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Synthesis, characterization and reactivity of tribenzylphosphine rhodium and iridium complexes

Vanessa R. Landaeta [a,b], Maurizio Peruzzini [b,*], Verónica Herrera [a], Claudio Bianchini [b,*], Roberto A. Sánchez-Delgado [a,c,*], Andrés E. Goeta [d], Fabrizio Zanobini [b]

[a] *Instituto Venezolano de Investigaciones Científicas (IVIC), Centro de Química, Apartado 21827, Caracas, 1020-A, Venezuela*
[b] *Istituto di Chimica dei Composti Organometallici (ICCOM – CNR), Area Ricerca CNR Firenze, Via Madonna del Piano 10, 50019 Sesto Fiorentino (FI), Italy*
[c] *Chemistry Department, Brooklyn College of The City University of New York Brooklyn, NY 11210, USA*
[d] *University of Durham, Department of Chemistry, Science Site, South Road, Durham DH1 3LE, UK*

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Abstract

New rhodium and iridium complexes, with the formula $[MCl(PBz_3)(cod)]$ [M = Rh (**1**), Ir (**2**)] and $[M(PBz_3)_2(cod)]PF_6$ [M = Rh (**3**), Ir (**4**)] (cod = 1,5-cyclooctadiene), stabilized by the tribenzylphosphine ligand (PBz_3) were synthesized and characterized by elemental analysis and spectroscopic methods. The molecular structures of **1** and **2** were determined by single-crystal X-ray diffraction. The addition of pyridine to a methanol solution of **1**or **2**, followed by metathetical reaction with NH_4PF_6, gave the corresponding derivatives $[M(py)(PBz_3)(cod)]PF_6$ [M = Rh (**5**), Ir (**6**)]. At room temperature in $CHCl_3$ solution, **4** converted spontaneously to the *ortho*-metallated complex $[IrH(PBz_3)(cod)\{\eta^2\text{-}P,C\text{-}(C_6H_4CH_2)PBz_2\}]PF_6$ (**7**) as a mixture of *cis*/*trans* isomers via intramolecular C–H activation of a benzylic phenyl ring. The reaction of **3** or **4** with hydrogen in coordinating solvents gave the dihydrido bis(solvento) derivative $[M(H)_2(S)_2(PBz_3)_2]PF_6$ (M = Rh, Ir; S = acetone, acetonitrile, THF), that transformed into the corresponding dicarbonyls $[M(H)_2(CO)_2(PBz_3)_2]PF_6$ by treatment with CO. Analogous *cis*-dihydrido complexes $[M(H)_2(THF)_2(py)(PBz_3)_2]PF_6$ (M = Rh, Ir) were observed by reaction of the py derivatives **5** and **6** with H_2.
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Keywords: Rhodium; Iridium; Tribenzylphosphine; C–H bond activation; X-ray crystallography; *Ortho*-metallation

1. Introduction

Excellent coordinating ability and easy-to-tune steric properties make tertiary phosphines the ligands of largest use in organometallic chemistry and homogeneous catalysis, especially in conjunction with late transition metals [1]. A variety of catalytic processes, in particular hydrogenation and hydroformylation reactions, involve metal precursors modified with tertiary phosphines, among which triphenylphosphine (PPh_3) plays a major role. Surprisingly, tribenzylphosphine (PBz_3) has received very little attention, which contrasts with the great potential stemming from its excellent nucleophilicity and peculiar steric properties. In a sense, PBz_3 lies midway between PPh_3 and PCy_3: it is more sterically demanding and a stronger Lewis base than the former [2–5] and less sterically demanding and less basic than the latter [6]. In this respect, studying whether PBz_3 complexes are efficient catalysts is of importance because, at variance with PPh_3 complexes, PCy_3 derivatives show low activity and are not currently used in metal catalyzed hydrogenation and hydroformylation.

* Corresponding authors. Tel.: +39 055 5225289; fax: +39 055 5225203.
E-mail addresses: maurizio.peruzzini@iccom.cnr.it, mperuzzini@iccom.cnr.it (M. Peruzzini), Claudio.bianchini@iccom.cnr.it (C. Bianchini), Rsdelgado@brooklyn.cuny.edu (R.A. Sánchez-Delgado).

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PBz_3 metal complexes have been reported with silver [7,8], osmium [9], palladium [2,10–14], platinum [2,11], nickel [11,15–17], copper [18–20], rhenium [21], and ruthenium [3,22–24], while catalytic applications of PBz_3 metal complexes are limited to the sole example of hydroformylation of allylbenzene by rhodium catalysts [25,26]. Remarkably, only one rhodium compound containing PBz_3, namely $RhCl(CO)(PBz_3)_2$ [4,27,28], has been described and no iridium derivative is known. This lack of data is surprising indeed as rhodium and iridium constitute the essential ingredients of most catalytic processes in homogeneous phase as well as of fundamental studies of organometallic reactions. Aimed at filling this gap, we decided to carry out a systematic study of the coordination ability of PBz_3 towards rhodium and iridium and to investigate both the organometallic chemistry and the application in homogeneous catalysis of the resultant complexes.

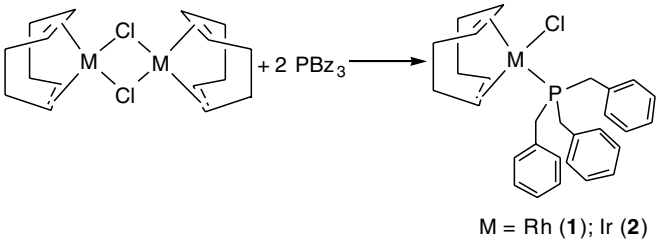
In this paper, we describe the synthesis and characterization of some rhodium and iridium complexes, starting from the parent compounds [MCl(PBz_3)(cod)] [M = Rh (**1**), Ir (**2**)] and [M(PBz_3)$_2$(cod)]PF_6 [M = Rh (**3**), Ir (**4**)] (cod = 1,5-cyclooctadiene). These precursors have proved amenable to investigating elementary organometallic reactions such as the activation of CO, H_2 and C–H bonds. In a concomitant paper, a study of the ability of the Rh and Ir complexes [M(PBz_3)$_2$(cod)]PF_6 [M = Rh, Ir] and [M(py)(PBz_3)(cod)]PF_6 [M = Rh, Ir; py = pyridine] to catalyze the hydrogenation of imines, will be reported [29].

2. Results and discussion

2.1. Synthesis and characterization of MCl(cod)(PBz_3) (M = Ir, Rh)

The binuclear precursors [MCl(cod)]$_2$ (M = Rh, Ir) react smoothly in dichloromethane with two equivalents of PBz_3 to give bright yellow crystals of the neutral complexes MCl(PBz_3)(cod) [M = Rh (**1**), Ir (**2**)] in high yield (>90%) (Scheme 1). Compounds **1** and **2** are air-stable in the solid state and are soluble in polar organic solvents.

The $^{31}P\{^1H\}$ NMR resonance of PBz_3 is a singlet in the spectrum of **2** and a doublet, with a J_{PRh} value of 150.5 Hz, typical for Rh(I) complexes, in the spectrum of **1** [30]. The CH and CH_2 groups of the COD ligand are magnetically inequivalent: four signals in the ^1H NMR spectrum are originated by four CH protons and two signals by the two methylenic protons. Four separated carbon resonances, due to the two pairs of CH and CH_2 carbons, are present in the $^{13}C\{^1H\}$ NMR spectrum. 2D-COSY and HMQC NMR spectra were helpful to unambiguously assign the network of proton and carbon resonances for these complexes as well as for all the new complexes described in this paper. Details of the spectral data and assignments are provided in Section 4.



Scheme 1.

Suitable crystals of **1** and **2** grown from dilute dichloromethane/ethanol solutions were subjected to X-ray diffraction analysis. An ORTEP drawing showing the molecular structure of the iridium derivative is given in Fig. 1. A summary of crystal data and a selection of bond distances and angles are collected in Tables 1 and 2. Both complexes crystallized in the same space group (monoclinic, $P2_1/n$) and are characterized by a strongly distorted square planar geometry due to the presence of the bulky PBz_3 ligand. M–P [2.292(1) Å for **1** and 2.303(2) Å for **2**] and M–Cl bond distances [2.377(1) Å for **1** and 2.365(2) Å for **2**] are within the range expected for this kind of complexes [31]. A comparison of the metrical data of **1** with that of *trans*-$RhCl(CO)(PBz_3)_2$ (d_{Rh-Cl} = 2.3654(15) Å; $d_{Rh-P(ave)}$ = 2.3164(15) Å) [4] shows a complete matching of the Rh–Cl separations, but somewhat different Rh–P distances, likely reflecting the different *trans* influence exerted by the phosphorus atoms and the carbon atoms of COD.

