)(CO)(PPh₃)(2-Ph₂PC₆H₄O-κO,P)] [1]. With the aim of weighing the O- and N-
basicities of 2-(diphenylphosphanyl)anilido and -phenolato ligands against those displayed by coordinatively unsaturated metal centers, we have extended our previous studies to the reactivity of the rhodium and iridium chelate complexes $\text{[M(CO)(PPh}_3\text{(2-Ph}_2\text{PC}_6\text{H}_4\text{X-}}\kappa\text{P},\kappa\text{X})\text{]} \ (X = \text{NH, NHCH}_3\text{, O})$ towards Brønsted acids which, different from HCl, possess non-coordinating or, at best, weakly coordination anions, e. g., HBF$_4$.

**Results and Discussion**

Treatment of CH$_2$Cl$_2$ solutions of the 16e chelate complexes $\text{[M(CO)(PPh}_3\text{(2-Ph}_2\text{PC}_6\text{H}_4\text{NR-}}\kappa\text{N},\kappa\text{P})\text{]} \ [2]$, where M/NR = Rh/NH (1), Rh/NCH$_3$ (2), Ir/NH (3), and Ir/NCH$_3$ (4), with one molar equivalent of HBF$_4$ (54\% in diethyl ether) resulted in smooth protonation of the amide functions to form the corresponding tetrafluoroborate salts $\text{[M(CO)(PPh}_3\text{(2-Ph}_2\text{PC}_6\text{H}_4\text{NHR-}}\kappa\text{N},\kappa\text{P})\text{]}\text{BF}_4$ (Scheme 1, 7 – 10). When allowed to interact with one additional equivalent of HBF$_4$, none of the four $d^8$ complexes 7 – 10 underwent any clean further transformation such as, e. g., protonation at rhodium or iridium with or without decoordination of the NH$_2$ and NHCH$_3$ donors. Instead, intractable mixtures of products were obtained.

In the infrared spectra, the moderately air-stable yellow complex salts 7 – 10 exhibit a single carbonyl stretch band in the 1980 – 2010 cm$^{-1}$ region, each positioned ca. 50 cm$^{-1}$ at higher wavenumbers than those of the neutral starting compounds 1 – 4 [2], along with a very strong absorption between 1050 and 1070 cm$^{-1}$ arising from the triply degenerate u(CO) vibration of the anion. The NHCH$_3$ and NH$_2$ groups manifest themselves by single and, respectively, split v(NH) absorptions around 3200 cm$^{-1}$ as well as by proton resonances observed as broad signals at $\delta$ ca. 5.0 and 5.5 for the two aniline complexes 7 and 9, and at $\delta$ ca. 4.3 and 5.1 for their $N$-methylated homologs 8 and 10. P,N-chelation in the $\text{[M(CO)(PPh}_3\text{(2-Ph}_2\text{PC}_6\text{H}_4\text{NHR-}}\kappa\text{N},\kappa\text{P})\text{]}^+$ cations is evident from the pronounced downfield shifts [6] of their Ph$_2$P$^{31}$P$^1$H resonances ($\delta$ ca. 47 for M = Rh; $\delta$ ca. 44 for M = Ir), which are approximately 66 – 69 ppm at lower field than those of the free 2-Ph$_2$PC$_6$H$_4$NHR ligands ($\delta$ ca. – 22) and thus closely resemble the $^{31}$P shift values observed for the two deprotonated P,N bidentates in the respective $\text{[M(CO)(PPh}_3\text{(2-Ph}_2\text{PC}_6\text{H}_4\text{NHR-}}\kappa\text{N},\kappa\text{P})\text{]}$ precursors ($\delta$ ca. 49 for M = Rh; $\delta$ ca. 38 for M = Ir) [2]. Coupling constants $^2J_{P,P}$ of 280 to 285 Hz indicate the PPh$_3$ and Ph$_2$P donors to be bonded in a monodentate fashion.

