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REACTIONS OF INTERNALLY METALLATED TRIS(TRIPHENYLPHOSPHINE)IRIDIUM(I) COMPLEX WITH CARBON MONOXIDE, HYDROGEN AND METHANOL

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Summary

The reaction of the internally metallated tris(triphenylphosphine)iridium(I) complex with CO, H_2, CH_3OH in solution gives rise to a new carbonyl, hydridocarbonyl and hydrido complexes of iridium(I) and iridium(III). The preparation and characterization of these compounds are reported. A new route to prepare the pure isomers *fac*- and *mer*-$[(C_6H_5)_3P]_3IrH_3$ is also described. The stereochemistries of the products have been assigned by a combination of IR and ^1H NMR spectroscopy.

Introduction

In a preliminary communication [1] we recently reported the preparation and characterization of the internally metallated tris(triphenylphosphine)iridium(I) complex. Subsequently we made a study of the reactions of this complex with a variety of simple molecules, such as CO, H_2 and CH_3OH. In this way new carbonyl, hydridocarbonyl and hydrido complexes of iridium(I) and iridium(III) were obtained, and this paper gives a full account of the preparation and characterization of these compounds. In addition, a new route for the preparation of both pure isomers *fac*- and *mer*-$[(C_6H_5)_3P]_3IrH_3$ by reaction of $[(C_6H_5)_3P]_2\underline{Ir[P(C}_6H_4)(C_6H_5)_2]$ with hydrogen and methanol, respectively, is reported.

Results and discussion

We [1] first isolated $[(C_6H_5)_3P]_2\underline{Ir[P(C}_6H_4)(C_6H_5)_2]$ (I) by treating $[(C_6H_5)_3P]_3IrCl$ with an excess of the lithium derivative of C(2)-substituted dicarba-*closo*-

TABLE 1

ANALYTICAL AND IR DATA FOR THE PREPARED IRIDIUM COMPLEXES

Nr.	Compound	Color	M.p. (°C)[a]
I	$(Ph_3P)_2\underline{Ir[P(C}_6H_4)Ph_2]$	Red-orange	186—187
II	$(Ph_3P)\underline{Ir[P(C}_6H_4)Ph_2](CO)$	Yellow	234—236
III	$(Ph_3P)_2\underline{Ir[P(C}_6H_4)Ph_2](CO)$	Yellow	239—240
IV	$(Ph_3P)\underline{Ir[P(C}_6H_4)Ph_2](CO)_2$	White	148—150
V	$(Ph_3P)\underline{Ir(H_2)[P(C}_6H_4)Ph_2](CO)$	Pale-yellow	[b]
VI	*fac*-$(Ph_3P)_3IrH_3$	White	213—214
VII	$(Ph_3P)_2\underline{Ir(H_2)[P(C}_6H_4)Ph_2]$	White	161—163
VIII	*mer*-$(Ph_3P)_3IrH_3$	White	221—222

[a] All compounds melt with decomposition in a capillary tube sealed under vacuum. Uncorrected values. [b] Mixture of isomers Va (~85%) and Vb. [c] s, strong; m, medium; w, weak; (sh), shoulder; nm, not measured.

dodecaborane(12) in diethyl ether at 0—25° C (eq. 1).

$$[(C_6H_5)_3P]_3IrCl + \text{Li-carb} \rightarrow \underset{(I)}{[(C_6H_5)_3P]_2\underline{Ir[P(C}_6H_4)(C_6H_5)_2]} + LiCl + \text{H-carb} \quad (1)$$

$(\text{carb} = 2\text{-R-}1,2\text{-}B_{10}C_2H_{10}^-;\ R = CH_3,\ C_6H_5)$

Complex I is a red-orange crystalline material, stable in solution and in the solid state in an inert atmosphere. It behaves as nonelectrolyte at 25° C in CH_2Cl_2 solution. Its analytical data are reported in Table 1. The IR spectrum (Nujol mull) of I shows no bands in the region 2800—1600 cm^{-1}, ruling out the possibility the carborane group is bonded to the metal atom. The bands at 1565 and 1570 cm^{-1} attributed to the $\nu(CC)$ absorptions in the spectrum of $[(C_6H_5)_3P]_3$-IrCl are replaced by bands centered at 1558, 1570 and 1585 cm^{-1} in the spectrum of I. A strong band is also observed at 725 cm^{-1}, which is in the range characteristic of the C—H out-of-plane deformation for *ortho*-disubstituted aromatics [2]. The ^1H NMR spectrum of I exhibits only a complex multiplet centered at τ 3.10 ppm (in CH_2Cl_2 solution) due to the phenyl protons of the phosphine ligands.