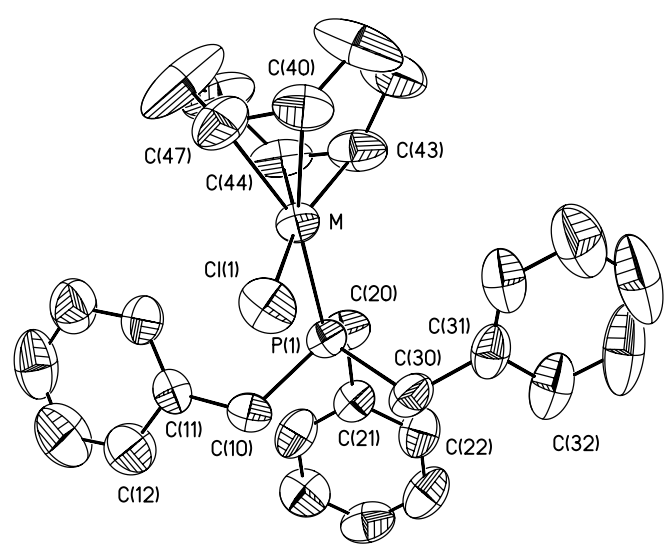


Fig. 1. ORTEP drawing of the complex IrCl(cod)(PBz_3) (**2**), with 50% probability displacement ellipsoids. The labeling scheme is the same for both complexes (M = Rh (**1**) and Ir (**2**)) and the displacement ellipsoids are very similar, slightly smaller for **1** due to the lower temperature of the experiment. Hydrogen atoms have been omitted for clarity.

Table 1
Summary of crystal data for RhCl(cod)(PBz_3) (**1**) and IrCl(cod)(PBz_3) (**2**)

Compound	**1**	**2**
Formula	$RhC_{29}H_{33}PCl$	$IrC_{29}H_{33}PCl$
Molecular weight	550.986	640.17
Cryst size (mm)	$0.72 \times 0.50 \times 0.40$	$0.575 \times 0.25 \times 0.20$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	10.626(3)	10.676(1)
b (Å)	13.208(3)	13.159(5)
c (Å)	18.795(5)	18.862(2)
β (°)	102.709(8)	101.95(1)
V (Å^3)	2573.2(12)	2592.4(11)
Z	4	4
d_{calc} (Mg/m^3)	1.422	1.640
Absorption coefficient (mm^{-1})	0.844	5.330
$F(000)$	1136	1264
θ Range (°)	1.90–28.29	1.90–24.99
Index ranges	$-14 \leqslant h \leqslant 14$, $-17 \leqslant k \leqslant 17$, $-24 \leqslant l \leqslant 25$	$-12 \leqslant h \leqslant 12$, $0 \leqslant k \leqslant 15$, $0 \leqslant l \leqslant 22$
Total number of data	28 161	4696
Number of unique data [$I \geqslant 2\sigma(I)$] (R_{int})	6384/4974 (0.0221)	4552/2979 (0.0264)
Goodness-of-fit on F^2, S	1.044	1.076
R_1 [$I \geqslant 2\sigma(I)$]	0.0307	0.0294
wR_2 (all)	0.0843	0.0737
Largest difference in peak and hole (e/Å^3)	0.409 and −0.368	0.576 and −0.501

Several rhodium(I) and iridium(I) complexes with sterically demanding phosphines (PCy_3, $PMePh_2$, PPr^i_3) or phosphites ($P(OMe)Ph_2$) share the primary structure of **1** and **2** [31,32].

Table 2
Selected bond distances (Å) and angles (°) for RhCl(cod)(PBz_3) (**1**) and IrCl(cod)(PBz_3) (**2**)

1		**2**	
Distances			
Rh–C(43)	2.106(3)	Ir–C(43)	2.097(7)
Rh–C(44)	2.107(3)	Ir–C(44)	2.106(7)
Rh–C(47)	2.192(3)	Ir–C(47)	2.179(6)
Rh–C(40)	2.212(3)	Ir–C(40)	2.182(6)
Rh–P(1)	2.292(1)	Ir–P(1)	2.303(2)
Rh–Cl(1)	2.377(1)	Ir–Cl(1)	2.365(2)
Angles			
P(1)–Rh–Cl(1)	86.75(3)	P(1)–Ir–Cl(1)	87.55(6)
C(43)–Rh–C(44)	38.56(13)	C(43)–Ir–C(44)	38.6(3)
C(43)–Rh–C(47)	94.61(14)	C(43)–Ir–C(47)	95.4(3)
C(44)–Rh–C(47)	81.72(12)	C(44)–Ir–C(47)	81.7(3)
C(43)–Rh–C(40)	81.53(12)	C(43)–Ir–C(40)	81.2(3)
C(44)–Rh–C(40)	92.06(12)	C(44)–Ir–C(40)	91.6(3)
C(47)–Rh–C(40)	36.00(13)	C(47)–Ir–C(40)	37.2(3)
C(43)–Rh–P(1)	95.69(9)	C(43)–Ir–P(1)	95.9(2)
C(44)–Rh–P(1)	95.10(8)	C(44)–Ir–P(1)	95.5(2)
C(47)–Rh–P(1)	158.94(11)	C(47)–Ir–P(1)	157.9(2)
C(40)–Rh–P(1)	164.62(9)	C(40)–Ir–P(1)	164.4(2)
C(43)–Rh–Cl(1)	160.91(11)	C(43)–Ir–Cl(1)	160.0(3)
C(44)–Rh–Cl(1)	160.23(11)	C(44)–Ir–Cl(1)	160.7(3)
C(47)–Rh–Cl(1)	89.49(10)	C(47)–Ir–Cl(1)	88.3(2)
C(40)–Rh–Cl(1)	91.10(8)	C(40)–Ir–Cl(1)	90.2(2)

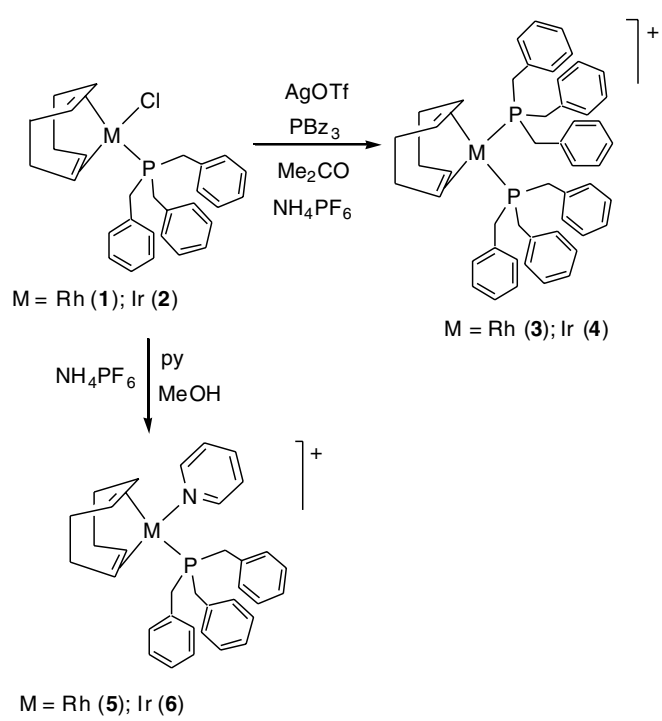
2.2. Reactivity of the neutral complexes MCl(PBz_3)(cod) (M = Rh, Ir)

Removal of the chloride ligand from **1** or **2** can be readily achieved either by reaction with silver salts or by straightforward ligand substitution using an excess of a strong σ-donor such as pyridine (py) in the presence of NH_4PF_6. Thus, the reaction of silver triflate with **1** or **2**, dissolved in acetone at room temperature, followed by addition of one equivalent of PBz_3, led to the formation of cationic derivatives that were isolated as PF_6^- salts, [M(PBz_3)$_2$(cod)]PF_6 [M = Rh (**3**); Ir (**4**)] (Scheme 2).

Complexes **3** and **4** contain two *cis*-PBz_3 ligands. PPh_3 rhodium compounds with similar structure, [M(PPh_3)$_2$-(cod)]PF_6 [M = Rh, Ir] have been reported by Haines and Singleton [33] and Osborn et al. [34], yet no bis-PCy_3 rhodium derivative has ever been reported in the literature. A series of comparable complexes with substituted triphenylphosphines [P(p-RC_6H_4)$_3$, R = Cl, F, CH_3, CH_3O] were also synthesized by Oro and co-workers [35].

The $^{31}P\{^1H\}$ NMR spectra of **3** and **4** contain, in addition to the high-field septuplet of PF_6^-, a single resonance for the two phosphine ligands (**4**, singlet at δ −6.40 ppm; **3**, doublet at δ 2.75ppm, $J_{RhP} = 143.5$ Hz). The equivalence of the two PBz_3 ligands makes the ^1H NMR spectra simpler than those of **1** or **2** as the CH and CH_2 protons of COD now appear as single signals.

