Ligand *vs.* Metal Basicity: Reactions of 2-(Diphenylphosphanyl)anilido and 2-(Diphenylphosphanyl)phenolato Complexes of Rhodium(I) and Iridium(I) with HBF_4

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

Treatment of [M(CO)(PPh_3)(2-$Ph_2PC_6H_4NR$-*κN*,*κP*)], where M/NR = Rh/NH (**1**), Rh/NCH_3 (**2**), Ir/NH (**3**), and Ir/NCH_3 (**4**), with $Et_2O{\cdot}HBF_4$ in CH_2Cl_2 resulted in protonation at nitrogen with formation of [M(CO)(PPh_3)(2-$Ph_2PC_6H_4NHR$-*κN*,*κP*)]BF_4 [M/NHR = Rh/NH_2 (**7**), Rh/$NHCH_3$ (**8**), Ir/NH_2 (**9**), Ir/$NHCH_3$ (**10**)]. Similar protonation of [Rh(CO)(PPh_3)(2-$Ph_2PC_6H_4O$-*κO*,*κP*)] (**5**) in CH_2Cl_2 afforded [Rh(CO)(PPh_3)(2-$Ph_2PC_6H_4OH$-*κO*,*κP*)]BF_4 (**11**), but furnished [Rh(CO)(PPh_3)($NCCH_3$)(2-$Ph_2PC_6H_4OH$-*κP*)]BF_4 (**12**) if carried out in CH_3CN. [Ir(CO)(PPh_3)(2-$Ph_2PC_6H_4O$-*κO*,*κP*)] (**6**) reacted with HBF_4 by protonation at the central metal atom and oxidative addition to give [IrH(FBF_3)(CO)(PPh_3)(2-$Ph_2PC_6H_4O$-*κO*,*κP*)] (**13**), the substitutionally labile BF_4^- ligand of which underwent smooth exchange with neutral donors L producing [IrH(CO)(L)(PPh_3)(2-$Ph_2PC_6H_4O$-*κO*,*κP*)]BF_4 with L = H_2O (**14**), CH_3CN (**15**) and PPh_3 (**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-$Ph_2PC_6H_4XH$ (X = O, S, NH, NCH_3) and deprotonated 2-$Ph_2PC_6H_4X^-$ 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)(PPh_3)(2-$Ph_2PC_6H_4NH$-*κN*,*κP*)] was seen to react with HCl in $CHCl_3$ 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)(PPh_3)(2-$Ph_2PC_6H_4NH_2$-*κN*,*κP*)]Cl, containing one of its NH groups hydrogen-bonded to Ir-Cl [2]. Treatment of the *N*-methylanilido compound [Ir(CO)(PPh_3)(2-$Ph_2PC_6H_4NCH_3$-*κN*,*κP*)] 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)(PPh_3)(2-$Ph_2PC_6H_4NH$-*κN*,*κP*)] into the stable ionic product [IrH(Cl)(CO)(PPh_3)(2-$Ph_2PC_6H_4NH_2$-*κN*,*κP*)]Cl, the protonation of the *N*-methylanilido ligand was followed by dissociation of the $NHCH_3$ group from the metal, allowing the chloride ion to coordinate with formation of the covalent ring-opened product [$IrHCl_2$(CO)(PPh_3)(2-$Ph_2PC_6H_4NHCH_3$-*κP*)], stabilized by intramolecular -N(CH_3)H···Cl-Ir hydrogen bonding [2]. In contrast, the ring-opened compound [$IrHCl_2$(CO)(PPh_3)(2-$Ph_2PC_6H_4POH$-*κP*)], resulting from combination of the chelated phenolato complex [Ir(CO)(PPh_3)(2-$Ph_2PC_6H_4O$-*κO*,*κP*)] 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)(PPh_3)(2-$Ph_2PC_6H_4O$-*κO*,*κP*)] [1]. With the aim of weighing the *O*- and *N*-

