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Synthesis and characterization of new pentamethylcyclopentadienyl iridium hydride complexes

María Talavera, Sandra Bolaño*, Jorge Bravo*, Jesús Castro, Soledad García-Fontán

Departamento de Química Inorgánica, Universidade de Vigo, Facultade de Química, Edificio de Ciencias Experimentales, 36310 Vigo, Spain

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ABSTRACT

Pentamethylcyclopentadienyl iridium dihydride complexes [Cp*Ir(H)$_2$(PR$_3$)]; (PR$_3$ = PPh$_2$Me, PTA) were prepared by reaction of [Cp*IrCl$_2$(PPh$_2$Me)] and [Cp*IrCl$_2$(PTA)], respectively, with an excess of sodium bis(2-methoxyethoxy)aluminium hydride (Red-Al). Protonation of the dihydride [Cp*Ir(H)$_2$(PPh$_2$Me)] with HBF$_4$·Et$_2$O at low temperature gave the classical trihydride complex [Cp*Ir(H)$_3$(PPh$_2$Me)]BF$_4$ that displays quantum mechanical exchange coupling. Reaction of [Cp*IrCl$_2$(PPh$_2$Me)] with CO gave the half-sandwich iridium carbonyl compound [Cp*IrCl(CO)(PPh$_2$Me)]Cl which, by reaction with NaBPh$_4$, yielded yellow microcrystals of [Cp*IrCl(PPh$_2$Me)(CO)]BPh$_4$ adequate for X-ray diffraction analysis.

1. Introduction

Interest in the chemistry of hydrido transition metal complexes is increasing in inorganic, biochemical and organometallic research owing to their reactivity and applications in areas such as catalysis and materials science, amongst others [1].

The reactivity of these compounds is highly dependent on the metal atom and the coligands that complete the coordination sphere of the metal. Appropriate design of this environment allows tuning both the steric and electronic properties of the resulting compound. The presence of a Cp* ligand on di- and polyhydride complexes will force hydride ligands to be in close contact, favouring their interaction and the possibility to be eliminated as H$_2$ and creating a free coordination site which is very important in metal catalysis [2]. On the other hand, di- and polyhydride complexes can display exchange couplings which, besides relevant theoretical aspects [3], may present applications as sensors of very weak interactions in solution or as temperature probes in NMR [4].

We report here the synthesis and characterization of a set of new half-sandwich iridium hydride complexes bearing the PPh$_2$Me phosphine or the water-soluble phosphine 1,3,5-triaza-7-phosphaadamantane (PTA), and their protonation studies. Attempts to characterize an unexpected carbonyl subproduct obtained in the synthesis of the dihydride [Cp*Ir(H)$_2$(PPh$_2$Me)] (**1**) prompted us to obtain the new half-sandwich iridium carbonyl compounds [Cp*IrCl(CO)(PPh$_2$Me)]A, A = Cl (**3**); BPh$_4$ (**4**). The X-ray structure of compound **4** was elucidated.

2. Results and discussion

2.1. Synthesis and characterization of the dihydrides [Cp*Ir(H)$_2$(PR$_3$)] PR$_3$ = PPh$_2$Me (1), PTA (2)

The dihydrides [Cp*Ir(H)$_2$(PPh$_2$Me)] (**1**) and [Cp*Ir(H)$_2$(PTA)] (**2**) [5] can be obtained by two different ways:

1) By reaction of toluene solutions of the chlorocomplexes [Cp*IrCl$_2$(PPh$_2$Me)] and [Cp*IrCl$_2$(PTA)], respectively, with an excess of sodium bis(2-methoxyethoxy)aluminium hydride (Red-Al) (Scheme 1);
2) By reaction of methanol solutions of the same chlorocomplexes with NaOMe [6].

The second method gives better yields for complex **2** but in the case of complex **1**, the reaction of [Cp*IrCl$_2$(PPh$_2$Me)] with NaOMe gives, besides to the dihydride compound **1** a non-identified subproduct, that was detected by NMR and IR spectroscopies (see below) but we were not able to isolate it because it easily decomposes during the workup of the mixture.

Compounds **1** and **2** were isolated as brown solids and are air-unstable [7]. They were characterized by IR and NMR spectroscopies.

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* Corresponding authors. Tel.: +34 986812275; fax: +34 986813798.
E-mail addresses: bgs@uvigo.es (S. Bolaño), jbravo@uvigo.es (J. Bravo).

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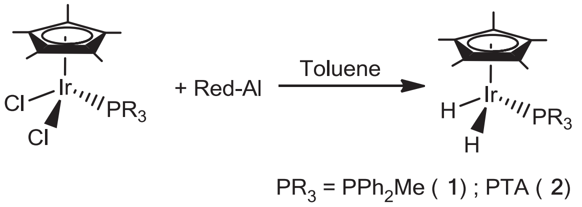


Scheme 1.