Complexes **1** and **2** reacted with an excess of pyridine and NH_4PF_6 in methanol to yield the cationic mixed phosphine-pyridine complexes [M(py)(PBz_3)(cod)]PF_6 [M = Rh



Scheme 2.

(**5**), Ir (**6**)] whose structure is quite similar to that of Crabtree's catalyst, $[Ir(py)(PCy_3)(cod)]PF_6$ (Scheme 2) [32].

2.3. Ortho-metallation of $[Ir(cod)(PBz_3)_2]PF_6$

On standing in $CHCl_3$ for three days under nitrogen, **4** transformed into off-white crystals of a new product that was later identified as the *ortho*-metallated complex *cis*-(*P*,*P*)-$[IrH(PBz_3)(cod)\{\eta^2\text{-}P,C\text{-}(C_6H_4CH_2)PBz_2\}]PF_6$ (*cis*-*P*,*P*-**7**).

The solution structure of *cis*-*P*,*P*-**7** was unequivocally established by 1D and 2D NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum consists of two doublets due to the inequivalent PBz_3 ligands (δ −2.86 and −9.97) which are mutually *cis* as shown by the small magnitude of the homonuclear coupling constant ($J_{PP} = 18.5$ Hz). The ^1H NMR spectrum contains an eight-line multiplet (ddd) in the hydride region due to coupling of the Ir–H hydride both to the two P atoms ($^2J_{HP1} = 102.3$ Hz, $^2J_{HP2} = 17.2$ Hz) and to one of the four CH protons of COD. ^{31}P broad-band decoupling collapses/the hydride resonance into a slightly broadened doublet ($^4J_{HH} = 6.3$ Hz), confirming that only one homonuclear H,H coupling is discernable. A 2D-HMQC NMR experiment showed the metallated carbon atom to appear as a doublet at δ 146.87 ($^2J_{CP} = 17.8$ Hz) in the ^{13}C NMR spectrum.

Incorporation of the NMR data led us to assign an octahedral coordination to *cis*-*P*,*P*-**7** where a terminal hydride is *trans* to the P atom of an *ortho*-metallated PBz_3 ligand (Scheme 3). COD, a phenyl ring and an intact PBz_3 complete the coordination geometry.

It is very likely that the intramolecular C–H oxidative addition leading to *cis*-*P*,*P*-**7** is a consequence of the large steric hindrance exerted by the two *cis*-disposed PBz_3 ligands in the precursor **4** [5]. Indeed, bulky arylphosphines tend to form *o*-metallated compounds via intramolecular C–H bond activation just to relief the steric congestion with bulky *cis* ligands [36]. Besides steric effects, *o*-metallation could be also promoted by electronic effects, associated with the enthalpy of formation of new M–C and M–H bonds as compared to the energy required to break a C–H bond. In this respect, it is not a case that the iridium complex **4** undergoes spontaneous *o*-metallation, whereas the analogous rhodium derivative **3** is fully stable in chloroform either even at reflux temperature [37].

Ortho-metallation of a phenyl ring from PPh_2Bz has been previously observed for nickel [15], and suggested for some ruthenium and palladium complexes with PBz_3 [23]; in no case, however, the process occurred spontaneously at room temperature as observed for **4**, but harsh reaction conditions were required for *o*-metallation.

Monitoring the stability of **4** in $CDCl_3$ by NMR spectroscopy at room temperature showed the bis-PBz_3 complex to convert to *cis*-*P*,*P*-**7** and to another complex, later identified as *trans*-(*P*,*P*)-$[IrH(PBz_3)(cod)\{\eta^2\text{-}P,C\text{-}(C_6H_4CH_2)PBz_2\}]PF_6$ (*trans*-*P*,*P*-**7**), which was initially the major product. In particular, **4** disappeared completely after 30 min, to form a ca. 1:1 mixture of the two products, and *trans*-*P*,*P*-**7** completely converted into *cis*-*P*,*P*-**7** in ca. 8 h at room temperature.

The identity of *trans*-*P*,*P*-**7** as a kinetic, geometric isomer of *cis*-*P*,*P*-**7** (Scheme 3) was readily established on the basis of its NMR parameters, for example the much larger homonuclear $^2J_{PP}$ coupling constant (18.5 Hz for *cis*-*P*,*P*-**7** and 238.0 Hz for *trans*-*P*,*P*-**7**) as well as a broad triplet at −13.38 ppm in the hydride region of the ^1H NMR spectrum with $^2J_{HP} = 19.8$ Hz.

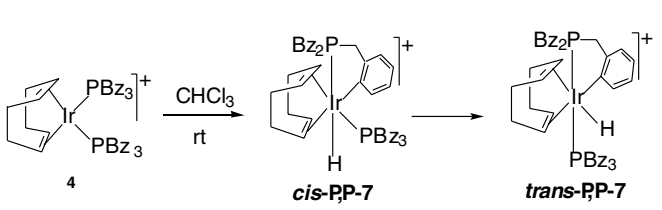
2.4. Reactions of $[M(PBz_3)_2(cod)]PF_6$ and $[M(py)(PBz_3)(cod)]PF_6$ with H_2

When dissolved in coordinating solvents such as acetone, acetonitrile or THF, **3** and **4** reacted rapidly with H_2 at room temperature to give the M(III) *cis*-dihydrides $[M(H)_2(S)_2(PBz_3)_2]PF_6$ (M = Rh, Ir; S = acetone, MeCN, THF). The formation of the latter complexes was accompanied by the reduction of COD to cyclooctane (COA).

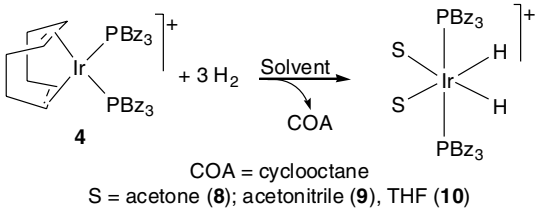
Both the acetone and the acetonitrile Ir adducts $[Ir(H)_2(S)_2(PBz_3)_2]PF_6$ (S = acetone, **8**; S = acetonitrile, **9**) could be isolated as cream-colored crystals (Scheme 4). Due to the better nucleophilic properties of acetonitrile versus acetone, **8** converted into **9** upon dissolution in acetonitrile, while the reverse reaction did not occur. In contrast, the THF adduct $[Ir(H)_2(THF)_2(PBz_3)_2]^+$ (**10**) was exclusively prepared in situ but could not be isolated in the solid state.

Octahedral iridium *cis*-dihydride complexes similar to **8**, **9** and **10** have been synthesized by Crabtree and co-workers by reaction of $[Ir(PPh_3)_2(cod)]PF_6$ with H_2 in coordinating solvents [38].

The $^{31}P\{^1H\}$ NMR spectra of the dihydrides **8**–**10** exhibit a sharp singlet for the P atoms, as expected for a *trans* disposition of the phosphines. In keeping with the presence of an Ir(III) center, the ^{31}P chemical shift is significantly low-field shifted with respect to the analogous resonance



Scheme 3.



Scheme 4.

of the Ir(I) precursor **4**. The ^{1}H NMR spectra contain high-field hydride triplets at −30.13 ppm ($^2J_{HP} = 15.3$ Hz), −21.45 ppm ($^2J_{HP} = 16.2$ Hz); δ −23.5 ($J_{HP} = 15.5$ Hz). The ^{1}H NMR spectra of all compounds contain also a virtual triplet for the methylenic PBz_3 protons, which is again consistent with *trans*-phosphines [39].

Related iridium hydrido complexes containing PPr^i_3 exhibit hydride signals with chemical shifts similar to those found for the present PBz_3 derivatives, specially if compared to the acetonitrile complex, **9** [40]. The analogous compound $[Ir(H)_2(PPr^i_3)(PMe_3)(CH_3CN)_2]BF_4$ displays a unique hydride signal at −22.26 ppm (dd, $J_{HP} = J_{HP'} = 17.0$ Hz), indicating similar steric and electronic properties between our ligand and PPr^i_3 in this complex.