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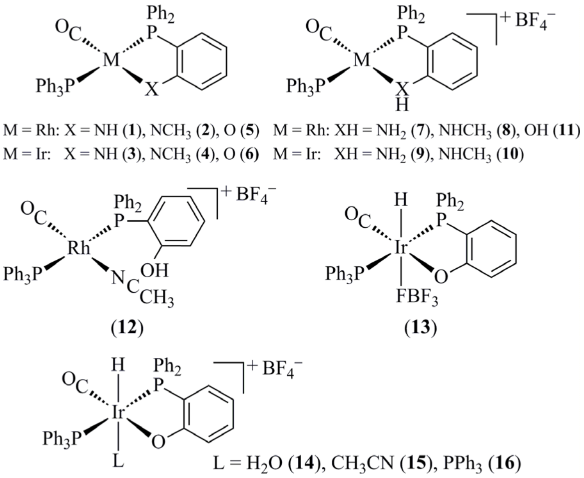
basicities of 2-(diphenylphosphanyl)anilido and -phenolato ligands against those displayed by coordinatively unsaturated metal centers, we have extended our previous studies to the reactivity of the rhodium and iridium chelate complexes [M(CO)(PPh_3)(2-$Ph_2PC_6H_4X$-$\kappa P,\kappa X$)] (X = NH, $NHCH_3$, 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_2Cl_2 solutions of the 16e chelate complexes [M(CO)(PPh_3)(2-$Ph_2PC_6H_4NR$-$\kappa N,\kappa P$)] [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 [M(CO)(PPh_3)(2-$Ph_2PC_6H_4NHR$-$\kappa N,\kappa P$)]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 ν(BF) vibration of the anion. The $NHCH_3$ and NH_2 groups manifest themselves by single and, respectively, split ν(NH) absorptions around 3200 cm^{-1} as well as by proton resonances observed as broad signals at δ *ca.* 5.0 and 5.5 for the two aniline complexes **7** and **9**, and at δ *ca.* 4.3 and 5.1 for their *N*-methylated homologs **8** and **10**. *P*,*N*-chelation in the [M(CO)(PPh_3)(2-$Ph_2PC_6H_4NHR$-$\kappa N,\kappa P$)]$^+$ cations is evident from the pronounced downfield shifts [6] of their Ph_2P $^{31}P\{^1H\}$ resonances (δ *ca.* 47 for M = Rh; δ *ca.* 44 for M = Ir), which are approximately 66–69 ppm at lower field than those of the free 2-$Ph_2PC_6H_4NHR$ ligands (δ *ca.* −22) and thus closely resemble the ^{31}P shift values observed for the two deprotonated *P*,*N* bidentates in the respective [M(CO)(PPh_3)(2-$Ph_2PC_6H_4NR$-$\kappa N,\kappa P$)] precursors (δ *ca.* 49 for M = Rh; δ *ca.* 38 for M = Ir) [2]. Coupling constants $^2J_{P,P}$ of 280 to 285 Hz indicate the PPh_3 and Ph_2P donors to be coordinated in mutual *trans* position [7].



Scheme 1.

Rhodium complex **5** similarly underwent protonation of its anionic 2-$Ph_2PC_6H_4O^-$ ligand when combined in CH_2Cl_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, [Rh(CO)(PPh_3)(2-$Ph_2PC_6H_4OH$-$\kappa O,\kappa P$)]BF_4 (**11**), have been established by IR and ^{31}P-NMR spectroscopy as outlined above for **7**–**10**: ν(BF) = 1098, ν(CO) = 2000 cm^{-1}; δ(Ph_2P) = 43.6, $^2J_{P,P}$ = 284.4 Hz. The presence of the phenolic OH group was evident from a broad ^1H resonance at δ = 10.1.

Dissociation of the OH function from the metal atom with formation of [Rh(CO)(PPh_3)($NCCH_3$)(2-$Ph_2PC_6H_4OH$-κP)]BF_4 (**12**) was observed when the reaction between **5** and an equimolar quantity of $Et_2O \cdot HBF_4$ 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 [Rh(CO)(PPh_3)($NCCH_3$)-(2-$Ph_2PC_6H_4OH$-κP)]$^+$ shown in Scheme 1 was confirmed by spectral data. In particular, the $^{31}P\{^1H\}$-NMR spectrum revealed very similar chemical shifts for the two *trans*-positioned phosphorus nuclei (δ = 25.3 and 31.5; $^2J_{P,P}$ = 292.2 Hz), which proves the 2-$Ph_2PC_6H_4OH$ ligand to be bonded 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 [Ir(CO)(PPh_3)(2-$Ph_2PC_6H_4O$-$\kappa O,\kappa P$)] (**6**) afforded the hydrido complex [IrH(FBF_3)(CO)(PPh_3)(2-$Ph_2PC_6H_4O$-