The IR spectra shows medium absorptions at 2109 and 1922 cm^{-1} for compound **1**, and strong absorptions at 2095 and 1896 cm^{-1} for compound **2**, attributable to the ν (Ir–H) vibrations [8,9]. The ^1H NMR spectrum shows a high field doublets at δ −17.83 ppm ($^2J_{H-P}$ = 31.4 Hz) (compound **1**), and at δ −17.91 ppm ($^2J_{H-P}$ = 32.5 Hz) (compound **2**), both integrating by two protons, suggesting the presence of two hydride ligands coupled to the phosphorus nucleus of the phosphane ligand.

However, to confirm this hypothesis, and to rule out other possibilities, such as a dynamic *cis* dihydride or a dihydrogen complex, we have carried out a variable temperature 400 MHz study. The relaxation time, T_1, of the hydride resonance in complexes **1** and **2** was measured as a function of temperature using a standard inversion recovery sequence. The minimum T_1 of 459 ms at 200 K for compound **1** and of 647 ms at 209 K for compound **2** was estimated by plotting ln T_1 vs 1000/T. Dihydrides and dihydrogen complexes can be distinguished by their minimum T_1 value by following the method of Halpern and co-workers [10]. The T_1 minimum values calculated for compounds **1** and **2** clearly indicate their nature as classical dihydride complexes.

The $^{31}P\{^1H\}$ NMR spectrum of the complexes shows a singlet at −5.57 ppm for compound **1** and at −68.29 ppm for compound **2**; and the $^{13}C\{^1H\}$ NMR spectrum displays, besides the signals correspondent to the R groups of the phosphane ligand (see Experimental part), signals at 10.9 ppm and 92.3 ppm (compound **1**) and at 11.9 ppm and 92.3 ppm (compound **2**) assigned to the Cp* ligand.

As it was previously mentioned, reaction of [Cp*$IrCl_2(PPh_2Me)$] with NaOMe gives, besides to the dihydride compound **1** a non-identified subproduct detected by NMR and IR spectroscopies. Figs. 1 and 2 show the $^{31}P\{^1H\}$ and ^1H NMR spectra of the mixture. It is remarkable the high similarity among the signals of both compounds, except for the low frequency part of the ^1H NMR spectrum, in which only the signal corresponding to the hydride nuclei of compound **1** is observed, indicating that the subproduct is not a hydride complex. On the other hand, the IR spectrum of the mixture shows a strong absorption at 1909 cm^{-1} and its $^{13}C\{^1H\}$ NMR spectrum displays a doublet at 182.7 ppm (J_{C-P} = 15.5 Hz). These facts indicate the presence of an iridium complex with, at least, carbonyl, Cp* and $PMePh_2$ ligands on its structure [11].

Bibliographic data [12] allows us to exclude the monocarbonylcompound [Cp*Ir(CO)(PPh_2Me)] [^1H (CD_2Cl_2): δ 7.6 (m, 10 H, C_6H_5), 1.82 (d, J_{PH} = 1.5 Hz, 15 H, Cp*) ppm; $^{31}P\{^1H\}$ ($CDCl_3$): δ = 25.18 (s) ppm], so we intended to synthesize the unknown carbonyl compound trying different strategies. First, we have refluxed a methanolic solution of the dihydride compound **1** to produce the expected carbonylation reaction. Unfortunately we have obtained a mixture of compounds that we were not able to identify, but none of the signals observed in the ^{31}P NMR spectrum were coincident with that observed for the aforementioned subproduct. In a second attempt we have reacted a methanolic solution of the chlorocomplex [Cp*$IrCl_2(PPh_2Me)$] with CO(g) at 75 °C under pressure, obtaining the Ir(III) carbonyl compound [Cp*IrCl(CO)(PPh_2Me)]Cl and its spectroscopic parameters were not coincident with those of the subproduct either (see next paragraph). To gather more experimental evidences about the nature of this compound, we have treated a solution of the mixture of the dihydride compound **1** and the unknown subproduct (in different solvents as MeOH or CH_2Cl_2 and with similar results, which indicates that the solvent does not play any important role in the mixture behaviour) with $NaBPh_4$ and also with $NaPF_6$, to see if the substitution of the counteranion helps the precipitation of the compound. Results were somewhat unexpected: There is no precipitation in any case but, when these reactions were monitored by NMR spectroscopy we have observed, in all cases, the progressive disappearance of the mixture ^1H and $^{31}P\{^1H\}$ NMR signals and the raising of new signals corresponding to the cationic hydride carbonyl compound [Cp*IrH(CO)(PPh_2Me)]$^+$, already reported in the literature although with a different counteranion (CF_3COO^-) [12,13]. All these results do not allow us to undoubtedly propose the structure of the unknown compound but we can assure the presence of CO, Cp* and $PMePh_2$ ligands bonded to the iridium centre.