Reactions of tris(triphenylphosphine)iridium(I) (I)

(a) Carbon monoxide. The complex $[(C_6H_5)_3P]_2\underline{Ir[P(C}_6H_4)(C_6H_5)_2]$ (I) reacts instantaneously with carbon monoxide in solution at room temperature

Analysis (Found (calcd.) (%))		ν(CO) (cm^{-1})		ν(IrH) ^{c} (cm^{-1})		Other bands ^{c} (cm^{-1}) Nujol
C	H	Nujol	CH_2Cl_2	Nujol	CH_2Cl_2	
66.05 (66.31)	4.74 (4.53)	—	—	—	—	1558m, 1570w, 1585m, 725s
59.80 (59.75)	4.07 (3.93)	1947s	1950s	—	—	1558w, 1570(sh) 1585m, 730s
65.54 (65.66)	4.32 (4.41)	1945s	1948s	—	—	1558w, 1570(sh) 1585m, 730s
58.47 (59.13)	3.38 (3.78)	1914s 1966s	1923s 1974s	—	—	1558w, 1570(sh) 1585m, 730s
59.33 (59.59)	4.13 (4.19)	1970s 1988w 2009(sh)	1974s 1998w	2114m 2054m	2090m	1562m, 1575w, 1589w, 730s
66.70 (66.04)	4.96 (4.92)	—	—	2100s	2088s	—
66.04 (66.17)	4.76 (4.73)	—	—	1742s	nm	1565m, 1570(sh), 1587w, 725s
65.77 (66.04)	4.73 (4.92)	—	—	2131m 1746s	2100m 1754s	—

and 1 atm. Depending on the experimental conditions, three carbonyl derivatives of iridium(I) can be obtained (complexes II—IV of Table 1). Thus, treatment of complex I with CO in CH_2Cl_2 solution at 25° C (1 atm) followed by recrystallization of the pale-yellow crude product under an inert atmosphere gives the yellow carbonyl $[(C_6H_5)_3P]\underline{Ir[P(C}_6H_4)(C_6H_5)_2](CO)$ (II). This complex appears to be stable in the solid state and in solution under an inert atmosphere. In agreement with the suggested formulation, the IR spectrum (Nujol mull) shows a strong band assignable to ν(CO) of a terminal carbonyl group at 1947 cm^{-1} and bands at 1558, 1570, 1585 and 730 cm^{-1}, which are characteristic of *ortho*-disubstituted aromatics. On the other hand, the yellow complex $[(C_6H_5)_3P]_2\underline{Ir[P(C}_6H_4)(C_6H_5)_2](CO)$ (III) is obtained in good yield from treatment of II with an excess of the free ligand triphenylphosphine in solution (eq. 2).

$$\underset{\text{(II)}}{[(C_6H_5)_3P]\underline{Ir[P(C}_6H_4)(C_6H_5)_2](CO)} + P(C_6H_5)_3 \rightleftharpoons \underset{\text{(III)}}{[(C_6H_5)_3P]_2\underline{Ir[P(C}_6H_4)(C_6H_5)_2](CO)} \qquad (2)$$

Complex III is stable in the solid state under an inert atmosphere, but in solution it undergoes extensive dissociation of one molecule of phosphine. Unfortunately, a study of the dissociation of III in solution by osmometric molecular weight determinations is not reliable because of its high air and moisture sensitivity. Its formulation was assigned on the analytical and infrared data (Table 1). The IR spectrum exhibits, other than the bands indicative of the presence of a disubstituted phenyl ring, a strong band at 1945 cm^{-1} due to $\nu(CO)$ of a terminal carbonyl group.