$\kappa O,\kappa P$)] (**13**) by oxidative addition of the acid. The outcome of this reaction, which parallels the oxidative addition of HBF_4 to *trans*-[IrCl(CO)(PPh_3)$_2$] [12], clearly shows the metal basicity of **6** to surpass that of the 2-$Ph_2PC_6H_4O^-$ chelate ligand. In agreement with the assignment of **13** as an iridium(III) complex containing a coordinated BF_4^- ion of C_{3v} 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} ($F_2 \rightarrow A_1 + E$). Coordination of the hydride *cis* to two mutually *trans*-positioned *P*-donors and *trans* to Ir-FBF_3 follows from both the $^{31}P\{^1H\}$-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 $\delta = -26.60$, *i. e.*, close to the chemical shift previously reported as $\delta = -26.5$ for *trans*-(*H*,*F*)-, *trans*-(*P*,*P*)-[IrH(Cl)(FBF_3)(CO)(PPh_3)$_2$] [12].

As observed for other transition metal tetrafluoroborato complexes, the BF_4^- ligand of **13** is substitutionally labile and is easily displaced by diverse hard and soft donors to produce aqua, nitrile and phosphane derivatives such as, *e. g.*, [IrH(CO)(OH_2)-(PPh_3)(2-$Ph_2PC_6H_4O$-$\kappa O,\kappa P$)]BF_4 (**14**), [IrH(CO)-($NCCH_3$)(PPh_3)(2-$Ph_2PC_6H_4O$-$\kappa O,\kappa P$)]BF_4 (**15**), and [IrH(CO)(PPh_3)$_2$(2-$Ph_2PC_6H_4O$-$\kappa O,\kappa P$)]BF_4 (**16**). While the preparation of **14** required complex **13** to be isolated and purified prior to the BF_4^-/H_2O exchange reaction, compounds **15** and **16** were also obtained from the *in situ* protonation, with HBF_4, of [Ir(CO)(PPh_3)(2-$Ph_2PC_6H_4O$-$\kappa O,\kappa P$)] (**6**) either in neat acetonitrile or in CH_2Cl_2 in the presence of added PPh_3.

Notwithstanding that the aqua complex **14** contains a non-coordinated BF_4^- ion, the infrared spectrum displays three BF stretch bands at 995, 1064, and 1097 cm^{-1}, which points to symmetry lowering from T_d to C_{2v} ($F_2 \rightarrow A_1 + B_1 + B_2$) as a result of O–H$\cdots$F hydrogen bonding between the complex cation and the BF_4^- counterion. 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)(OH_2)(CO)(PPh_3)$_2$]BF_4 [12], [Cr(CCH_3)(CO)$_3${P(CH_3)$_3$}(OH_2)]BF_4 [13], [(η^7-C_7H_7)Mo(acac)(OH_2)]BF_4 [14], and [Re(CO)$_3$-{(CH_3)$_2NCH_2CH_2N$(CH_3)$_2$}(OH_2)]BF_4 [15].

The geometry of the cation **16**$^+$ has been concluded from its NMR features displaying (i) $^{31}P\{^1H\}$ *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 $^{13}C\{^1H\}$ carbonyl resonance, and (iii) an IrH doublet of virtual triplets characterized by *trans*-$^2J_{P,H}$ = 148.0 Hz and $|cis\text{-}^2J_{P,H} + cis\text{-}^2J_{P',H}|$ = 31.8 Hz.

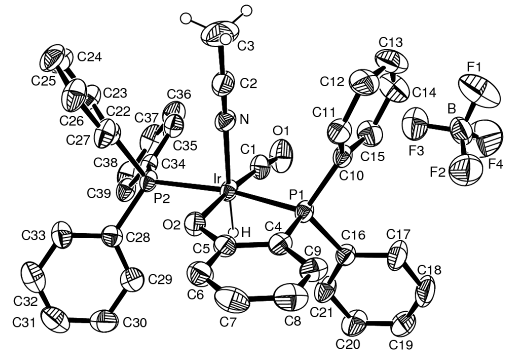


Fig. 1. Molecular structure of [IrH(CO)($NCCH_3$)(PPh_3)(2-$Ph_2PC_6H_4O$-$\kappa O,\kappa P$)]BF_4 (**15**) in the crystal (aryl H atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Ir–P(1) 2.322(2), Ir–P(2) 2.381(2), Ir–O(2) 2.053(4), Ir–N 2.134(5), Ir–C(1) 1.831(8), Ir–H, 1.6 (calcd.); P(1)–Ir–P(2) 169.26(6), P(1)–Ir–O(2) 84.0(1), P(1)–Ir–N 90.3(1), P(1)–Ir–C(1) 92.7(2), P(2)–Ir–O(2) 85.9(1), P(2)–Ir–N 92.5(1), P(2)–Ir–C(1) 97.2(2), O(2)–Ir–N 86.3(2), O(2)–Ir–C(1) 175.3(2), N–Ir–C(1) 97.1(3).