*2.2. Synthesis and characterization of the carbonyl complexes [Cp*IrCl(CO)(PPh_2Me)]A, A = Cl (**3**); BPh_4 (**4**)*

Compound [Cp*IrCl(CO)(PPh_2Me)]Cl (**3**) was prepared by treating a methanolic solution of the chlorocomplex [Cp*$IrCl_2(PPh_2Me)$] with CO(g) at 75 °C under pressure (Scheme 2). A yellow solid was obtained and characterized by IR and NMR spectroscopies. The IR spectrum shows a strong band at 2042 cm^{-1} attributable to the ν_{CO} band. The $^{31}P\{^1H\}$ NMR spectrum displays a singlet at −12.26 ppm corresponding to the phosphorus nuclei of the phosphine ligand and the $^{13}C\{^1H\}$ NMR spectrum shows, apart from the signals corresponding to the Cp* and PPh_2Me ligands, a low field doublet (δ = 166.1 ppm; $^2J_{C-P}$ = 14.3 Hz) assignable to the carbonyl ligand.

Treating a methanol solution of this complex with $NaBPh_4$ yielded yellow microcrystals of [Cp*IrCl(PPh_2Me)(CO)]BPh_4 (**4**) adequate for X-ray diffraction analysis.

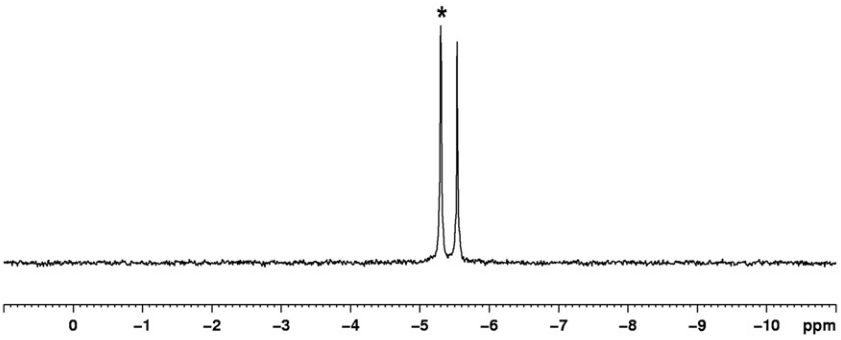


Fig. 1. $^{31}P\{^1H\}$ NMR spectrum of the mixture of compound **1** and the unknown subproduct (*) obtained by reaction of [Cp*$IrCl_2(PPh_2Me)$] with NaOMe.

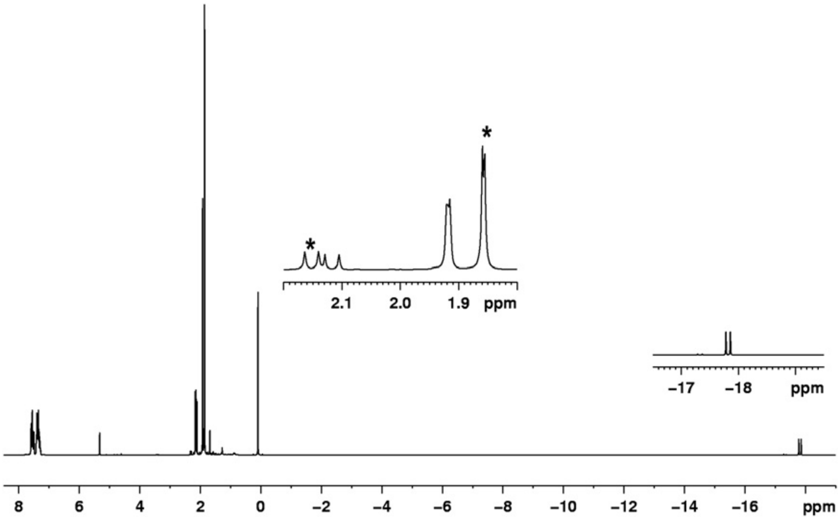


Fig. 2. ^1H NMR spectrum of the mixture of compound **1** and the unknown subproduct (*) obtained by reaction of [$Cp^*IrCl_2(PPh_2Me)$] with NaOMe.