Rhodium complex 5 similarly underwent protonation of its anionic 2-Ph$_2$PC$_6$H$_4$O$^-\text{O}$ ligand when combined in CH$_2$Cl$_2$ with ethereal HBF$_4$ in 1 : 1 stoichiometry. Both the P,O-chelated identity and the trans-P-Rh-P geometry of the resulting ionic product, $\text{[Rh(CO)(PPh}_3\text{(2-Ph}_2\text{PC}_6\text{H}_4\text{OH-}}\kappa\text{O,} \kappa\text{P})\text{]}\text{BF}_4$ (11), have been established by IR and $^{31}$P-NMR spectroscopy as outlined above for 7 – 10: $\nu(\text{BF}) = 1098$, $\nu(\text{CO}) = 2000$ cm$^{-1}$; $\delta$(Ph$_2$P) = 43.6, $^2J_{P,P} = 284.4$ Hz. The presence of the phenolic OH group was evident from a broad $^1$H resonance at $\delta = 10.1$.

Dissociation of the OH function from the metal atom with formation of $\text{[Rh(CO)(PPh}_3\text{(NCCH}_3\text{)}\text{)](2-Ph}_2\text{PC}_6\text{H}_4\text{OH-}}\kappa\text{O,} \kappa\text{P})\text{]}\text{BF}_4$ (12) was observed when the reaction between 5 and an equimolar quantity of Et$_2$O-HBF$_4$ was conducted in acetonitrile as a strongly donating solvent rather than in dichloromethane, which has only poor coordinating abilities [8 – 11]. The overall geometry of the cation $\text{[Rh(CO)(PPh}_3\text{(NCCH}_3\text{)}\text{)](2-Ph}_2\text{PC}_6\text{H}_4\text{OH-}}\kappa\text{P})\text{]}^+$ shown in Scheme 1 was confirmed by spectral data. In particular, the $^{31}$P$^1$H-NMR spectrum revealed very similar chemical shifts for the two trans-positioned phosphorus nuclei ($\delta$ = 25.3 and 31.5; $^2J_{P,P} = 292.2$ Hz), which proves the 2-Ph$_2$PC$_6$H$_4$OH ligand to be coordinated in a monodentate fashion.

Whereas the phenolato rhodium complex 5 reacted with HBF$_4$ in different solvents by protonation at oxygen to give 11 or 12, the very same reaction of the phenolato iridium(I) compound $\text{[Ir(CO)}$-$\text{(PPh}_3\text{)](2-Ph}_2\text{PC}_6\text{H}_4\text{O-}}\kappa\text{O,} \kappa\text{P})\text{]}$ (6) afforded the hydrid complex $\text{[IrH(FBF}_3\text{(CO)(PPh}_3\text{)](2-Ph}_2\text{PC}_6\text{H}_4\text{O-}}\kappa\text{O,} \kappa\text{P})\text{]}$. 

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by oxidative addition of the acid. The outcome of this reaction, which parallels the oxidative addition of HBF₄ to trans-[IrCl(CO)(PPh₃)₂] [12], clearly shows the metal basicity of 6 to surpass that of the 2-Ph₂PC₆H₄O⁻ chelate ligand. In agreement with the assignment of 13 as an iridium(III) complex containing a coordinated BF₄⁻ ion of C₃ᵥ symmetry, the IR-active triply degenerate ν(BF) vibration of the free anion is now seen to be split into two components absorbing at 924 and 1125 cm⁻¹ (F₂ → A₁ + E). Coordination of the hydride cis to two mutually trans-positioned P-donors and trans to Ir-FBF₄ follows from both the ³¹P{¹H}-NMR spectrum consisting of two doublets split by 313.5 Hz and the ¹H-NMR spectrum containing a cis-P,P,Coupled IrH pseudotriplet at δ = -26.60, i.e., close to the chemical shift previously reported as δ = -26.5 for trans-(H,F)-, trans-(P,P)-, trans-(P,P)-, and [IrH(CI)(BF₄)](CO)(PPh₃)] [12].