Complex **15** was isolated as the addition compound **15**·$2C_3H_6O$ by crystallizing the residue of an evaporated reaction mixture of **6** and an equimolar quantity of $Et_2O \cdot HBF_4$ in CH_3CN from an acetone/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-$NCCH_3$ 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)-(PPh_3)(2-$Ph_2PC_6H_4O$-$\kappa O,\kappa P$)] (**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)-

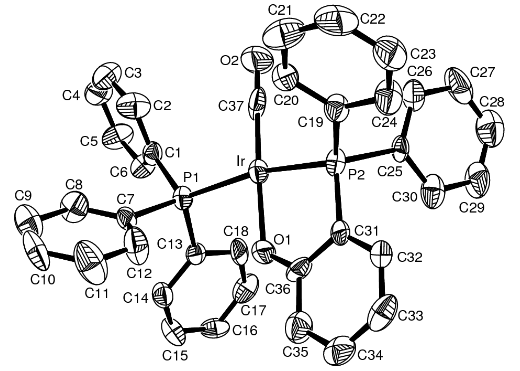


Fig. 2. Molecular structure of [Ir(CO)(PPh_3)(2-$Ph_2PC_6H_4O$-$\kappa O,\kappa P$] (**6**) in the crystal (H atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Ir–P(1) 2.336(2), Ir–P(2) 2.297(2), Ir–O(1) 2.039(4), Ir–C(37) 1.785(8); P(1)–Ir–P(2) 167.27(7), P(1)–Ir–O(1) 85.2(1), 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).

(PPh_3)(2-$Ph_2PC_6H_4O$-$\kappa O,\kappa P$)] and [Ir(CO)(PPh_3)(2-$Ph_2PC_6H_4NHCH_3$-$\kappa N,\kappa P$)], the structures of which have been reported previously [1, 2].

Concluding Remarks

A comparative investigation of the reaction of HBF_4 with Vaska-type 2-(diphenylphosphanyl)anilido complexes of rhodium(I) and iridium(I), [M(CO)(PPh_3)(2-$Ph_2PC_6H_4NR$-$\kappa N,\kappa P$)] (R = H, CH_3), 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)(PPh_3)(2-$Ph_2PC_6H_4NHR$-$\kappa N,\kappa P$)]BF_4. The 2-(diphenylphosphanyl)phenolato precursors [Rh(CO)(PPh_3)(2-$Ph_2PC_6H_4O$-$\kappa O,\kappa P$)] and [Ir(CO)(PPh_3)(2-$Ph_2PC_6H_4O$-$\kappa O,\kappa P$)] displayed divergent reactivity towards HBF_4: the rhodium(I) compound, dissolved in CH_2Cl_2 or CH_3CN, was protonated by the acid at the phenolato function producing [Rh(CO)(PPh_3)(2-$Ph_2PC_6H_4OH$-$\kappa O,\kappa P$)]BF_4 and [Rh(CO)(PPh_3)($NCCH_3$)(2-$Ph_2PC_6H_4OH$-κP)]BF_4, respectively. In marked contrast, the iridium(I) complex underwent protonation at the central metal atom with formation of hydridoiridium(III) products, [IrH(FBF_3)(CO)(PPh_3)(2-$Ph_2PC_6H_4O$-$\kappa O,\kappa P$)] and [IrH(CO)(L)(PPh_3)(2-$Ph_2PC_6H_4O$-$\kappa O,\kappa P$)]BF_4 (L = H_2O, CH_3CN, PPh_3), under all conditions studied.

In conclusion, it has been demonstrated that the Brønsted basicity towards HBF_4 of the anionic anilido chelate ligands of the 16e complexes [M(CO)(PPh_3)(2-$Ph_2PC_6H_4NR$-$\kappa N,\kappa P$)] (R = H, CH_3) exceeds the metal basicity of both Rh(I) and Ir(I), whereas the ligand basicity of the 2-$Ph_2PC_6H_4O^-$ chelate is superior to that of the central metal atom of [M(CO)(PPh_3)(2-$Ph_2PC_6H_4O$-$\kappa O,\kappa P$)] for M = Rh, but inferior for M = Ir.