An ORTEP view of this complex is shown in Fig. 3 together with the labelling scheme while selected bond distances and angles are listed in Table 1. The structure of the complex consists of a tetraphenyl borate anion (not represented in the figure) and a cation formed by an iridium atom η^5-coordinated to a pentamethylcyclopentadienyl ligand (Cp*), and to three monodentate ligands leading to the formation of a "three-legged piano stool" structure. These ligands are a chloride ligand, a carbonyl ligand and a diphenylmethylphosphane ligand. The geometry of the complex is pseudo octahedral and is marked by near 90° values for the angles C(0)–Ir–P(1), C(0)–Ir–Cl(1) and P(1)–Ir–Cl(1), less than 1° far from the regularity.

The centroid of Cp* ligand is situated at 1.8814(4) Å from the iridium atom, and the average Ir–C bond distances for the Cp* ligand is 2.2403(9) Å (Table 2), being both values similar to those found in the literature [14].

The Ir–C(0) and Ir–Cl bond lengths [1.89(2) Å and 2.383(3) Å, respectively] are in good agreement with the scarce values found in the literature for structures based on the {Cp*Ir(CO)Cl} fragment [15]. Less data were found containing the {$Cp^*Ir(PMePh_2)$} fragment, but the Ir–P bond length [2.334(2) Å], compares well with that found in the cation [$Cp^*Ir(PMe_3)$(mesityl)(CO)]$^+$ [14b]. The disposition of the phosphane ligand is in such a way that the methyl group is situated *pseudo-trans* to the chlorine ligand, perhaps due the steric hindrance of the Cp* ligand.

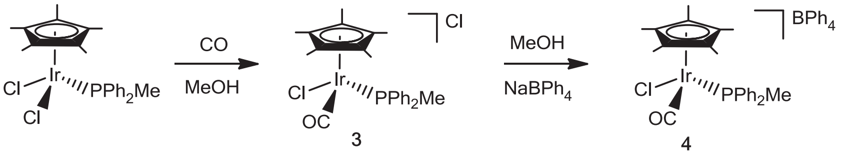
2.3. Protonation studies of compounds **1** and **2**

With the aim of obtaining dihydrogen compounds by protonation of the dihydride complexes **1** and **2**, we treated a diethyl ether solution of the dihydrides with slight excess of $HBF_4 \cdot Et_2O$. The reaction was carried out at low temperature due to the low thermal stability of most of the dihydrogen complexes [16]. Reaction of the dihydride **2** yielded a brown solid insoluble in the common solvents that cannot be identified [17]. In the case of compound **1** the protonation reaction gave the trihydride complex [$Cp^*IrH_3(PPh_2Me)$]BF_4 (**5**) as a brown solid that immediately precipitated (Scheme 3).

The spectral parameters of complex **5** show that the protonation site is the metal centre and not a hydride ligand. This reaction can be reverted by adding Et_3N. The ^1H NMR spectrum of the complex **5** displays a doublet resonance at −13.01 ppm, integrating by three protons with a coupling constant $^2J_{H-P} = 9.2$ Hz. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at −8.30 ppm, corresponding to the phosphorous nucleus of the phosphine ligand. A variable temperature ^1H NMR study shows that the spectra are temperature dependent. The presence of a single resonance at 298 K that progressively converts into two signals consistent with a A_2BX spin system (X = ^{31}P) agrees with the presence of a thermally activated exchange process which renders the three hydrides equivalent, at the NMR time scale, at room temperature. This behaviour was already observed for other four-legged piano stool iridium trihydrides [18]. In Fig. 4 we present the ^{31}P decoupled ^1H NMR spectra of the hydride region of compound **5** at different temperatures. At 298 K, the spectrum shows a singlet that broadens when the temperature of the sample is lowered. At 238 K, a decoalescence occurs and, at 218 K, a well resolved A_2B spin system is observed. Line-shape analysis performed using gNMR software, allowed us to establish that this system is defined by chemical shifts of $\delta_A = -13.6$ and $\delta_B = -12.3$ ppm and a coupling constant $J_{AB} = 173.5$ Hz.

When the temperature is further lowered from 218 to 178 K, the values of the chemical shifts do not change significantly with the temperature but the value of J_{AB} decreases from 173.5 Hz at 218 K to 81.7 Hz at 178 K. The high value of J_{AB} and its variation with the temperature indicates that this compound displays quantum mechanical exchange coupling between H_A and H_B [4].

The T_1 values of the hydrogen nuclei of the IrH_3 unit of **5** were determined over the temperature range 298–178 K. $T_{1(\mathrm{min})}$ values of 137 ms for H_A, and 151 ms for H_B were obtained at 204 K and



Scheme 2.