As observed for other transition metal tetrafluoroborate complexes, the BF₄⁻ ligand of 13 is substitutionally labile and is easily displaced by diverse hard and soft donors to produce amines, nitride and phosphane derivatives such as, e.g., [IrH(CO)(OH₂)₂-(PPh₃)](2-Ph₂PC₆H₄O⁻-κO,kP)BF₄ (14), [IrH(CO)-(NCCH₃)(PPh₃)](2-Ph₂PC₆H₄O⁻-κO,kP)BF₄ (15), and [IrH(CO)(PPh₃)](2-Ph₂PC₆H₄O⁻-κO,kP)BF₄ (16). While the preparation of 14 required complex 13 to be isolated and purified prior to the BF₄⁻ exchange reaction, compounds 15 and 16 were also obtained from the in situ protonation, with HBF₄, of [Ir(CO)(PPh₃)](2-Ph₂PC₆H₄O⁻-κO,kP) (6) either in neat acetonitrile or in CH₂Cl₂ in the presence of added PPh₃.

Notwithstanding that the aqua complex 14 contains a non-coordinated BF₄⁻ ion, the infrared spectrum displays three BF stretch bands at 995, 1064, and 1097 cm⁻¹, which points to symmetry lowering from T₄ to C₂ᵥ (F₂ → A₁ + B₁ + B₂) as a result of O–H···F hydrogen bonding between the complex cation and the BF₄⁻ countercation. Such hydrogen bonding interactions have previously been established, by vibrational spectroscopy and X-ray crystallography, for several related aqua complexes, representative examples of which are given by [IrH(Cl)(OH₂)₂(CO)(PPh₃)]BF₄ [12], [Cr(CCH₃)(CO)₃(PC₆H₆)](OH₂)BF₄ [13], [(η²-C₇H₇)Mo(acac)(OH₂)]BF₄ [14], and [Re(CO)₅{(CH₃)₂NCH₂CH₂N(CH₃)₂}(OH₂)]BF₄ [15].

The geometry of the cation 16 has been concluded from its NMR features displaying (i) ³¹P{¹H} ABX-type splitting with trans- and cis-P,P couplings of 291.0, 15.3, and 13.3 Hz, respectively, (ii) pseudoquartet multiplicity of the ¹⁵C{¹H} carbonyl resonance, and (iii) an IrH doublet of virtual triplets characterized by trans-²Jₚₕₕ = 148.0 Hz and |cis-²Jₚₕₕ + cis-²Jₚₕₕ| = 31.8 Hz.

Complex 15 was isolated as the addition compound 15·2C₃H₆O by crystallizing the residue of an evaporated reaction mixture of 6 and an equimolar quantity of Et₂O-HBF₄ in CH₃CN from an acetonitrile/pentane solvent mixture. X-Ray crystal structure analysis confirmed the presence of a distorted octahedral cation in which the acetonitrile ligand is bonded trans to Ir–H (Fig. 1). The Ir–N distance, 2.134(5) Å, is within the range of 2.10 to 2.15 Å previously measured for various other cationic iridium(III) complexes possessing trans-H-Ir-NCC(H) building blocks [16–19]. Ir–P and Ir–O bond lengths within the five-membered chelate ring, 2.322(2) and 2.053(4) Å, are slightly longer than the Ir–P and Ir–O distances of 2.297(2) and 2.039(4) Å observed for [Ir(CO)(PPh₃)](2-Ph₂PC₆H₄O⁻-κO,kP) (6), the crystal structure of which has been determined for comparison (Fig. 2).

Molecule 6 displays the expected four-coordinate planar coordination geometry about the central metal atom as evidenced from the sum of the four interligand cis angles, 360.2°. Metal-to-ligand bond lengths and valence angles at the central metal atom reveal a close relation to [Rh(CO)₃Cl]²⁻.
Fig. 2. Molecular structure of [(CO)(PPh3)(2-Ph2PC6H4O−κO,κP)] (6) in the crystal (H atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Ir–P(1) 2.336(2), Ir–P(2) 2.297(2), Ir–O(1) 2.039(4), Ir–C(37) 1.785(8); P(1)–Ir–P(2) 167.27(7), P(1)–Ir–O(1) 85.2(1), P(1)–Ir–C(37) 96.0(2), P(2)–Ir–O(1) 82.6(1), P(2)–Ir–C(37) 96.4(2), O(1)–Ir–C(37) 177.1(3).