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 – NMR: Bruker DPX 300 (300.1 MHz for ^1H, 75.5 MHz for ^{13}C, and 121.5 MHz for ^{31}P) with $SiMe_4$ as internal or H_3PO_4 as external standards (downfield positive) at ambient temperature ("m" = deceptively simple multiplet). Complexes [M(CO)(PPh_3)(2-$Ph_2PC_6H_4NR$-$\kappa N,\kappa P$)] [M = Rh: R = H (**1**), CH_3 (**2**); M = Ir: R = H (**3**), CH_3 (**4**)] and [M(CO)(PPh_3)(2-$Ph_2PC_6H_4O$-$\kappa O,\kappa P$] [M = Rh (**5**), Ir (**6**)] were prepared as previously described [1, 2].

[Rh(CO)(PPh_3)(2-$Ph_2PC_6H_4NH_2$-$\kappa N,\kappa P$)]BF_4 (7)

A solution of 100 mg (0.15 mmol) of **1** in 10 mL of CH_2Cl_2 was treated with 21 μL of HBF_4 (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 **7** as yellow microcrystals. – IR (KBr): ν = 3218/3120 (NH_2), 2004 (CO), 1067 (BF_4) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 4.97 (br, 2 H, NH_2), 7.5 (m, 29 H, aryl H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 147.8 (dd, $^2J_{P,C}$ = 23.1 Hz, $^3J_{P,C}$ = 5.3 Hz, phenylene C-1), 190.0 ("dt", $^1J_{Rh,C}$ = 70.8 Hz, $|cis\text{-}^2J_{P,C} + cis\text{-}^2J_{P',C}|$= 31.0 Hz, CO). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 31.0 (dd, $^1J_{Rh,P}$ = 126.5 Hz, *trans*-$^2J_{P,P}$ = 285.3 Hz, PPh_3), 47.1 (dd, $^1J_{Rh,P}$ = 123.9 Hz, Ph_2P). – $C_{37}H_{31}BF_4NOP_2Rh$ (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**.

[Rh(CO)(PPh_3)(2-$Ph_2PC_6H_4NHCH_3$-$\kappa N,\kappa P$)]BF_4 (8)

From 140 mg (0.21 mmol) of **2** and 28 μL of 54 % ethereal HBF_4 (0.21 mmol) in 10 mL of CH_2Cl_2. – Yield: 140 mg (86 %). – IR (KBr): ν = 3244 (NH), 1996 (CO), 1057 (BF_4) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 2.15 (d, $^3J_{H,H}$ = 6.0 Hz, 3 H, CH_3), 4.33 (br, 1 H, NH), 7.6 (m, 29 H, aryl H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 45.4 (s, CH_3), 154.7 (dd, $^2J_{P,C}$ = 22.0 Hz, $^3J_{P,C}$ = 3.5 Hz, phenylene C-1), 189.9 ("dt", $^1J_{Rh,C}$ = 69.7 Hz, $|cis\text{-}^2J_{P,C} + cis\text{-}^2J_{P',C}|$= 32.4 Hz, CO). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 31.1 (dd, $^1J_{Rh,P}$ = 128.8 Hz, *trans*-$^2J_{P,P}$ = 280.1 Hz, PPh_3), 44.2 (dd, $^1J_{Rh,P}$ = 126.4 Hz, Ph_2P). – $C_{38}H_{33}BF_4NOP_2Rh$ (771.34): calcd. C 59.17, H 4.31, N 1.82; found C 59.16, H 4.33, N 1.79.