Unlike iridium, rhodium does not form any bis-solvento dihydride possible to isolate in the solid state. $[Rh(H)_2(CD_3CN)_2(PBz_3)_2]^+$ (**11**), generated by hydrogenation of **3** in acetonitrile-d_3, was stable in solution only under a protective H_2 atmosphere. The hydride signal appears as a doublet of triplets in the ^{1}H NMR spectrum, while the $^{31}P\{^1H\}$ spectrum consists of a doublet [30,41]. The formation of COA was put in evidence by a ^{1}H NMR singlet at 1.39 ppm as well as a GC/MS analysis. The bis(acetone) derivative $[Rh(H)_2(Me_2CO\text{-}d_6)_2(PBz_3)_2]^+$ (**12**) (δ_P 32.48; $J_{RhP} = 122.1$ Hz), was prepared analogously. However, this complex was unstable even under 1 bar H_2 and readily equilibrated with the square-planar Rh(I) cation $[Rh(Me_2CO\text{-}d_6)_2(PBz_3)_2]^+$ (**13**) (δ_P 38.36; $J_{RhP} = 149.3$ Hz), which apparently forms by reductive elimination of H_2 from **12** (Scheme 5). This behavior has some precedents in rhodium chemistry, for example with the couple $[Rh(H)_2(MeOH)_2(PR_3)_2]^+/[Rh(MeOH)_2(PR_3)_2]^+$ (R = Ph, *p*-tolyl) [34,42]. Increasing the H_2 pressure to 10 bar with the use of a HP-NMR sapphire tube inhibited the reductive elimination of H_2 from **12** and no formation of **13** was observed.

A similar behavior was observed for the hydrogenation of **3** in THF. Again, an equilibrium concentration (ca. 1:1) of $[Rh(H)_2(THF)_2(PBz_3)_2]^+$ (**14**) and $[Rh(THF)_2(PBz_3)_2]^+$ (**15**) was detected by NMR analysis under 1 bar H_2.

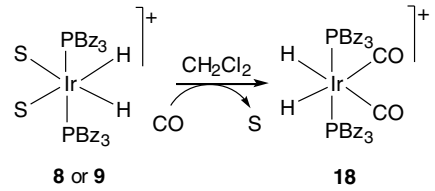
cis-Dihydride bis-THF complexes, $[M(H)_2(THF)_2(py)(PBz_3)]PF_6$ [M = Rh (**16**); Ir (**17**)], were also obtained by hydrogenation of $[M(py)(PBz_3)(cod)]PF_6$ in THF. These compounds were exclusively prepared in solution and characterized in situ by NMR spectroscopy (see Section 4).

The lower stability of Rh(III) dihydrides versus their Ir(III) congeners is well known and has been rationalized on the basis of the greater strength of Ir–H bonds versus Rh–H bonds [43].

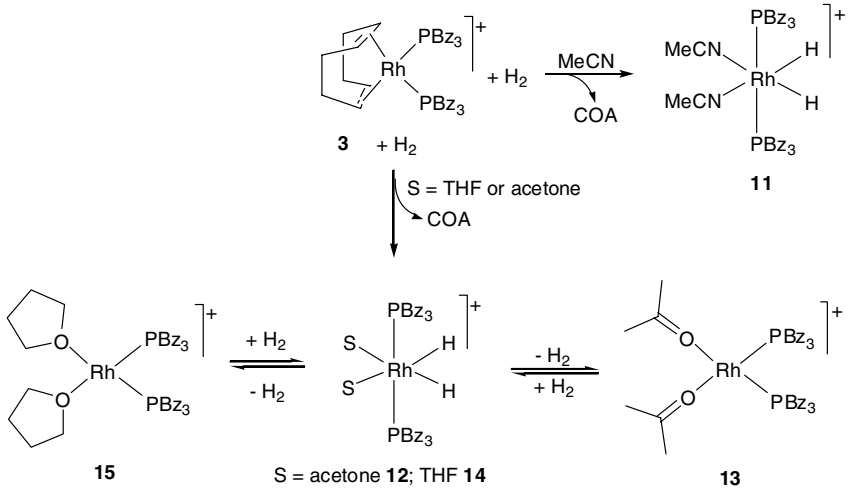
2.5. Reactions of $[M(PBz_3)_2(cod)]PF_6$ with CO

The reactions of the dihydrides **8** and **9** with CO were followed by in situ NMR spectroscopy (Scheme 6). The replacement of either acetone or MeCN by 1 bar CO was fast and complete to give $[Ir(H)_2(CO)_2(PBz_3)_2]^+$. A bulk preparative experiment allowed the isolation of the octahedral complex $[Ir(H)_2(CO)_2(PBz_3)_2]PF_6$ (**18**), featured inter alia by ν_{CO} bands at 2002 and 2004 cm^{-1}. A similar compound with $P(p\text{-}CH_3C_6H_4)_3$ has been described showing ν_{CO} bands at 2070 and 2040 cm^{-1} [35]. Also, the monocarbonyl dihydride species $[IrH_2(PPr^i_3)(CO)(NCCH_3)_2]BF_4$, displays a strong ν_{CO} band at 2015 cm^{-1} [40].

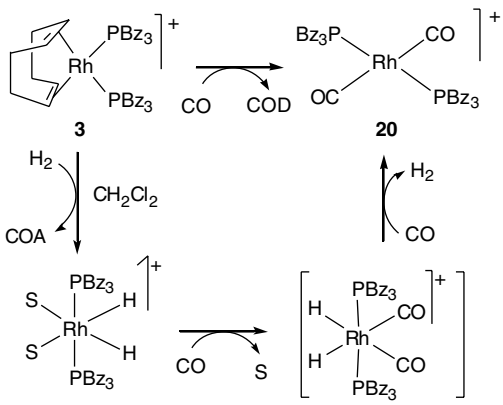
The rhodium dihydrides **11**, **12** and **14**, generated in situ in the appropriate deuterated solvent, reacted analogously



Scheme 6.



Scheme 5.



S = acetone **11**; acetonitrile **12**; THF **14**

COD = 1,5 - cyclooctadiene
COA = cyclooctane

Scheme 7.

with CO yielding the dicarbonyl dihydride $[Rh(H)_2(CO)_2(PBz_3)_2]^+$ (**19**), which was unstable and rapidly converted to *trans*-$[Rh(CO)_2(PBz_3)_2]PF_6$ (**20**) (Scheme7).

Due to its low solubility in dichloromethane, the latter complex separated from the solution in almost quantitative yield. Compound **20** was also independently prepared by carbonylation of **3** in THF solution. The assignment of the *trans* arrangement of the two carbonyl ligands in **20** is confirmed by the presence of a single strong ν_{CO} band at 2022 cm^{-1} in the solid-state IR spectrum, which slightly moves to 2019 cm^{-1} in DMSO solution. The $^{31}P\{^1H\}$ NMR displays a doublet at 48.6 ppm in DMSO-d_6 (J_{RhP} = 75.1 Hz).

A similar Rh(I) complex with PPh_3 has been synthesized from cationic rhodium-nitrosyl species and shows similar IR features [44]. Also, a tricarbonyl iridium species with $P(p\text{-}CH_3C_6H_4)_3$ was reported, and the presence of three carbonyls sitting in the equatorial plane of a trigonal-bipyramidal polyhedron was confirmed by the presence of a unique ν_{CO}-band (2010 cm^{-1}) [35]. A computational study carried on a series of *cis*- and *trans*-$[Rh(CO)_2X_2]^+$ complexes (X = PH_3, PF_3, PCl_3, PBr_3, PI_3 or PMe_3) suggests that more the ligand size and the donor properties of the phosphine increase, more the *trans*-isomers become stable [45]. ν_{CO} frequencies for these complexes were compared, showing single bands for *trans*-compounds ranging from 2083 to 2040 cm^{-1}. Generally, the CO absorptions move to lower frequencies as the ligand size increases [45]. These facts, altogether with our experimental evidence, provide a further strong confirmatory evidence of the *trans*-geometry of **20**.

3. Conclusions

This paper reports the synthesis and reactivity of a family of rhodium and iridium complexes with tribenzylphosphine. This ligand has been scarcely investigated in organometallic chemistry and almost completely ignored in homogeneous catalysis. The preparations and reactions described in this paper highlight the versatility of the PBz_3 ligand which combines the steric hindrance of triarylphosphines with the basicity of trialkylphosphines, thus providing a further tool to look for improved activity and selectivity.

The reactivity of the rhodium and iridium PBz_3 complexes towards H_2 or CO has been investigated and compared with related complexes bearing either substituted triphenylphosphines or PPr^i_3 [35,40,45]. Although the reactivity does not generally differ from that reported in the literature, our complexes are more air and moisture stable likely due to the presence of PBz_3 ligand. In a concomitant paper, a study of the hydrogenation of imines catalyzed by Rh and Ir complexes with PBz_3, will be reported showing that the latter is able to generate more efficient catalysts than the ones known with PPh_3 [29].