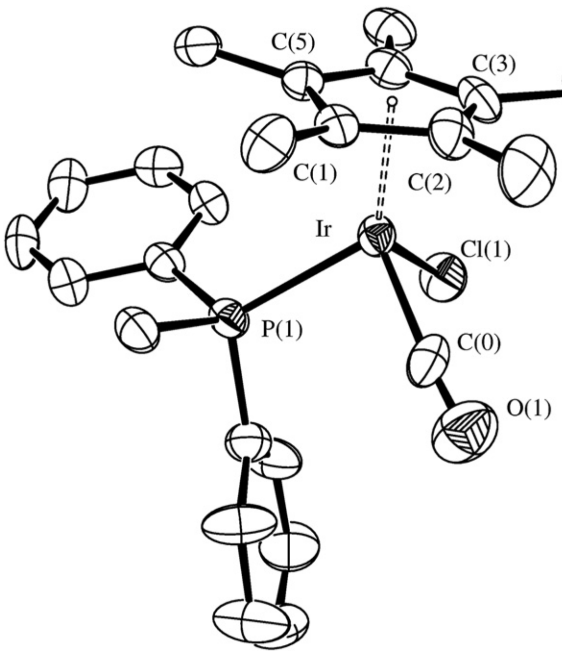


Fig. 3. ORTEP view of the cationic complex $[Cp^*IrCl(PPh_2Me)(CO)]^+$ drawn at 30% probability level. Hydrogen atoms are omitted for clarity.

206 K respectively, supporting the classical trihydride character of **5** [19].

3. Experimental

3.1. General procedures, methods and materials

All experiments were carried out under an atmosphere of argon by Schlenk techniques. Solvents were dried by the usual procedures [20] and distilled under argon prior to use. The starting materials $[Cp^*IrCl_2(PPh_2Me)]$ [21], $[Cp^*IrCl_2(PTA)]$ [22] were prepared as described in the literature. All reagents were obtained from commercial sources. Unless stated, NMR spectra were recorded at room temperature on Bruker ARX-400 instrument, with resonating frequencies of 400 MHz (^1H), 161 MHz ($^{31}P\{^1H\}$), and 100 MHz ($^{13}C\{^1H\}$) using the solvent as the internal lock. ^1H and $^{13}C\{^1H\}$ signals are referred to internal TMS and those of $^{31}P\{^1H\}$ to 85% H_3PO_4; downfield shifts (expressed in ppm) are considered positive. ^1H and $^{13}C\{^1H\}$ NMR signal assignments were confirmed by ^1H-COSY, HSQC ($^1H-^{13}C$), HMBC ($^1H-^{13}C$) and DEPT experiments. Low-temperature measurements were made by cooling the probe with a stream of N_2. NMR spectra were simulated using *gNMR* 4.1 software [23]. T_1 relaxation times for the hydridic resonances of complexes were measured in CD_2Cl_2 or Toluene-d_8 as a function of temperature at 400 MHz using a standard inversion-recovery methodology. Coupling constants are given in Hertz. Infrared spectra were run on a Jasco FT/IR-6100 spectrometer using KBr pellets. C, H, and N analyses were carried out in Carlo Erba 1108 analyzer. High resolution electrospray mass spectra were acquired using an Apex-Qe spectrometer.

Table 1
Selected bond lengths (Å) and angles (°) for compound **4**.

Ir—C(0)	1.886(12)	Ir—P(1)	2.334(2)
Ir—Cl(1)	2.383(3)	Ir—CT*	1.8814(4)
Ir—C(1)	2.197(8)	Ir—C(2)	2.234(9)
Ir—C(3)	2.237(9)	Ir—C(4)	2.261(9)
Ir—C(5)	2.268(9)		
CT*—Ir—C(0)	126.6(3)	CT*—Ir—P(1)	127.95(6)
CT*—Ir—Cl(1)	121.51(7)	C(0)—Ir—P(1)	89.2(3)
C(0)—Ir—Cl(1)	90.1(3)	P(1)—Ir—Cl(1)	90.17(9)
O(1)—C(0)—Ir	175.3(12)		

CT* refers to the centroid of Cp* ligand.

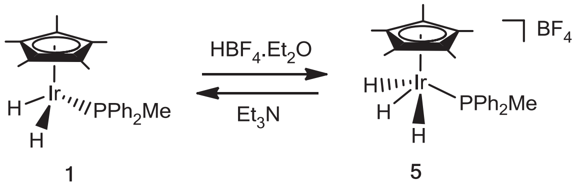
Table 2
Crystal data and structure refinement for $[Cp^*IrCl(PPh_2Me)(CO)]BPh_4$ (**4**).