Concluding Remarks

A comparative investigation of the reaction of HBF4 with Vaska-type 2-(diphenylphosphanyl)anilido complexes of rhodium(I) and iridium(I), [(CO)(PPh3)(2-Ph2PC6H4O−κO,κP)] (R = H, CH3), has shown that, irrespective of the nature of the central metal atom, protonation occurs at nitrogen to form ionic 2-(diphenylphosphanyl)aniline derivatives [M(CO)(PPh3)(2-Ph2PC6H4NH2−κN,κP)]BF4 and [M(CO)(PPh3)(2-Ph2PC6H4NHC6H4−κN,κP)]BF4 (L = 1H, CO). – 31P NMR (CDCl3): δ = 45.4 (s, CH3), 154.7 (dd, 2JPC = 3.5 Hz, phenylene C-1), 190.0 (“dt”, 1JPC = 70.8 Hz, “cis-2JPC + cis-2JPC” = 31.0 Hz, CO). – 31P (1H) NMR (CDCl3): δ = 31.0 (dd, 1JRH,P = 126.5 Hz, 2JSP = 285.3 Hz, PPh3), 47.1 (dd, 1JRH,P = 123.9 Hz, 2JSP = 87.4 Hz, PPh3). – C37H31BF4NOP2Rh (757.32): calcd. C 58.68, H 4.13, N 1.85; found C 58.86, H 4.09, N 1.79.

Experimental Section

All manipulations were performed under nitrogen using standard Schlenk techniques. Solvents were distilled from the appropriate drying agents prior to use. – IR: Mattson Polaris – Bruker DFX 300 (300.1 MHz for 1H, 75.5 MHz for 13C, and 28 MHz for 31P) with SiMe4 as internal or external standards (downfield positive) at ambient temperature (“m” = deceptively simple multiplet). Complexes [M(CO)(PPh3)(2-Ph2PC6H4H2−κN,κP)] (M = Rh; R = H (1), CH3 (2); M = Ir; R = H (3), CH3 (4)) and [M(CO)(PPh3)(2-Ph2PC6H4O−κO,κP)] (M = Rh (5), Ir (6)) were prepared as previously described [1, 2].

A solution of 100 mg (0.15 mmol) of 1 in 10 mL of CH2Cl2 was treated with 21 µL of HBF4 (54 % in diethyl ether; 0.15 mmol) and stirred for 1 h at r.t. Evaporation of all volatiles left a pale-yellow oil which was triturated with pentane to give 103 mg (90 %) of [(CO)(PPh3)(2-Ph2PC6H4NH2−κN,κP)]BF4 (7). – 1HNMR (CDCl3): δ = 4.97 (br, 2 H, NH2), 7.5 (m, 29 H, aryl H). – 13C NMR (CDCl3): δ = 147.8 (dd, 2JPC = 23.1 Hz, 3JPC = 5.3 Hz, phenylene C-1), 190.0 (“dt”, 1JPC = 70.8 Hz, “cis-2JPC + cis-2JPC” = 31.0 Hz, CO). – 31P (1H) NMR (CDCl3): δ = 31.0 (dd, 1JRH,P = 126.5 Hz, 2JSP = 285.3 Hz, PPh3), 47.1 (dd, 1JRH,P = 123.9 Hz, 2JSP = 87.4 Hz, PPh3). – C37H31BF4NOP2Rh (757.32): calcd. C 58.68, H 4.13, N 1.85; found C 58.86, H 4.09, N 1.54.

Similar procedures were used for the preparation of complexes 8–10.