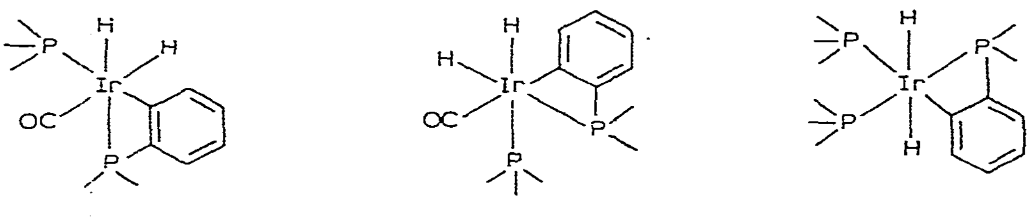
The white crystalline dicarbonyl derivative $[(C_6H_5)_3P]\underline{Ir[P(C}_6H_4)(C_6H_5)_2](CO)_2$ (IV), can be obtained on treating the complexes I or II with CO (1 atm) at 25°C in solution taking care to perform any subsequently purification step under a CO atmosphere. Recently, the crystal and molecular structure of the solvated complex $[(C_6H_5)_3P]\underline{Ir[P(C}_6H_4)(C_6H_5)_2](CO)_2 \cdot THF$ was reported, but characterization and the method of preparation were not described [3]. Complex IV is stable in the solid state under inert atmosphere but dissociation of one molecule of CO occurs in solution (eq. 3). This carbonylation is reversed on

$$\underset{(II)}{[(C_6H_5)_3P]\underline{Ir[P(C}_6H_4)(C_6H_5)_2](CO)} + CO \rightleftharpoons \underset{(IV)}{[(C_6H_5)_3P]\underline{Ir[P(C}_6H_4)(C_6H_5)_2](CO)_2} \quad (3)$$

flushing with dry argon. Thus, when a solution of II in CH_2Cl_2 is treated under a CO atmosphere, the colour rapidly changes from bright-yellow to pale-yellow. On sweeping with argon the solution regains its initial bright-yellow color, and resaturation with CO restores the pale-yellow color. The IR spectrum of IV is in agreement with the reported formulation, showing, in addition to the bands due to the phosphine ligands, two strong bands at 1914 and 1966 cm^{-1}, appropriate for stretching vibrations of terminal carbonyl groups.

Carbon monoxide insertion into the iridium—carbon bond was never observed in the course of these carbonylation reactions; this is in contrast to the behaviour shown by the corresponding internally metallated rhodium(I) complex [4].

The stable monocarbonyl complex II reacts quantitatively and irreversibly with hydrogen or deuterium giving a pale-yellow compound which was formulated as the dihydride or dideuteride $[(C_6H_5)_3P]\underline{Ir(H_2 \text{ or } D_2)[P(C}_6H_4)(C_6H_5)_2](CO)$ (V) (Table 1). However, the IR and ^1H NMR spectra indicate that the oxidative addition of hydrogen to complex II is not stereospecific, yielding a mixture of the stereoisomers Va and Vb (Fig. 1). The IR spectrum (Nujol mull) of the product formulated as V shows bands at 1562, 1575 and 1589 cm^{-1} due to $\nu(CC)$ and a band at 730 cm^{-1} assignable to C—H out-of-plane deformation for *ortho*-disubstituted aromatics, indicating that the iridium—carbonium bond of the exocycle $\underline{Ir—P—(C}_6H_4)$ is unaffected by the hydrogenation. This spectrum also exhibits two medium bands attributed to $\nu(IrH)$ at 2054 and 2114 cm^{-1}, indicating that the hydride ligands are mutually *cis*, and bands due to $\nu(CO)$ at 1970 (s), 1988 (w) and 2009 (sh) cm^{-1}. In CH_2Cl_2 solution the $\nu(CO)$ absorp-



(Va) (Vb) (VII)

Fig. 1.

tions occur at 1974 and 1998 cm^{-1}. This is consistent with a mixture of two stereoisomers resulting from *cis*-addition, and their formation was confirmed by NMR studies carried out both on the crude and on the recrystallized reaction product. Thus, the ^1H NMR spectrum of V in $CDCl_3$ exhibits, in addition to a multiplet due to the phenyl protons centered at τ 2.74 ppm, two doublets of doublets centered at τ 17.14 and 22.70 ppm and two doublets of doublets centered at τ 18.72 and 21.77 ppm, respectively. Each peak of these signals is further split into two lines by H—H coupling (J(HH) 1.8 Hz). The signals at τ 17.14 and 22.70 ppm are attributed to the hydride resonances of the isomer having the configuration Va.