Empirical formula	$C_{48}H_{48}BClOPIr$
Formula weight	910.29
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 15.8833(14)$ Å
	$b = 11.0778(10)$ Å
	$c = 23.751(2)$ Å
	$\beta = 94.102(2)°$
Volume	4168.4(6) Å [3]
Z	4
Density (calculated)	1.451 Mg/m^3
Absorption coefficient	3.340 mm^{-1}
F(000)	1832
Crystal size	0.18 × 0.11 × 0.10 mm
Theta range for data collection	1.49–28.01°
Index ranges	$-20 \leq h \leq 20$; $-14 \leq k \leq 10$; $-25 \leq l \leq 31$
Reflections collected	27 125
Independent reflections	9959 [R(int) = 0.0971]
Reflections observed (>2σ)	4111
Data completeness	0.987
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456/0.6484
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9959/0/481
Goodness-of-fit on F^2	0.959
Final R indices [I > 2σ (I)]	$R_1 = 0.0513$ $wR_2 = 0.1058$
R indices (all data)	$R_1 = 0.1825$ $wR_2 = 0.1572$
Largest diff. peak and hole	1.006 and −1.885 $eÅ^{-3}$

3.2. X-ray diffraction analysis

Crystallographic data of $[Cp^*IrCl(PPh_2Me)(CO)]BPh_4$ (**4**) were collected on a Bruker Smart 1000 CCD diffractometer at CACTI (Universidade de Vigo) using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å), and were corrected for Lorentz and polarisation effects. The software SMART [24] was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT [25] for integration of intensity of reflections and scaling, and SADABS [26] for empirical absorption correction.

The crystallographic treatment of the compound was performed with the Oscail program [27]. The structure was solved by direct methods and refined by a full-matrix least-squares based on F^2 [28]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters. Details of crystal data and structural refinement are given in Table 2.



Scheme 3.

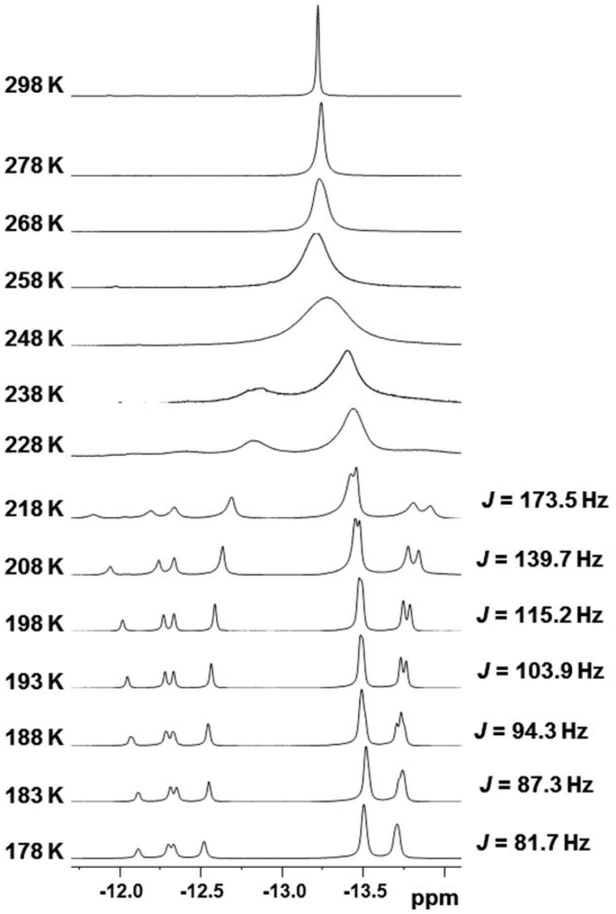


Fig. 4. NMR $^1H\{^{31}P\}$ NMR spectra (400 MHz) in CD_2Cl_2 at various temperatures in the hydride region of $[Cp^*IrH_3(PPh_2Me)]BF_4$ (**5**).