*[Ir(CO)(PPh$_3$)(2-Ph$_2$PC$_6$H$_4$NH$_2$-κN,κP)]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$_2$Cl$_2$. – Yield: 145 mg (86 %). – IR (KBr): ν = 3244/3176 (NH$_2$), 1980 (CO), 1069 (BF$_4$) cm^{-1}. – ^{1}H NMR (CDCl$_3$): δ = 5.45 (br, 2 H, NH$_2$), 7.5 (m, 29 H, aryl H). – ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 147.5 (dd, $^2J_{\mathrm{P,C}}$ = 21.0 Hz, $^3J_{\mathrm{P,C}}$ = 6.3 Hz, phenylene C-1), 175.1 ("t", $|cis\text{-}^2J_{\mathrm{P,C}}+cis\text{-}^2J_{\mathrm{P',C}}|$ = 20.8 Hz, CO). – ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 28.1 (PPh$_3$), 42.6 (Ph$_2$P); both d, *trans*-$^2J_{\mathrm{P,P}}$ = 283.1 Hz. – C$_{37}$H$_{31}$BF$_4$IrNOP$_2$ (846.63): calcd. C 52.49, H 3.69, N 1.65; found C 51.69, H 3.81, N 1.51.

*[Ir(CO)(PPh$_3$)(2-Ph$_2$PC$_6$H$_4$NHCH$_3$-κN,κP)]BF$_4$ (**10**)*

From 130 mg (0.18 mmol) of **4** and 24 μL of 54 % ethereal HBF$_4$ (0.18 mmol) in 10 mL of CH$_2$Cl$_2$. – Yield: 140 mg (96 %). – IR (KBr): ν = 3227 (NH), 1987 (CO), 1057 (BF$_4$) cm^{-1}. – ^{1}H NMR (CDCl$_3$): δ = 2.20 (d, $^3J_{\mathrm{H,H}}$ = 5.8 Hz, 3 H, CH$_3$), 5.07 (br, 1 H, NH), 7.7 (m, 29 H, aryl H). – ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 47.1 (s, CH$_3$), 155.7 (dd, $^2J_{\mathrm{P,C}}$ = 20.4 Hz, $^3J_{\mathrm{P,C}}$ = 2.0 Hz, phenylene C-1), 174.3 ("t", $|cis\text{-}^2J_{\mathrm{P,C}}+cis\text{-}^2J_{\mathrm{P',C}}|$ = 21.2 Hz, CO). – ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 28.6 (PPh$_3$), 40.0 (Ph$_2$P); both d, *trans*-$^2J_{\mathrm{P,P}}$ = 281.2 Hz. – C$_{38}$H$_{33}$BF$_4$IrNOP$_2$ (860.66): calcd. C 53.03, H 3.86, N 1.63; found C 52.73, H 4.03, N 1.13.

*[Rh(CO)(PPh$_3$)(2-Ph$_2$PC$_6$H$_4$OH-κO,κP)]BF$_4$ (**11**)*

160 mg (0.24 mmol) of **5** and 33 μL of 54 % ethereal HBF$_4$ (0.24 mmol) were combined in 10 mL of CH$_2$Cl$_2$. Stirring at ambient conditions and subsequent work-up as described for compound **7** afforded 169 mg (91 %) of **11** as yellow crystals. – Yield: 165 mg (91%). – IR (KBr): ν = 2000 (CO), 1098 (BF$_4$) cm^{-1}. – ^{1}H NMR (CDCl$_3$): δ = 7.1–7.6 (m, 29 H, aryl H), 10.1 (br, 1 H, OH). – ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 161.2 (dd, $^2J_{\mathrm{P,C}}$ = 18.0 Hz, $^3J_{\mathrm{P,C}}$ = 3.6 Hz, phenylene C-1), 188.6 ("dt", $^1J_{\mathrm{Rh,C}}$ = 82.1 Hz, $|cis\text{-}^2J_{\mathrm{P,C}}+cis\text{-}^2J_{\mathrm{P',C}}|$ = 32.2 Hz, CO). – ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 28.0 (dd, $^1J_{\mathrm{Rh,P}}$ = 125.9 Hz, *trans*-$^2J_{\mathrm{P,P}}$ = 284.4 Hz, PPh$_3$), 43.6 (dd, $^1J_{\mathrm{Rh,P}}$ = 118.1 Hz, Ph$_2$P). – C$_{37}$H$_{30}$BF$_4$O$_2$P$_2$Rh (758.30): calcd. C 58.61, H 3.99; found C 57.58, H 3.87.