While the doublet of doublets centered at low field (τ 17.14 ppm) is due to the hydride proton mutually *cis* to the both phosphine ligands (J(PH) 18.3 and 16.5 Hz), the resonance at τ 22.70 ppm is assignable to a hydride proton *trans* to one phosphine ligand ($J(PH_{trans})$ 141 Hz; $J(PH_{cis})$ 14.6 Hz). Once the phosphine and the hydride ligands in the octahedral isomer Va were shown to be both mutually *cis*, the remaining stereochemistry was confirmed by IR spectroscopy. Thus, the corresponding dideuteride complex was also prepared and an increase in $\nu(CO)$ of 35 cm^{-1} was observed in going from the hydride to the deuteride, indicating that CO is *trans* to a H ligand [5,6], providing further support for the configuration Va. On the other hand, the hydride resonances at τ 18.72 ppm ($J(PH_{cis})$ 14.5, $J(PH_{trans})$ 137.0) and at τ 21.77 ppm ($J(PH_{cis})$ 16.0, $J(PH_{trans})$ 139.0 Hz) together with the J(PH) values found are in agreement with the configuration Vb, in which the two hydride ligands are mutually in *cis* position and are both *trans* to the phosphine ligands. The relative intensities of these signals indicate that the isomers Va and Vb are formed in the course of hydrogenation of II in a molar ratio of ca. 6/1.

(b) Hydrogen. The complex I reacts instantaneously and irreversibly with hydrogen. The reaction occurs with cleavage of the iridium—carbon bond and appears to be stereospecific, yielding quantitatively white crystals of the pure isomer *fac*-$[(C_6H_5)_3P]_3IrH_3$ (VI). The IR and ^1H NMR spectra are in agreement with the suggested configuration. The ^1H (hydride) NMR pattern consists of a complex centro-symmetrical multiplet at τ 22.23 ppm (in $CDCl_3$) interpretable in terms of a non-fluxional structure, and is similar to that reported for the corresponding diethylphenylphosphino derivative [7].

(c) Methanol. The tris(triphenylphosphine)iridium(I) complex (I) reacts irreversibly with methanol at room temperature, giving initially white crystals of the internally metallated dihydro derivative $[(C_6H_5)_3P]_2\underline{Ir(H_2)[P(C}_6H_4)(C_6H_5)_2]$ (VII) and formaldehyde. On further treatment with methanol, complex VII undergoes cleavage of the "internal" iridium—carbon bond to give the trihydride *mer*-$[(C_6H_5)_3P]_3IrH_3$ (VIII) (eq. 4).

$$\begin{tikzcd} \underset{\text{(I)}}{[(C_6H_5)_3P]_2\underline{Ir|P(C}_6H_4)(C_6H_5)_2]} \arrow[r, "CH_3OH", "-H_2CO"'] & \underset{\text{(VII)}}{[(C_6H_5)_3P]_2\underline{Ir(H_2)[P(C}_6H_4)(C_6H_5)_2]} \arrow[d, "CH_3OH", "-H_2CO"'] \\ & mer\text{-}[(C_6H_5)_3P]_3IrH_3 \text{ (VIII)} \end{tikzcd} \quad (4)$$

Iridium-methoxides are probably reaction intermediates, and a hydride ion is then probably transferred to the metal from the coordinated methoxide, giving the hydrido derivatives found and formaldehyde [8]. The complexes VII and VIII are white crystalline light-sensitive materials, and their configurations were assigned on the basis of IR and ^{1}H NMR data. The infrared spectrum (Nujol mull) of VII exhibits in addition to bands at 1565, 1570, 1587 and 725 cm^{-1} which provide evidence for an *ortho*-disubstitution of one of the phenyl groups of the phosphine ligands a strong band centered at 1742 cm^{-1} due to ν(IrH) absorptions, which suggests that the hydrogens are mutually *trans*. This configuration is confirmed by the ^{1}H (hydride) NMR spectrum which shows a 1/3/3/1 quartet centered at τ 17.77 ppm (J(PH) 15.0 Hz). This pattern and the