3.3. Synthesis and characterization of the complexes

*3.3.1. Preparation of [Cp*Ir(H)$_2$(PPh$_2$Me)](**1**)*

An orange solution of $[Cp^*IrCl_2(PPh_2Me)]$ (515 mg, 0.86 mmol) in 15 mL of toluene was treated with Red-Al (1.5 mL, 6 equiv). The reaction mixture was stirred for 15 min. After that, the solvent was vacuum removed and the resulting "gum" was dissolved in hexane/THF (5:1 v/v). This solution was filtered through a silica column using hexane/THF (5:1 v/v) as eluent. The solvent was vacuum removed and the brown solid obtained was washed with pentane (3 × 2 mL) and dried in vacuum. Yield: 168.0 mg (37%). Anal. Calcd. for $C_{23}H_{30}IrP$ (529.68 g/mol): C 52.15, H 5.71; found: C 52.51, H 5.83. MS (*m*/*z*, referred to the most abundant isotopes): 527 $[M - 2H]^+$. IR (cm^{-1}): ν (Ir–H) 2109 (m), 1922 (m). $T_{1(min)}$: 459 ms (200 K). ^1H NMR (CD_2Cl_2): δ −17.83 (d, 2H, $^2J_{H-P} = 31.4$ Hz, Ir–*H*); 1.91 (d, 15H, $^4J_{H-P} = 2.0$ Hz, C_5CH_3); 2.11 (d, 3H, $^2J_{H-P} = 9.6$ Hz, PPh_2CH_3); 7.25–7.38 (m, 6H, PPh_2CH_3); 7.47–7.55 (m, 4H, PPh_2CH_3) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −5.57 (s, PPh_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 10.9 (s, C_5CH_3); 24.7 (d, $^1J_{C-P} = 41.9$ Hz PPh_2CH_3); 92.3 (d, $^2J_{C-P} = 3.0$ Hz, C_5CH_3); 127.9 (d, $^3J_{C-P} = 9.9$ Hz, *C* PPh_2Me); 129.4 (d, $^4J_{C-P} = 2.3$ Hz, *C* PPh_2Me); 132.6 (d, $^2J_{C-P} = 10.9$ Hz, *C* PPh_2Me); 139.3 (d, $^1J_{C-P} = 51.4$ Hz, C_{ipso}) ppm.

*3.3.2. Preparation of [Cp*Ir(H)$_2$(PTA)] (**2**)*

Method (a): A yellow solution of $[Cp^*IrCl_2(PTA)]$ (300 mg, 0.54 mmol) in 15 mL of toluene was treated with Red-Al (2.5 mL, 15 equiv). The reaction mixture was stirred for 2 h at room temperature. Solvent was vacuum removed and the resulting oil was dissolved in hexane/THF (5:1 v/v). This solution was filtered through a silica column using methanol as eluent. After that, the solvent was vacuum removed and the light brown solid obtained was washed with pentane (3 × 5 mL) and dried in vacuum. Yield: 126.3 mg (49%).

Method (b): $[Cp^*IrCl_2(PTA)]$ (300 mg, 0.54 mmol) was added to a vigorously stirred solution of sodium methoxide prepared by dissolving sodium (150 mg, 12.75 equiv) in 25 mL of methanol. The solution was allowed to react for 2 h at reflux temperature, and then, the solvent was vacuum removed. The residue obtained was dissolved in toluene (20 mL) and filtered through a Celite® column. The solvent was vacuum removed again and the brown solid obtained was washed with pentane (3 × 5 mL) and dried in vacuum. Yield: 150 mg (57%).

Anal. Calcd for $C_{16}H_{29}N_3IrP$ (486.62 g/mol): C 39.49, H 6.01, N 8.64; found: C 39.93, H 6.07, N 8.69. MS (*m*/*z*, referred to the most abundant isotopes): 486 $[M]^+$. IR (cm^{-1}): ν (Ir–H) 2095 (s), 1896 (s). $T_{1(min)}$: 647 ms (209 K). ^1H NMR (C_6D_6): δ −17.91 (d, 2H, $^2J_{H-P} = 32.5$ Hz, Ir–H); 2.11 (d, 15H, $^4J_{H-P} = 0.6$ Hz, C_5CH_3); 3.63 (s, 6H, PCH_2N); 3.99–4.34 (AB system, 6H, NCH_2N) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −68.29 (s, *P*-PTA) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 11.9 (s, C_5CH_3); 59.2 (d, $^1J_{C-P} = 25.1$ Hz, PCH_2N); 73.6 (d, $^3J_{C-P} = 7.0$ Hz, NCH_2N); 92.3 (s, C_5CH_3) ppm.

*3.3.3. Preparation of [Cp*IrCl(PPh$_2$Me)(CO)]Cl (**3**)*

A nitrogen-purged orange solution of $[Cp^*IrCl_2(PPh_2Me)]$ (100 mg, 0.17 mmol) in 15 mL of methanol was placed in a Schlenk flask equipped with a Teflon stopcock under an atmosphere of CO ($P_{CO} = 1$ atm). The Schlenk tube was tightly closed and heated at 75 °C for 90 min. Removal of the solvent under vacuum and precipitation of the residue with Et_2O (3 × 5 mL) gave a yellow solid. The solid was finally dried in vacuum. Yield: 80 mg (75%). Anal. Calcd for $C_{24}H_{28}OCl_2IrP$ (626.68 g/mol): C 45.96, H 4.47; found: C 45.72, H 4.50. IR (cm^{-1}): ν (CO) 2042 (s). ^1H NMR (CD_2Cl_2): δ 1.85 (d, 15H, $^4J_{H-P} = 2.4$ Hz, C_5CH_3); 2.54 (d, 3H, $^2J_{H-P} = 11.2$ Hz, PPh_2CH_3); 7.50–7.68 (m, 10H, PPh_2CH_3) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −12.26 (s, PPh_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 9.4 (s, C_5CH_3); 15.1 (d, $^1J_{C-P} = 42.6$ Hz, PPh_2CH_3); 105.6 (s, C_5CH_3); 127.6 (d, $^1J_{C-P} = 61.8$ Hz, C_{ipso}); 129.0 (d, $^1J_{C-P} = 61.7$ Hz, C_{ipso}); 129.4–129.8 (*C* PPh_2Me); 132.6–133.3 (*C* PPh_2Me); 166.1 (d, $^2J_{C-P} = 14.3$ Hz, *C*O) ppm.