*[Rh(CO)(PPh$_3$)(NCCH$_3$)(2-Ph$_2$PC$_6$H$_4$OH-κP)]BF$_4$ (**12**)*

Treatment of a suspension of 160 mg (0.24 mmol) of **5** in 10 mL of acetonitrile with 33 μL of 54 % ethereal HBF$_4$ (0.24 mmol) gave a clear solution which was stirred for 1 h at ambient conditions. Removal of the volatiles left the product as a bright-yellow solid which was washed with pentane and dried under vacuum. – Yield: 188 mg (98 %). – IR (KBr): ν = 3394 (OH), 2296 (CN), 1999 (CO), 1094 (BF$_4$) cm^{-1}. – ^{1}H NMR (CDCl$_3$): δ = 1.98 (s, 3 H, CH$_3$), 2.6 (br, 1 H, OH), 7.0 – 8.1 (m, 29 H, aryl H). – ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 1.6 (s, CH$_3$), 120.6 (s, CN), 188.0 (unresolved, CO). – ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 25.3 (dd, $^1J_{\mathrm{Rh,P}}$ = 121.2 Hz, *trans*-$^2J_{\mathrm{P,P}}$ = 292.2 Hz, PPh$_3$), 31.5 (dd, $^1J_{\mathrm{Rh,P}}$ = 121.2 Hz, Ph$_2$P). – C$_{39}$H$_{33}$BF$_4$NO$_2$P$_2$Rh (799.34): calcd. C 58.60, H 4.16, N 1.75; found C 59.06, H 4.62, N 1.56.

*[IrH(FBF$_3$)(CO)(PPh$_3$)(2-Ph$_2$PC$_6$H$_4$O-κO,κP)] (**13**)*

A mixture of 180 mg (0.24 mmol) of **6** and 33 μL of 54 % ethereal HBF$_4$ (0.24 mmol) in 10 mL of CH$_2$Cl$_2$ was stirred for 1 h at r. t. Evaporation of the solvent followed by treatment of the residue with pentane left 195 mg (96 %) of **13** as a pale-yellow solid. – IR (KBr): ν = 2054 (CO), 1125/924 (FBF$_3$) cm^{-1}. – ^{1}H NMR (CDCl$_3$): δ = −26.60 ("t" (br), 1 H, IrH), 6.8, 7.2 (both m, 2 H each, C$_6$H$_4$), 7.6 (m, 25 H, C$_6$H$_5$). – ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 14.6 (PPh$_3$), 36.6 (Ph$_2$P); both d, *trans*-$^2J_{\mathrm{P,P}}$ = 313.5 Hz. – C$_{37}$H$_{30}$BF$_4$IrO$_2$P$_2$ (847.62): calcd. C 52.43, H 3.57; found C 52.53, H 3.80.

*[IrH(CO)(OH$_2$)(PPh$_3$)(2-Ph$_2$PC$_6$H$_4$O-κO,κP)]BF$_4$ (**14**)*

A solution of 140 mg (0.17 mmol) of **13** in 10 mL of CH$_2$Cl$_2$ 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), 1097/1064/995 (BF$_4$) cm^{-1}. – ^{1}H NMR (CDCl$_3$): δ = −21.57 ("t", $|cis\text{-}^2J_{\mathrm{P,H}}+cis\text{-}^2J_{\mathrm{P',H}}|$ = 22.2 Hz, 1 H, IrH), 3.5 (br, 2 H, H$_2$O), 6.5, 7.0 (both m, 2 H each, C$_6$H$_4$), 7.3 (m, 25 H, C$_6$H$_5$). – ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 13.4 (PPh$_3$), 35.3 (Ph$_2$P); both d, *trans*-$^2J_{\mathrm{P,P}}$ = 314.0 Hz. – C$_{37}$H$_{32}$BF$_4$IrO$_3$P$_2$ (865.63): calcd. C 51.34, H 3.73; found C 51.12, H 3.69.

*[IrH(CO)(NCCH$_3$)(PPh$_3$)(2-Ph$_2$PC$_6$H$_4$O-κO,κP)]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 cystals which were identified as the acetone solvate **15**·2C$_3$H$_6$O by X-ray structure analysis.

*[IrH(CO)(PPh$_3$)$_2$(2-Ph$_2$PC$_6$H$_4$O-κO,κP)]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$_2$Cl$_2$, 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