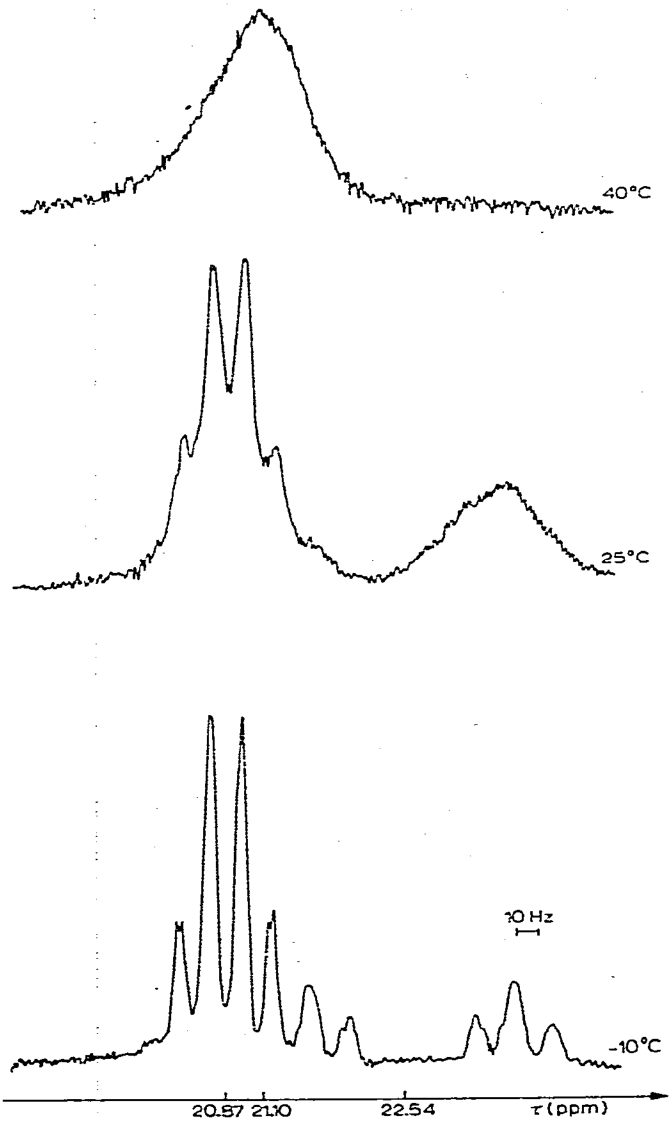


Fig. 2. ^{1}H NMR spectrum (60 MHz) of *mer*-$(Ph_3P)_3IrH_3$ in $CDCl_3$ solution at three different temperatures.

low J(PH) values are in agreement with a structure in which two hydride ligands are in mutual *trans* positions and are both *cis* to the phosphine ligands.

The ^{1}H(hydride) NMR spectra of *mer*-[(C$_6$H$_5$)$_3$P]$_3$IrH$_3$ (VIII) recorded in CDCl$_3$ between −10 and 40°C are shown in Fig. 2. Previously, the ^{1}H(hydride) NMR pattern of this isomer was reported to be a symmetrical quartet [9]. We now find that the NMR spectrum of this compound exhibits a much more complex pattern, similar to those reported for the corresponding trihydrides *mer*-L$_3$IrH$_3$, where L = PEt$_2$Ph or PEt$_3$ [7]. Moreover, the NMR spectrum of VIII appears to be temperature dependent. Thus, at −10°C, the spectrum is sharp showing at τ 20.87 ppm a quartet (each peak is further split into two lines by H—H coupling, J(HH) 2.7 Hz) due to the two equivalent hydrogens which are in mutual *trans* position and are both *cis* to three phosphine ligands (J(PH) 15.8 Hz) and a doublet of triplets centered at τ 22.54 ppm. The latter resonance is assignable to the hydrogen *trans* to one phosphorus nucleus (J(PH) 113.5 Hz) and *cis* to two equivalent ^{31}P nuclei (J(PH) 20.1 Hz). On raising the temperature to 40°C the hydride spectrum broadens and collapses reversibly to give only one large signal centered at τ 21.10 ppm. The observed spectral behaviour is indicative of either an inter- or intra-molecular exchange process, but further mechanistic information is not available because the low solubility of VIII limits the concentration range which can be used in the NMR experiments.