*3.3.4. Preparation of [Cp*IrCl(PPh$_2$Me)(CO)]BPh$_4$ (**4**)*

A metathesis reaction carried out by treating complex **3** dissolved in warm MeOH with an excess of $NaBPh_4$ yielded complex **4**. Yellow crystals of **4** were obtained by slow evaporation of the solvent. ^1H NMR (CD_2Cl_2): δ 1.66 (d, 15H, $^4J_{H-P} = 2.4$ Hz, C_5CH_3); 2.32 (d, 3H, $^2J_{H-P} = 11.2$ Hz, PPh_2CH_3); 6.80–6.89 (m, 4H, BPh_4); 6.99 (t, 8H, $J_{H-B} = 7.4$ Hz, BPh_4); 7.25–7.34 (m, 8H, BPh_4); 7.44–7.71 (m, 10H, PPh_2CH_3) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −11.93 (s, PPh_2CH_3) ppm.

*3.3.5. Preparation of [Cp*IrH$_3$(PPh$_2$Me)]BF$_4$ (**5**)*

A brown solution of $[Cp^*Ir(H)_2(PPh_2Me)]$ (130 mg, 0.25 mmol) in 4 mL of diethyl ether was cooled in an ice bath and then $HBF_4 \cdot Et_2O$ (35.9 μL, 0.295 mmol) was added. Immediately, a brown solid appeared. This solid was separated by decantation, washed with diethyl ether (3 × 2 mL) and dried in vacuum. Yield: 108.9 mg (70%). Anal. Calcd for $C_{23}H_{31}BF_4IrP$ (617.50 g/mol): C 44.74, H 5.06; found: C 44.55, H 5.13. MS (*m*/*z*, referred to the most abundant isotopes): 531 $[M-H_3-BF_4]^+$. IR (cm^{-1}): ν (Ir–H) 2143 (m), 2101 (w). $T_{1(min)}$: 137 ms and 151 ms. ^1H NMR (CD_2Cl_2): δ −13.01 (d, 3H, $^2J_{H-P} = 9.2$ Hz, Ir–*H*); 2.05 (d, 15H, $^4J_{H-P} = 1.7$ Hz, C_5CH_3); 2.35 (d, 3H, $^2J_{H-P} = 10.9$ Hz, PPh_2CH_3); 7.40–7.50 (m, 4H, PPh_2CH_3); 7.50–7.57 (m, 6H, PPh_2CH_3) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −8.30

(s, $P\mathrm{Ph_2CH_3}$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 10.1 (s, C_5CH_3); 22.2 (d, $^1J_{C-P}$ = 46.6 Hz, PPh_2CH_3); 103.7 (s, C_5CH_3); 129.5 (d, $^2J_{C-P}$ = 11.6 Hz, C PPh_2Me); 131.3 (d, $^1J_{C-P}$ = 65.9 Hz, C_{ipso}); 131.9 (d, $^3J_{C-P}$ = 10.9 Hz, C PPh_2Me); 132.6 (d, $^4J_{C-P}$ = 2.8 Hz, C PPh_2Me) ppm.

4. Conclusions

The synthesis of half-sandwich dihydride complexes of iridium(III) containing P-donor ligands such as PPh_2Me and 1,3,5-triaza-7-phosphaadamantane (PTA) has been achieved using [Cp*Ir(Cl)$_2$(PR$_3$)]; (PR$_3$ = PPh$_2$Me, PTA) as a precursor. Protonation of [Cp*Ir(H)$_2$(PPh$_2$Me)] with $HBF_4 \cdot Et_2O$ does not give an η^2-H_2 complex but proceeds with the formation of the classical trihydride [Cp*Ir(H)$_3$(PPh$_2$Me)](BF$_4$) which displays quantum mechanical exchange coupling between the hydrogen nuclei. Preliminary results indicate that the new neutral and cationic hydride complexes display a noticeable chemical inertness.

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Appendix A. Supplementary material

CCDC 865154 contains 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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