(BF$_4$) cm^{-1}. – ^{1}H NMR (CDCl$_3$): δ = −9.01 ("dt", *trans*-$^2J_{\mathrm{P,H}}$ = 148.0 Hz, $|cis\text{-}^2J_{\mathrm{P,H}} + cis\text{-}^2J_{\mathrm{P',H}}|$ = 31.8 Hz, 1 H, IrH), 6.8–7.8 (m, 44 H, aryl H). – ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 164.0 ("q", $\Sigma|cis\text{-}^2J_{\mathrm{P,C}}|$ = 24.0 Hz, CO), 176.9 ("dt", $^2J_{\mathrm{P,C}}$ = 18.9 Hz, $|^3J_{\mathrm{P,C}} + {}^3J_{\mathrm{P',C}}|$ = 11.8 Hz, phenylene C-1). – ^{31}P{^{1}H} NMR (CDCl$_3$): δ = −13.2, −0.6, 22.8 (*ABX* system, *trans*-$^2J_{\mathrm{P,P}}$ = 291.0 Hz, *cis*-$^2J_{\mathrm{P,P}}$ = 15.3 and 13.3 Hz). – $C_{55}H_{45}BF_4IrO_2P_3$ (1109.91): calcd. C 59.52, H 4.09; found C 58.90, H 3.85.

X-Ray structure determinations

Single crystals of **6** (0.30 × 0.15 × 0.13 mm^3) and **15**·2C$_3$H$_6$O (0.45 × 0.35 × 0.25 mm^3) 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 MoK_α radiation (λ = 0.71073 Å); orientation matrices and unit cell parameters from the setting angles of 25 centered medium-angle reflections; collection of the diffraction intensities by ω scans; data empirically corrected for absorption using ψ scans [20] (**6**: T$_{\mathrm{min}}$ = 0.349, T$_{\mathrm{max}}$ = 0.596; **15**·2C$_3$H$_6$O: T$_{\mathrm{min}}$ = 0.332, T$_{\mathrm{max}}$ = 0.507). The structures were solved by Direct Methods and subsequently refined by full-matrix least-squares procedures on F^2 with allowance for anisotropic thermal motion of all non-hydrogen atoms employing the WINGX package [21] with the programs SIR-97 [22], SHELXL-97 [23], and ORTEP-3 [24] implemented therein. – **6**: $C_{37}H_{29}IrO_2P_2$ (759.74); monoclinic, $P2_1/n$, a = 10.022(9), b = 14.861(4), c = 20.903(5) Å, β = 94.71(4)°, V = 3103(3) Å^3, Z = 4, D_{calcd} = 1.63 g cm^{-3}, μ(MoK_α) = 4.4 mm^{-1}, F(000) = 1496; 2.58° ≤ Θ ≤ 25.02°, 5618 reflections collected ($-11 \le h \le +11$, $0 \le k \le +17$, $0 \le l \le +24$), 5463 unique (R_{int} = 0.0381); $wR(F^2)$ = 0.0492 for all data and 379 parameters, $R(F)$ = 0.0349 for 2504 structure factors $F_{\mathrm{o}} \ge 4\sigma(F_{\mathrm{o}})$; weighting scheme applied: $w = 1/[\sigma^2(F_{\mathrm{o}}) + (0.0094P)^2]$, where $P = (F_{\mathrm{o}}{}^2 + 2F_{\mathrm{c}}{}^2)/3$; largest peak and hole in final difference map: 0.871 and −0.863 e Å^{-3}. – **15**·2C$_3$H$_6$O: $C_{45}H_{45}BF_4IrNO_4P_2$ (1004.77); triclinic, $P\bar{1}$, a = 9.164(6), b = 14.700(2), c = 16.515(2) Å, α = 91.26(1), β = 93.28(3), γ = 94.74(2)°, V = 2212.7(15) Å^3, Z = 2, D_{calcd} = 1.51 g cm^{-3}, μ(MoK_α) = 3.1 mm^{-1}, F(000) = 1004; 2.53° ≤ Θ ≤ 26.96°, 9966 reflections collected ($-11 \le h \le +11$, $-18 \le k \le +18$, $0 \le l \le +21$), 9626 unique (R_{int} = 0.0284); $wR(F^2)$ = 0.1098 for all data, 529 parameters, and 16 restraints, $R(F)$ = 0.0493 for 7160 structure factors $F_{\mathrm{o}} \ge 4\sigma(F_{\mathrm{o}})$; weighting scheme applied: $w = 1/[\sigma^2(F_{\mathrm{o}}) + (0.0512P)^2]$, where $P = (F_{\mathrm{o}}{}^2 + 2F_{\mathrm{c}}{}^2)/3$; largest peak and hole in final difference map: 1.746 and −1.035 e Å^{-3}.

CCDC 753417 (**6**) and CCDC 753418 (**15**·2C$_3$H$_6$O) 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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