Experimental

Reagent grade solvents were further purified by standard methods and were dried and degassed before use. The lithiocarboranes were prepared by treating the carboranes with butyllithium [10]. (Ph$_3$P)$_3$IrCl was prepared by a published method [11]. All the reactions involving iridium(I) complexes were carried out under argon. The ^{1}H NMR spectra were recorded at ca. 27°C and at 60 MHz in CDCl$_3$ and 90 MHz in CH$_2$Cl$_2$ with the WP-60 FTNMR and HFX-90 Bruker spectrometers, respectively. τ-Values ± 0.02 ppm; J(PH)-values ± 0.5 Hz; J(HH)-values ± 0.1 Hz. ^{1}H shifts are relative to internal TMS (τ 10.00 ppm). Infrared spectra were obtained with a Perkin—Elmer Model 457 and calibrated against polystyrene film. Molecular weight measurements were carried out with a Mechrolab 301A osmometer.

(Ph$_3$P)$_2$$\underline{\text{Ir}[\text{P}(\text{C}}$$_6H_4$)Ph$_2$] (I)

A solution of 2.7 mmol of 1-Li-2-R-1,2-B$_{10}$C$_2$H$_{10}$ (R = CH$_3$, C$_6$H$_5$) in 20 ml of anhydrous diethyl ether was slowly added to a suspension of 1 g (0.98 mmol) of (Ph$_3$P)$_3$IrCl in 20 ml of anhydrous diethyl ether at room temperature. The mixture was stirred for 2 h, and the orange-red product so formed was filtered and washed with diethyl ether and dried in vacuo. The crude product was recrystallized from CH$_2$Cl$_2$/n-hexane. The yield of pure orange-red crystals was 0.75 g (80%); m.p. 186—187°C (dec.).

(Ph$_3$P)$\underline{\text{Ir}[\text{P}(\text{C}}$$_6H_4$)Ph$_2$](CO) (II)

A suspension of 0.6 g (0.62 mmol) of (Ph$_3$P)$_2$$\underline{\text{Ir}[\text{P}(\text{C}}$$_6H_4$)Ph$_2$] in 10 ml of dry benzene was treated at 25°C with carbon monoxide at 1 atm. The red colour rapidly turned to yellow and a homogeneous solution was formed. The CO atmosphere was then replaced by an argon atmosphere and the solution was further stirred for 30 min. A microcrystalline yellow precipitate was thus formed which, after addition of 15 ml of n-hexane, was separated by filtration, washed with n-hexane and dried. The product was purified by recrystallization under argon from CH_2Cl_2/n-hexane. The yield of pure bright-yellow crystals was 0.4 g (85%), m.p. 234—236° C (dec.).

$(Ph_3P)_2\underline{Ir[P(C}_6H_4)Ph_2](CO)$ *(III)*

This complex was prepared as above by treatment of a solution of 0.3 g (0.31 mmol) of $(Ph_3P)_2\underline{Ir[P(C}_6H_4)Ph_2]$ in 10 ml of dry benzene with carbon monoxide at 1 atm. Purification of the fine precipitate by recrystallization from CH_2Cl_2/n-hexane in the presence of a large excess of the free triphenylphosphine ligand afforded pure pale-yellow crystals; yield 0.26 g (85%) of III, m.p. 239—240° C (dec.).

$(Ph_3P)\underline{Ir[P(C}_6H_4)Ph_2](CO)_2$ *(IV)*

A stirred solution of 0.3 g (0.29 mmol) of $(Ph_3P)\underline{Ir[P(C}_6H_4)Ph_2](CO)$ in 10 ml of anhydrous benzene was treated at 25° C with carbon monoxide at 1 atm. The bright-yellow solution rapidly turned pale-yellow. Addition of 15 ml of n-hexane caused separation of a white product which was collected by filtration under CO atmosphere and washed with n-hexane. The crude product was recrystallized under CO atmosphere from CH_2Cl_2/n-hexane. The yield of white crystals of the pure dicarbonyliridium(I) complex IV was essentially quantitative, m.p. 148—150° C (dec.).

Absorption of CO by $(Ph_3P)_2\underline{Ir[P(C}_6H_4)Ph_2]$

In a standard gas absorption apparatus 10 ml of dry benzene was saturated with carbon monoxide at 1 atm pressure and 25° C. Then, the iridium(I) complex I (~0.1 g) was tipped in and the additional carbon monoxide uptake at 25° C was measured. The uptake stopped after 3 min and the absorption was found to correspond to 1.24 mol of CO/mol of complex I (62% of the calculated value for the dicarbonyl adduct). The isolated product was identified as complex IV, m.p. 148—150° C (dec.).