From 140 mg (0.21 mmol) of 2 and 28 µL of 54 % ethereal HBF4 (0.21 mmol) in 10 mL of CH2Cl2. – Yield: 140 mg (86 %), – IR (KBr): ν = 3244 (NH), 1996 (CO), 1057 (BF4) cm−1. – 1H NMR (CDCl3): δ = 2.15 (d, 2JHH = 6.0 Hz, 3 H, CH3), 4.33 (br, 1 H, NH), 7.6 (m, 29 H, aryl H). – 13C NMR (CDCl3): δ = 45.4 (s, CH3), 154.7 (dd, 2JPC = 22.0 Hz, 3JPC = 3.5 Hz, phenylene C-1), 189.9 (“dt”, 1JRH,P = 69.7 Hz, “cis-2JPC + cis-2JPC” = 32.4 Hz, CO). – 31P (1H) NMR (CDCl3): δ = 31.1 (dd, 1JRH,P = 128.8 Hz, 2JSP = 280.1 Hz, PPh3), 44.2 (dd, 1JRH,P = 126.4 Hz, 2JSP = 87.4 Hz, PPh3). – C37H31BF4NOP2Rh (771.34): calcd. C 59.17, H 4.31, N 1.82; found C 59.16, H 4.33, N 1.79.

[Rh(CO)(PPh3)(2-Ph2PC6H4H2−κN,κP)]BF4 (8)

[Ir(H)2BF4(CP)(PPh3)(2-Ph2PC6H4−κO,κP)] and [Ir(H)2(CP)(PPh3)(2-Ph2PC6H4−κO,κP)]BF4, respectively. In marked contrast, the iridium(I) complex underwent protonation at the central metal atom with formation of hydridoiridium(III) products, [Ir(H2BF4)(CP)(PPh3)(2-Ph2PC6H4O−κO,κP)] and [Ir(CO)(L)(CP)(PPh3)(2-Ph2PC6H4O−κO,κP)]BF4 (L = H2O, CH3CN, PPh3), under all conditions studied.

In conclusion, it has been demonstrated that the Bronsted basicity towards HBF4 of the anionic anilido chelate ligands of the 16e complexes [M(CO)(PPh3)(2-Ph2PC6H4−κN,κP)] (R = H, CH3) exceeds the metal basicity of both Rh(I) and Ir(I), whereas the ligand basicity of the 2-Ph2PC6H4O−κO,κP] chelate is superior to that of the central metal atom of [M(CO)(PPh3)(2-Ph2PC6H4O−κO,κP)] for M = Rh, but inferior for M = Ir.
$[Ir(CO)(PPh_3)(2-Ph_2PC_6H_4HN_2-kN,kP)]BF_4$ (9)

From 150 mg (0.20 mmol) of 3 and 27 µL of 54% ethereal HBF_4 (0.21 mmol) in 10 mL of CH_2Cl_2. – Yield: 145 mg (86%). – IR (KBr): ν = 3244/1716 (NH_2), 1980 (CO), 1069 (BF_4) cm$^{-1}$. – 1H NMR (CDCl_3): 8 = 5.45 (br, 2 H, NH_2), 7.5 (m, 29 H, aryl H) – 13C{1H} NMR (CDCl_3): δ = 147.5 (dd, 2J_P,C = 21.0 Hz, 3J_P,C = 6.3 Hz, phenylene C-1), 175.1 (v’t, 2J_P,C = 20.8 Hz, CO), – 31P{1H} NMR (CDCl_3): δ = 28.1 (PPh_3), 42.6 (Ph_2P); both d, 2J_P,P = 283.1 Hz. – C_{39}H_{33}BF_4IrN_2O_2P_2Rh (799.34); calcd. C 58.60, H 4.16, N 1.75; found C 59.06, H 4.62, N 1.56.