4. Experimental

All reactions and manipulations were routinely performed under dry nitrogen or argon atmosphere using standard Schlenk techniques. Unless otherwise stated, all solvents were distilled just prior to use from appropriate drying agents. Methanol was distilled from $CaSO_4$, dichloromethane and acetonitrile from P_2O_5, and tetrahydrofuran (THF) from sodium/benzophenone. Diethylether and petroleum ether were dried with sodium. Hydrogen was purified passing it through two columns in series containing CuO/Al_2O_3 and $CaSO_4$, respectively. Deuterated solvents were dried over 4 Å molecular sieves prior to use. All other chemicals were commercial products and used as received without further purification. Literature methods were employed for the synthesis of $[RhCl(cod)]_2$ [46], $[IrCl(cod)]_2$ [47]. The solid complexes were collected on a sintered glass-frit and washed with ethanol and light petroleum ether (b.p. 40–60 °C) or pentane before being dried in a stream of nitrogen. ^1H, and $^{13}C\{^1H\}$ NMR spectra were recorded either on a Bruker ACP 200 (200.13 and 50.32 MHz), a Bruker AM 300 (300.13 and 75.47 MHz) or a Bruker Avance DRX-500 (500.13 and 125.80 MHz) spectrometers. Peak positions are relative to tetramethylsilane and were calibrated against the residual solvent resonance (^1H) or the deuterated solvent multiplet (^{13}C). $^{31}P\{^1H\}$ NMR spectra were recorded on the same instruments operating at 81.01, 121.49, and 202.53 MHz, respectively. Chemical shifts were measured relative to external 85% H_3PO_4, with downfield shifts considered positive. All the NMR spectra were recorded at room temperature (25 °C) unless otherwise stated. The high-pressure NMR (HP-NMR) spectra were recorded by using a standard 10-mm probe tuned to ^{31}P and ^1H nuclei on a BRUKER AC 200 spectrometer operating at 81 MHz. The HPNMR experiments were performed in a 10 mm-OD sapphire tube (Saphikon Inc., NH). 2D NMR spectra were recorded on a Bruker Avance DRX-500, operating at 500.13, 202.46 and 125.77 MHz, respectively, for ^1H, ^{31}P and ^{13}C. 2D ^1H DQF-COSY [48], and proton detected ^1H–^{31}P and

^{1}H–^{13}C correlations (HMQC [49] and HMBC [50]) using nonspinning samples. 2D NMR spectra were recorded using pulse sequences suitable for phase-sensitive representations using TPPI. *CAUTION: All manipulations involving high pressures are potentially hazardous. Safety precautions must be taken at all stages of NMR studies involving high pressure tubes*. Infrared spectra were recorded either on a Perkin–Elmer 1600 series or a Nicolet Magna IR 560 FT-IR spectrometers, using samples mulled in Nujol between KBr plates or in KBr disk. Elemental analyses (C, H, N) were performed using a Carlo Erba model 1106 elemental analyser by the Microanalytical Service of the Department of Chemistry at the University of Florence.

4.1. Tribenzylphosphine (PBz_3)

PBz_3 was prepared using a modification of the reported method [51]. The Grignard reagent, BzMgCl, was prepared by slowly adding benzyl chloride (100.0 g, 0.89 mol), to a cold suspension of magnesium turnings (22.0 g, 0.90 mol) in dry diethylether (750 mL) under vigorous stirring. The resulting mixture was slowly brought to the boiling temperature and refluxed for 2 h. To the clear ethereal Grignard solution, PCl_3 (42 g, 0.31 mol) was dropped slowly, while vigorously stirring, within 2 h. The mixture was left overnight under a nitrogen atmosphere before 500 mL of aqueous saturated solution of NH_4Cl (60 g) was added to the cooled mixture, which caused the separation of two phases. After separation of the organic layer, the aqueous phase was washed two times with cold diethyl ether (100 mL each) and discharged. The organic phase and the two Et_2O washings were combined and dried with $NaSO_4$. The filtered ethereal solution was concentrated to 250 mL and left standing overnight to allow for the separation of ivory colored crystals of the phosphine. The solid was collected on a Buchner funnel by filtration in the air and dried under vacuum. Yield: 55 g, 60%. ^{1}H NMR (200.13 MHz; $CDCl_3$): δ 2.78 (s, 6H, CH_2), δ 7.15–7.32 (m, 15H, aromatics). $^{31}P\{^{1}H\}$ (81.01 MHz; $CDCl_3$): δ −11.3 (s, PBz_3). Anal. Calc. for $C_{21}H_{21}P$: C, 82.87; H, 6.95. Found: C, 82.89; H, 6.75%.

4.2. RhCl(PBz_3)(cod) (**1**)

$[RhCl(cod)]_2$ (500 mg; 1.01 mmol) and PBz_3 (680 mg, 2.23 mmol) were dissolved in dichloromethane (15 mL) and stirred vigorously for 30 min. Ethanol (20 mL) was added, and the solution was concentrated under vacuum until a shiny yellow solid precipitated. Yield: 1.00 g, 90%. ^{1}H NMR (CD_2Cl_2, 300.13 MHz): δ 1.85 (m, 2H, CH_2 COD); δ 2.00 (m, 2H, CH_2 COD); δ 2.18 (m, 2H, CH_2 COD); δ 2.35 (m, 2H, CH_2 COD); δ 3.02 (d, 6H, CH_2 PBz_3, $J_{HP} = 9.3$ Hz); δ 3.20 (m, 2H, CH COD); δ 5.50 (br s, 2H, CH COD); δ 7.20–7.80 (m, 15H, CH aromatic protons). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 121.49 MHz): δ 24.2 (d, 1P, $J_{Rh-P} = 150.5$ Hz). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 75.47 MHz): δ 28.1 (CH_2 PBz_3, d, $J_{CP} = 19.2$ Hz); δ 28.5 (CH_2 COD); δ 32.9 (CH_2 COD); δ 68.8 (CH COD *trans* to Cl, d, $J_{CRh} = 13.5$ Hz); δ 103.7 (CH COD *trans* to P, dd, $J_{CRh} = 11.9$ Hz, $^{2}J_{CP} = 4.7$ Hz); δ 126.7, δ 129.0, δ 130.6 (CH aromatic carbons); δ 135.0 (C *ipso*). IR (KBr): ν(Rh–Cl) 478 cm^{-1}(m). Anal. Calc. for $C_{29}H_{33}ClPRh$: C, 63.22; H, 6.03. Found: C, 63.25; H, 5.95%.

4.3. IrCl(PBz_3)(cod) (**2**)

$[IrCl(cod)]_2$ (300 mg; 0.45 mmol) and PBz_3 (300 mg; 0.99 mmol) were dissolved in dichloromethane (15 mL) and stirred vigorously for 30 min. Ethanol (20 mL) was added, and the solution was concentrated under vacuum until a shiny yellow solid precipitated. Yield: 437 mg, 77%. ^{1}H NMR (CD_2Cl_2, 300.13 MHz): δ 1.62 (m, 2H, CH_2 COD); δ 1.84 (m, 2H, CH_2 COD); δ 2.08 (m, 2H, CH_2 COD); δ 2.22 (m, 2H, CH_2 COD); δ 2.86 (m, 2H, CH COD); δ 3.22 (d, 6H, CH_2 PBz_3, $J_{HP} = 9.7$ Hz); δ 5.11 (m, 2H, CH COD); δ 7.25–7.60 (m, 15H, aromatic protons). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 121.49 MHz): δ 8.72 (s, 1P). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 75.47 MHz): δ 27.83 (d, CH_2 PBz_3, $J_{CP} = 25.4$ Hz); δ 29.3, δ 33.5 (CH_2 COD); δ 52.0 (s, CH COD *trans* to Cl); δ 91.7 (d, CH COD *trans* to P, $J_{CP} = 14.0$ Hz); δ 126.6, δ 128.2, δ 130.8 (s, CH, aromatic carbons); δ 134.2 (C *ipso*, $^{2}J_{CP} = 4.5$ Hz). IR (KBr): ν(Rh–Cl) 479 cm^{-1}(m). Anal. Calc. for $C_{29}H_{33}ClIrP$: C, 54.40; H, 5.19. Found: C, 54.56; H, 5.11%.