$(Ph_3P)\underline{IrH_2[P(C}_6H_4)Ph_2](CO)$ *(V)*

Complex II (0.5 g; 0.67 mmol) was dissolved in CH_2Cl_2 (10 ml) under argon and then hydrogen was bubbled through the stirred solution at 25° C for 3 h. The bright-yellow solution turned pale-yellow. Addition of n-hexane caused separation of a pale-yellow solid, which was filtered off and recrystallized from CH_2Cl_2/n-hexane under hydrogen. The yield of pale-yellow crystals (mixture of isomers Va and Vb) was 0.4 g (81%). The corresponding dideuteride was prepared similarly using deuterium. Anal. Found: C, 58.13; H, 4.06. $C_{37}H_{29}D_2P_2O$-Ir calcd.: C, 59.43; H, 4.12%. A band due to ν(CO) was seen at 2005s cm^{-1} in Nujol.

fac-$(Ph_3P)_3IrH_3$ *(VI)*

Complex I (0.3 g; 0.31 mmol) was dissolved in CH_2Cl_2 (10 ml) under argon and then hydrogen was bubbled through the solution at room temperature for

5 min. The initially red-orange solution rapidly turned colourless. Addition of n-hexane (10 ml) precipitated a white solid, which was recrystallized from CH_2Cl_2/n-hexane to give a quantitative yield of white crystals of *fac*-$(Ph_3P)_3IrH_3$ (VI) m.p. 213—214° C (dec.).

$(Ph_3P)_2Ir(H_2)[P(C_6H_4)Ph_2]$ (VII)

A stirred suspension of 0.5 g (0.51 mmol) of I in 5 ml of CH_2Cl_2 was treated with 7 ml of pure deoxygenated methanol at room temperature. After 3 h, 10 ml of n-hexane was added and the precipitate was separated by filtration and washed with n-hexane. The crude product was recrystallized from CH_2Cl_2/n-hexane to give white crystals of the dihydride VII (0.4 g, 80%), m.p. 161—163° C (dec.).

Formaldehyde was also identified as a reaction product by gas-chromatographic analysis of the solution.

mer-$(Ph_3P)_3IrH_3$ (VIII)

(a) A solution of 0.5 g (0.51 mmol) of I in 10 ml of CH_2Cl_2 was treated with 7 ml of pure deoxygenated methanol at room temperature. The mixture was stirred for 24 h and the white crystalline product formed was separated, washed with methanol and was further purified by recrystallization from CH_2Cl_2/CH_3OH. Pure white crystals, yield 80% of *mer*-$(Ph_3P)_3IrH_3$ (VIII) (m.p. 221—222° C (dec.)) were obtained.

(b) Complex VIII was also obtained by treatment of 0.4 g (0.41 mmol) of VII in 10 ml of CH_2Cl_2 with 10 ml of CH_3OH at room temperature. The mixture was stirred for 24 h and the precipitate was purified as described above. The yield of pure *mer*-trihydride (VIII) was 75% m.p. 221—222° C (dec.). GLC analysis revealed that the methanol had been dehydrogenated to formaldehyde in the course of the reaction.

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References

1 B. Longato, F. Morandini and S. Bresadola, J. Organometal. Chem., 88 (1975) C7.
2 L.S. Bellamy, The Infrared Spectra of Complex Molecules, Methuen, London, 1958, p. 77.
3 G. Perego, G. Del Piero, M. Cesari, M.G. Clerici and E. Perrotti, J. Organometal. Chem., 54 (1973) C51.
4 W. Keim, J. Organometal. Chem., 19 (1969) 161.
5 A.J. Deeming and B.L. Shaw, J. Chem. Soc. A, (1969) 1128.
6 B. Longato, F. Morandini and S. Bresadola, Inorg. Chem., 15 (1976) 650.
7 B.E. Mann, C. Master and B.L. Shaw, J. Inorg. Nucl. Chem., 33 (1971) 2195.
8 J. Chatt and B.L. Shaw, J. Chem. Soc., (1962) 5075.
9 J. Chatt, R.S. Coffey and B.L. Shaw, J. Chem. Soc., (1965) 7391.
10 P.M. Garrett, J.C. Smart and M.F. Hawthorne, J. Amer. Chem. Soc., 91 (1969) 4707.
11 M.A. Bennett and D.L. Milner, J. Amer. Chem. Soc., 91 (1969) 6983.