$[Ir(H)(BF_4)_2(CO)(PPh_3)(2-Ph_2PC_6H_4O-kO,kP)]$ (13)

A mixture of 180 mg (0.04 mmol) of 6 and 33 µL of 54% ethereal HBF_4 (0.04 mmol) in 10 mL of CH_2Cl_2 was stirred for 1 h at r.t. Evaporation of the solvent followed by treatment with pentane left 195 mg (96%) of 13 as a pale-yellow solid. – IR (KBr): ν = 2054 (CO), 1125/924 (BF_4) cm$^{-1}$. – 1H NMR (CDCl_3): δ = 26.70 (v’(t), 1 H, IrH), 6.8, 7.2 (both m, 2 H each, C_6H_5), 7.6 (m, 25 H, C_6H_5). – 31P{1H} NMR (CDCl_3): δ = 14.6 (PPh_3), 36.6 (Ph_2P); both d, 2J_P,P = 313.5 Hz. – C_{37}H_{31}BF_4IrO_2P_2 (847.62); calcd. C 52.43, H 3.57; found C 52.53, H 3.80.

$[Ir(CO)(OH)(PPh_3)(2-Ph_2PC_6H_4O-kO,kP)]BF_4$ (14)

A solution of 140 mg (0.17 mmol) of 13 in 10 mL of CH_2Cl_2 was treated with 3 µL of water. Stirring the mixture for 1 h at r.t. followed by evaporation to dryness afforded 143 mg (99%) of compound 14 as a pale-yellow solid which was washed with pentane and dried. – IR (KBr): ν = 3408 (OH), 2276 (IrH), 2045 (CO), 1097/164995 (BF_4) cm$^{-1}$. – 1H NMR (CDCl_3): δ = -21.57 (v’(t), 2J_RH + 2J_PH = 22.2 Hz, 1 H, IrH), 3.5 (br, 2 H, H_2O), 6.5, 7.0 (both m, 2 H each, C_6H_5), 7.3 (m, 25 H, C_6H_5). – 31P{1H} NMR (CDCl_3): δ = 13.4 (PPh_3), 35.3 (Ph_2P) d, 2J_P,P = 314.0 Hz. – C_{37}H_{32}BF_4IrO_2P_2 (865.63); calcd. C 51.34, H 3.73; found C 51.12, H 3.69.

$[Ir(CO)(NCCH_3)(PPh_3)(2-Ph_2PC_6H_4O-kO,kP)]BF_4$ (15)

This compound was obtained from equimolar quantities of 6 and 54% ethereal HBF_4 in acetonitrile using a procedure similar to the one outlined above for the rhodium complex 12. The oily residue remaining after evaporation of the solvent was re-dissolved in acetone. Addition of pentane resulted in the gradual deposition of some off-white crystals which were identified as the acetone solvate 15 2C_6H_5O by X-ray structure analysis.

$[Ir(CO)(PPh_3)(2-Ph_2PC_6H_4O-kO,kP)]BF_4$ (16)

Addition of 100 µL of 54% ethereal HBF_4 (0.73 mmol) and 83 mg (0.32 mmol) of PPh_3 to 240 mg (0.17 mmol) of 6, dissolved in 10 mL of CH_2Cl_2 produced a colorless solution which was stirred at ambient conditions for 1 h and then evaporated. Complex 16 was left as an off-white residue which was washed with pentane and dried. – Yield: 355 mg (quantitative). – IR (KBr): ν = 2127 (IrH), 2040 (CO), 1092
X-Ray structure determinations

Single crystals of 6 (0.30 × 0.15 × 0.13 mm³) and 15·2C₃H₆O (0.45 × 0.25 mm²) were grown from toluene/pentane and, respectively, acetone/pentane solvent mixtures. Diffraction measurements were made at ambient temperature on an Enraf-Nonius CAD-4 MACH 3 diffractometer using graphite-monochromatized MoKα radiation (λ = 0.71073 Å); orientation matrices and unit cell parameters from the setting angles of 25 centered non-hydrogen atoms employing the WINGX package [21] and CCDC 753417 (6) and CCDC 753418 (15·2C₃H₆O) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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