4.4. [Rh(PBz_3)$_2$(cod)]PF_6 (**3**)

A solution of RhCl(PBz_3)(cod) (1.00 g, 1.81 mmol) in acetone (20 mL) was treated with $AgOSO_2CF_3$ (475 mg, 2.90 mmol), and stirred for 30 min at room temperature. The AgCl that separated was filtered out, and one equivalent of solid PBz_3 (800 mg, 2.63 mmol) was added under stirring to afford an orange solution. Addition of an excess of NH_4PF_6 (700 mg, 4.20 mmol) dissolved in ethanol (20 mL) and concentration under a brisk current of nitrogen precipitated a yellow solid. Yield: 1.56 g, 72%. ^{1}H NMR ($CDCl_3$, 200.13 MHz): δ 1.62 (m, 2H, CH_2 COD); δ 1.84 (m, 2H, CH_2 COD); δ 2.08 (m, 2H, CH_2 COD); δ 2.22 (m, 2H, CH_2 COD); δ 2.86 (m, 2H, CH COD); δ 3.22 (d, 6H, CH_2 PBz_3); δ 5.11 (m, 2H, CH COD); δ 7.25-7.60 (m, 15H, CH aromatic protons). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 81.015 MHz): δ 2.75 (d, 2P, $J_{Rh-P} = 143.5$ Hz); δ −143.6 (sept, PF_6, $J_{P-F} = 712.1$ Hz). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75.47 MHz): δ 31.1 (s, CH_2 COD); δ 33.1 (ps t, CH_2 PBz_3,); δ 99.0 (CH COD); δ 128.5, δ 129.9, δ 130.7 (CH, aromatic carbons); δ 133.3 (C *ipso*). IR (Nujol mull): ν(P–F) 840 cm^{-1} (s). Anal. Calc. for $C_{50}H_{54}F_6P_3Rh$: C, 62.25; H, 5.64. Found: C, 62.07; H, 5.55%.

4.5. [Ir(PBz_3)$_2$(cod)]PF_6 (**4**)

A solution of IrCl(PBz_3)(cod) (1.00 g, 1.56 mmol) in acetone (40 mL) was treated with $AgOSO_2CF_3$(450 mg, 1.73 mmol), and stirred for 30 min. The AgCl that sepa-

rated was filtered out, and one equivalent of solid PBz_3 (700 mg, 2.34 mmol) was added to afford a red solution. Addition of an excess of NH_4PF_6 (500 mg, 3.13 mmol) dissolved in ethanol (20 mL) and concentration under a brisk current of nitrogen precipitated a carmine red solid. Yield: 1.52 g, 92%. ^{1}H NMR ($CDCl_3$, 200.13 MHz): δ 1.85 (m, 8H, CH_2 COD); δ 3.37 (d, 12H, CH_2 PBz_3, $J_{HP} = 7.2$ Hz); δ 4.31 (br s, 4H, CH COD); δ 7.23–7.40 (m, 30H, CH aromatic protons). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81.01 MHz): δ −6.40 (s, 2P); δ −143.6 (sept, PF_6). IR (Nujol mull): ν(P–F) 845 cm^{-1} (s). Anal. Calc. for $C_{50}H_{54}F_6P_3Ir$: C, 56.97; H, 5.16. Found: C, 57.10; H, 5.19%.

4.6. [Rh(py)(PBz$_3$)(cod)]PF$_6$ (5)

A solution of RhCl(PBz_3)(cod) (500 mg, 0.910 mmol) in methanol (20 mL) was stirred until the solid dissolved completely and it was then treated with an excess of pyridine (0.6 mL, 7.58 mmol) in methanol (5 mL) for 60 min to afford an orange solution. A solution of NH_4PF_6 in methanol (5 mL) was added. Concentration under vacuum separated an orange solid which after filtration was washed with water (5 mL) and methanol (5 mL) before being dried under vacuum. Yield: 600 mg, 89% ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 2.14 (m, 4H, CH_2 COD); δ 2.59 (m, 4H, CH_2 COD); δ 2.72 (d, 6H, CH_2 PBz_3, $J_{HP} = 7.8$ Hz); δ 4.16 (br s, 2H, CH COD); δ 4.67 (br s, 2H, CH COD); δ 7.10–8.00 (m, 20H, aromatic + pyridine protons). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.49 MHz): δ 9.30 (d, 2P, $J_{RhP} = 153.3$ Hz); δ −142 (sept, PF_6, $J_{P-F} = 711.0$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.47 MHz): δ 29.0 (d, CH_2 PBz_3); δ 29.4, δ 32.4 (CH_2 COD); δ 79.3 (d, CH COD *trans* to py, $J_{CRh} = 12.2$ Hz); δ 104.6 (dd, CH COD *trans* to P, $J_{CP} = 8.2$ Hz, $J_{CRh} = 8.0$ Hz); δ 126.4, δ 128 (CH aromatic + pyridine carbons); δ 129.4 (CH, aromatic + para pyridine carbons); δ 130.14 (d, CH ortho aromatic carbons, $^3J_{CP} = 6.2$ Hz); δ 133.2 (d, C *ipso*, $^2J_{CP} = 5.1$ Hz); δ 138.4 (CH meta pyridine carbons); δ 151.3 (CH ortho pyridine carbons). IR (Nujol mull): ν(P–F) 847 cm^{-1} (s). Anal. Calc. for $C_{34}H_{38}NF_6P_2Rh$: C, 52.93; H, 5.44; N, 1.99. Found: C, 52.70; H, 5.33; N, 1.85%.

4.7. [Ir(py)(PBz$_3$)(cod)]PF$_6$ (6)

A solution of IrCl(PBz_3)(cod) (500 mg, 0.781 mmol) in methanol (20 mL) was stirred until the solid dissolved completely and it was then treated with an excess of pyridine (0.6 mL, 7.58 mmol) in methanol (5 mL) for 60 min to afford an orange solution. A solution of NH_4PF_6 in methanol (5 mL) was added. Concentration under vacuum separated an orange solid which after filtration was washed with water (5 mL) and methanol (5 mL) before being dried under vacuum. Yield: 550 mg, 85%. ^{1}H NMR (CD_2Cl_2, 300.13 MHz): δ 2.12 (m, 4H, CH_2 COD); δ 2.52 (m, 4H, CH_2 COD); δ 2.99 (d, 6H, CH_2 PBz_3, $J_{HP} = 8.9$ Hz); δ 4.13 (m, 2H, CH COD); δ 4.25 (m, 2H, CH COD); δ 7.14–7.71 (m, 20H, aromatic + pyridine protons). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.49 MHz): δ −3.05 (s, 1P); −143.22 (sept, PF_6, $J_{P-F} = 711.0$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.47 MHz): δ 29.3 (d, CH_2 PBz_3, $J_{CP} = 26.7$ Hz); δ 29.9, δ 33.2 (CH_2 COD); δ 65.0 (CH COD *trans* to py); δ 93.8 (d, CH COD *trans* to P, $J_{CP} = 12.3$ Hz); δ 127, δ 128 (CH aromatic + *para* pyridine carbons); δ 129.5 (CH, aromatic carbons); δ 130.4 (d, CH *ortho* aromatic carbons, $^3J_{CP} = 6.3$ Hz); δ 133.0 (d, C *ipso*, $^2J_{CP} = 4.6$ Hz); δ 138.7 (CH *meta* pyridine carbons); δ 150.3 (CH *ortho* pyridine carbons). IR (KBr): ν(P–F) 842 cm^{-1} (s). Anal. Calc. for $C_{34}H_{38}NF_6IrP_2$: C, 46.97; H, 4.83; N, 1.77. Found: C, 47.12; H, 4.67; N, 1.68%.

4.8. [IrH(PBz$_3$)(cod){η^2-P,C-($C_6H_4CH_2$)PBz$_2$}]PF$_6$ (7)

4.8.1. cis-(P,P)-[IrH(PBz$_3$)(cod){η^2-P,C-($C_6H_4CH_2$)PBz$_2$}]PF$_6$ (cis-7)

A solution of [Ir(PBz_3)$_2$(cod)]PF_6 (500 mg, 0.475 mmol) in chloroform (5 mL) was left under nitrogen for 3 days. After this period, the white crystals that separated out were filtered and washed with cold chloroform and pentane before being dried in vacuum. Yield: 485 mg, 97%. ^{1}H NMR (acetone-d_6, 500.13 MHz): δ 4.93 (td, 1H, CH COD, $^3J_{HP1} = {}^3J_{HH} = 9.2$ Hz, $^3J_{HH} = 5.9$ Hz); δ 4.81 (ddd, 1H, CH COD, $^3J_{HP2} = 2.3$ Hz, $^3J_{HH} = 8.5$ Hz, $^3J_{HH} = 6.2$ Hz); δ 4.40 (dd, 1H, CH_2 PBz_3, $^2J_{HP1} = 6.5$ Hz, $^2J_{HH} = 14.5$ Hz); δ 4.03 (dd, 1H, CH_2 PBz_3, $^2J_{HP1} = 8.9$ Hz, $^2J_{HH} = 14.5$ Hz); δ 4.17 (m, 1H, CH COD); δ 4.01 (m, 1H, CH COD); δ 3.41 (dd, 1H, CH_2 PBz_3, $^2J_{HP2} = 9.1$ Hz, $^2J_{HH} = 14.6$ Hz); δ 3.16 (dd, 1H, CH_2 PBz_3, $^2J_{HP2} = 8.6$ Hz, $^2J_{HH} = 14.6$ Hz); δ 3.96 (dd, 1H, CH_2 PBz_3, $^2J_{HP1} = 4.9$ Hz, $^2J_{HH} = 14.6$ Hz); δ 3.95 (dd, 1H, CH_2 PBz_3, $^2J_{HP1} = 3.0$ Hz, $^2J_{HH} = 14.6$ Hz); δ 2.76 (m, 1H, CH_2 COD); δ 1.75 (m, 1H, CH_2 COD); δ 1.80 (m, 1H, CH_2 COD); δ 1.57 (m, 1H, CH_2 COD); δ 3.36 (t, 1H, CH_2 COD, $^4J_{HP1} = J_{HH} = 8.6$ Hz); δ 2.96 (m, 1H, CH_2 COD); δ 3.13 (m, 1H, CH_2 COD); δ 2.72 (m, 1H, CH_2 COD); δ 3.73 (dd, 1H, CH_2 PBz_3, $^2J_{HP1} = 6.6$ Hz, $^2J_{HH} = 15.1$ Hz); δ 3.18 (m, 1H, CH_2 PBz_3); δ −7.82 (ddd, 1H, hydride, $^2J_{HP1} = 102.3$ Hz, $^2J_{HP2} = 17.2$ Hz, $^4J_{HH} = 6.3$ Hz); δ 7.20 (tq, 1H, CH aromatic, $J_{HH} = 7.2$ Hz, $^4J_{HP1} = J_{HH} = 2.9$ Hz); δ 7.67 (m, 1H, CH aromatic); δ 6.38 (m, 1H, CH aromatic); δ 7.43 (m, 1H, CH aromatic). $^{31}P\{^1H\}$ NMR (acetone-d_6, 202.46 MHz): δ −2.86 (d, 1P, $^2J_{PP} = 18.5$ Hz); δ −9.97 (d, 1P, $^2J_{PP} = 18.5$ Hz). $^{13}C\{^1H\}$ NMR (acetone-d_6, 125.77 MHz): δ 26.32 (CH_2 COD); δ 27.17 (CH_2 COD); δ 32.11 (d, CH_2 PBz_3, $J_{CP1} = 20.9$ Hz); δ 32.68 (d, CH_2 PBz_3, $J_{CP2} = 27.5$ Hz); δ 35.39 (CH_2 COD); δ 36.70 (d, CH_2 PBz_3, $J_{CP1} = 18.7$ Hz); δ 37.68 (CH_2 COD); δ 37.95 (d, CH_2 PBz_3, $J_{CP1} = 35.1$ Hz); δ 81.24 (d, CH COD, $^2J_{CP2} = 15.2$ Hz); δ 81.81 (CH COD); δ 83.55 (CH COD); δ 98.22 (d, CH COD, $^2J_{CP2} = 9.6$ Hz); δ 128.88 (C *ipso* aromatic); δ 130.43 (CH aromatic); δ 130.59 (CH aromatic); δ 131.18 (CH aromatic); δ 146.87 (d, metalated aromatic C, $^2J_{CP1} = 17.8$ Hz). IR (Nujol

mull): ν(Ir–H) 2100 cm^{-1} (m). Anal. Calc. for $C_{50}H_{54}F_6P_3Ir$: C, 56.97; H, 5.16. Found: C, 57.15; H, 5.12%.

4.8.2. trans-(P,P)-[IrH(PBz$_3$)(cod) {η^2-P,C-($C_6H_4CH_2$)-PBz$_2$}]PF$_6$ (trans-7)

Compound *trans*-**7**, which forms together with *cis*-**7**, could not be isolated (see text). It was characterized in solution by NMR spectroscopy: ^{1}H NMR ($CDCl_3$, 200.13 MHz): δ −13.38 (ps t, 1H, hydride, $^2J_{HP}$ = 19.8 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81.014 MHz): δ 27.81 (d, 1P, $^2J_{PP}$ = 238.0 Hz); δ −27.61 (d, 1P).

4.9. [Ir(H)$_2$(Me$_2$CO)$_2$(PBz$_3$)$_2$]PF$_6$ (8)

H_2 was bubbled through an acetone (40 mL) solution of [Ir(PBz$_3$)$_2$(cod)]PF$_6$ (1.00 g, 0.950 mmol). After 15 min, the solution became colorless. At this point the H_2 flow was replaced by nitrogen and the solution was concentrated to 15 mL. Addition of petroleum ether (15 mL), precipitated a white-off solid. Yield: 920 mg; 91%. ^{1}H NMR (CD_2Cl_2, 200.13 MHz): δ −30.13 (t, 2H, hydrides, J_{HP} = 15.3 Hz); 2.00 (s, 12H, CH_3 acetone); δ 3.20 (t, 12H, CH_2 PBz$_3$, $^2J_{HP}$ = 7.4 Hz); δ 6.92 (br t, 12H, *ortho* aromatic protons); δ 7.24–7.32 (m, 18H, *meta* + *para* aromatic protons). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 81.015 MHz): δ 14.58 (s, 2P); δ −143.8 (sept, PF_6, J_{P-F} = 713.0 Hz). IR (Nujol mull): ν(Ir–H) 2130 cm^{-1} (s); ν(C=O)$_{acetone}$ 1750 cm^{-1} (s); ν(P–F) 840 cm^{-1} (s). Anal. Calc. for $IrC_{48}H_{56}O_2P_3F_6$: C, 54.15; H, 5.30. Found: C, 54.51; H, 5.14%.

4.10. [Ir(H)$_2$(MeCN)$_2$(PBz$_3$)$_2$]PF$_6$ (9)

Replacing acetone with acetonitrile in the above preparation gave **9** after identical work-up. Yield: 930 mg; 95%. ^{1}H NMR (CD_2Cl_2, 300.13 MHz): δ −21.45 (t, 2H, hydrides, J_{HP} = 16.2 Hz); 1.82 (s, 12H, CH_3 acetonitrile); δ 3.29 (t, 12H, CH_2 PBz$_3$, $^2J_{HP}$ = 3.3 Hz); δ 6.92 (br t, 12H, *ortho* aromatic protons); δ 7.16–7.35 (m, 18H, *meta* + *para* aromatic protons). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ 1.18 (s, 2P); δ −143.22 (sept, PF_6, J_{P-F} = 711.0 Hz). IR (KBr): ν(Ir–H) 2150 cm^{-1} (s); ν(C≡N)$_{acetonitrile}$ 2410 cm^{-1} (s); ν(P–F) 850 cm^{-1} (s). Anal. Calc. for $IrC_{46}H_{50}N_2P_3F_6$: C, 53.64; H, 4.89; N, 2.72. Found: C, 53.81; H, 4.72; N, 2.59%.

4.11. In situ reaction of [Ir(PBz$_3$)$_2$(cod)]PF$_6$ (4) with H$_2$ in THF

Complex **4** (30 mg, 0.032 mmol) was dissolved in THF-d_8 (1 mL) and the solution was introduced into a 5 mm NMR tube under an inert atmosphere. After the tube was cooled to 0 °C, H_2 was gently bubbled into the solution for 5 min. ^{1}H and $^{31}P\{^1H\}$ NMR spectra showed the formation of $[Ir(H)_2(THF)_2(PBz_3)_2]^+$ (**10**). All our attempts to isolate **10** by scaling up the reaction were unsuccessful. In all cases, products without hydride ligands were detected.

4.11.1. Selected NMR data for 10

^{1}H NMR (THF-d_8, 300.13 MHz): δ −23.5 (t, hydrides, J_{HP} = 15.5 Hz). $^{31}P\{^1H\}$ NMR (THF-d_8, 121.49 MHz): δ 9.83 (s).

4.12. In situ reactions of [Rh(PBz$_3$)$_2$(cod)]PF$_6$ (3) with H$_2$

Complex **3** (30 mg; 0.031 mmol) was dissolved in an NMR tube, under an inert atmosphere, in the appropriate solvent (acetone-d_6, THF-d_8 or CD_3CN, 1 mL) and cooled to 0 °C. H_2 was gently bubbled into the solution with a long syringe needle for 5 min. ^{1}H and $^{31}P\{^1H\}$ NMR spectra were recorded and showed the formation of the bis-solvento *cis*-dihydrides **11**, **12**, or **14**, depending on the solvent used. All our attempts to isolate **11**, **12** or **14** by scaling up the reactions were unsuccessful. In all cases, mixtures of products were obtained, but no hydride species were detected.

4.12.1. Selected NMR data for [Rh(H)$_2$(CD$_3$CN)$_2$(PBz$_3$)$_2$]PF$_6$ (11)

^{1}H NMR (CD_3CN, 200.13 MHz): δ −18.21 (dt, hydrides, J_{HP} = 14.0 Hz; J_{RhH} = 17.2 Hz). $^{31}P\{^1H\}$ NMR (CD_3CN, 81.01 MHz): δ 33.85 (d, J_{RhP} = 113.4 Hz).

4.12.2. Selected NMR data for [Rh(H)$_2$(acetone)$_2$(PBz$_3$)$_2$]PF$_6$ (12)

^{1}H NMR (acetone-d_6, 200.13 MHz): δ −22.38 (dt, hydrides, J_{HP} = 15.9 Hz; J_{RhH} = 26.0 Hz). $^{31}P\{^1H\}$ NMR (acetone-d_6, 81.01 MHz): δ 32.48 (d, J_{RhP} = 122.1 Hz).

4.12.3. Selected NMR data for [Rh(H)$_2$(THF)$_2$(PBz$_3$)$_2$]PF$_6$ (14)

^{1}H NMR (THF-d_8, 300.13 MHz): δ −23.30 (dt, hydrides, J_{HP} = 15.9 Hz; J_{RhH} = 25.8 Hz). $^{31}P\{^1H\}$ NMR (THF-d_8, 121.49 MHz): δ 34.23 (d, J_{RhP} = 122.7 Hz).

4.13. In situ reaction of [Rh(py)(PBz$_3$)(cod)]PF$_6$ (5) with H$_2$

Complex **5** (30 mg; 0.045 mmol) was dissolved in THF-d_8 (1 mL) under an inert atmosphere in a 5 mm NMR tube and cooled to 0 °C, H_2 was gently bubbled into the solution for 5 min. ^{1}H and $^{31}P\{^1H\}$ NMR spectra at room temperature showed the selective formation of $[Rh(H)_2(THF)_2(py)(PBz_3)]^+$ (**16**). All our attempts to isolate **16** were unsuccessful.

4.13.1. Selected NMR data for 16

^{1}H NMR (THF-d_8, 300.13 MHz): δ −22.62 (dd, hydrides, J_{HP} = 15.7 Hz; J_{RhH} = 26.3 Hz). $^{31}P\{^1H\}$ NMR (THF-d_8, 121.49 MHz): δ 39.23 (d, J_{RhP} = 121.9 Hz).

4.14. In situ reaction of [Ir(py)(PBz$_3$)(cod)]PF$_6$ (6) with H$_2$

Complex **6** (30 mg; 0.040 mmol) was dissolved in THF-d_8 (1 mL) under an inert atmosphere in a 5 mm NMR tube.

H_2 was gently bubbled into the NMR solution for 5 min at 0 °C. ^{1}H and ^{31}P{^{1}H} NMR spectra showed the formation of $[Ir(H)_2(THF)_2(py)(PBz_3)]^+$ (**17**). All our attempts to isolate **17** by scaling up the reaction were unsuccessful. In all cases, mixtures of products were obtained, but no hydride species were detected.

4.14.1. Selected NMR data for 17

^{1}H NMR (THF-d_8, 200.13 MHz): δ −19.8 (d, hydrides, $J_{HP} = 16.8$ Hz). ^{31}P{^{1}H} NMR (THF-d_8, 81.01 MHz): δ 8.23 (s).

4.15. [Ir(H)$_2$(CO)$_2$(PBz$_3$)$_2$]PF$_6$ (18)

A solution of **8** (250 mg, 0.24 mmol) in CH_2Cl_2 (40 mL) was treated with 1 bar CO for 15 min. After concentration to ca. 15 mL and addition of petroleum ether (15 mL), **15** separated as a white solid. Yield: 200 mg, 85%. ^{1}H NMR (CD_2Cl_2, 200.13 MHz): δ −11.50 (t, 2H, hydrides, $J_{HP} = 15.3$ Hz); δ 3.45 (t, 12H, CH_2 PBz_3, $^2J_{HP} = 3.7$ Hz); 7.24–7.32 (m, 30H, aromatic protons). ^{31}P{^{1}H} NMR (CD_2Cl_2, 81.01 MHz): δ 10.15 (s, 2P); δ −143.7 (sept, PF_6 $J_{P-F} = 711.0$ Hz). IR (Nujol mull): ν(Ir–H) 2120 cm^{-1}; ν(C≡O) 2002 cm^{-1} (s); ν(C≡O) 2004 cm^{-1} (s); ν(P–F) 847 cm^{-1} (s). Anal. Calc. for $IrC_{44}H_{44}O_2P_3F_6$: C, 52.60; H, 4.41. Found: C, 52.75; H, 4.35%.

4.16. trans-[Rh(CO)$_2$(PBz$_3$)$_2$]PF$_6$ (20)

A solution of $[Rh(cod)(PBz_3)_2]PF_6$ (250 mg; 0.26 mmol) in THF (40 mL) was treated with carbon monoxide at 60 °C for 15 min, and an off-white solid precipitated. This solid was collected on a frit under nitrogen and washed with cold THF (5 mL) and petroleum ether (5 mL) before being dried under vacuum (yield: 200 mg; 85%). ^{1}H NMR (DMSO-d_6, 25 °C, 300.13 MHz): δ 3.45 (broad s, 12H, CH_2 PBz_3); 6.90–7.73 (m, 30H, aromatics PBz_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C, 121.5 MHz): δ 48.6 (d, 2P, $J_{RhP} = 75.1$ Hz); δ −143.0 (septuplet, PF_6^-). IR (KBr): ν(CO) = 2022 cm^{-1} (s). IR (DMSO): ν(CO) = 2019 cm^{-1} (s). Anal. Calc. for $RhC_{44}H_{42}O_2P_3F_6$: C, 57.91; H, 4.64. Found: C, 57.25; H, 4.65%.

4.17. In situ reaction of [Rh(cod)(PBz$_3$)$_2$]PF$_6$ (3) with H$_2$ (HP-NMR tube test, $P_{H_2} = 10$ bar)

Complex **3** (30 mg, 0.031 mmol) was dissolved, under an inert atmosphere, in acetone-d_6 (2 mL) in a sapphire HP-NMR 10 mm tube. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded. Then, the sample was removed from the spectrometer and pressurized with H_2 (10 bar). A new series of ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded which confirmed the quantitative formation of **11**. After removal of the sample from the spectrometer, the HP-NMR tube was depressurized, vented with N_2 and checked again by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy which established the complete loss of H_2 from **11** and the quantitative formation of **12**.

4.18. X-ray diffraction studies

Summary of crystal data and structure refinement parameters for RhCl(cod)(PBz_3) (**1**) and IrCl(cod)(PBz_3) (**2**) are reported in Table 1. Selected distances and angles for both compounds are summarized in Table 2.

4.18.1. RhCl(cod)(PBz$_3$) (1)

Single crystal structure determination of **1** was carried out from data collected using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$) on a Bruker SMART-1K CCD area detector diffractometer equipped with a Cryostream N_2 flow cooling device [52]. Series of narrow ω-scans (0.3°) were performed at several ϕ-settings in such a way as to cover a sphere of data to a maximum resolution of 0.75 Å. Data collection was carried out at 260 K. Cell parameters were determined and refined from the centroids of 956 reflections within the range $5.4° < 2\theta < 42.0°$ using the SMART software [53]. Raw frame data were integrated using the SAINT program [54]. The structure was solved using Direct Methods and refined by full-matrix least-squares on F^2 using SHELXTL [55]. No absorption correction was applied to data from (**1**). All non-hydrogen atoms were refined with anisotropic displacement parameters (adps). Hydrogens atoms were geometrically placed and allowed to ride on their parent C atom with $U_{iso}(H) = 1.2U_{eq}(C)$. Idealized C–H distances were fixed at 0.93 Å (for C–H in phenyl groups), 0.97 Å (for C–H in CH_2 groups) and 0.98 Å (C–H in the 1,5-cyclooctadiene group). A phenyl ring from one of the benzyl groups has been modelled as disordered over two positions (occupancies of 0.63(4) and 0.37(4)), with distances between carbon atoms restrained to 1.39 Å with an s.u. of 0.005 Å.

4.18.2. IrCl(cod)(PBz$_3$) (2)

Crystallographic data for **2** were collected on a CAD4 diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.7107$ Å) at room temperature. A set of 25 carefully centered reflections in the range $7° < \theta < 9°$ was used for determining the lattice constants. As a general procedure, the intensity of three standard reflections were measured periodically every 200 reflections for orientation and intensity control. This procedure revealed an 8% decay of intensities during the data collection period, for which the intensities were corrected. The data were corrected for Lorentz and polarization effects. Atomic scattering factors were those tabulated by Cromer and Waber [56] with anomalous dispersion corrections taken from Ref. [57]. An empirical absorption correction was applied via ψ scan with correction factors in the range 0.8401–0.8977. The computational work was carried out using the program SHELX-97 [58]. All non-hydrogen atoms were refined with anisotropic displacement parameters (adps). Hydrogens atoms were geometrically placed and refined following the same procedure described above for the Rh complex (**1**).

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 272989 and 272990. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033 or e-mail: deposit@ccdc.cam.ac.uk).

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