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SOME IRIDIUM(I) AND IRIDIUM(III) COMPLEXES WITH THE TRIPOD-LIKE LIGAND $CH_3C(CH_2PPh_2)_3$ (triphos) AND THE X-RAY CRYSTAL STRUCTURE OF [IrCl(CO)(triphos)] *

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Summary

The compound [IrCl(CO)(triphos)] (**1**), has been reinvestigated and its X-ray crystal structure is reported. The crystals are orthorhombic, space group *Pbca*, with a 18.941(6), b 22.193(8), c 17.501(7) Å, $Z = 8$. The structure was solved by the heavy atom method and refined by full-matrix least-squares to the conventional R factor value of 0.074 for 6462 reflections. The metal atom coordination is trigonal bipyramidal, with the three phosphorus atoms occupying one axial and two equatorial positions. The other equatorial position is occupied by CO while Cl is coordinated axially.

Compound **1** readily undergoes a series of oxidative-addition reactions with H_2, HCl and Cl_2, giving $[IrH_2(CO)(triphos)]^+$ (**4**) $[IrHCl(CO)(triphos)]^+$ (**3**), and $[IrCl_3(triphos)]$ (**5**), respectively. Compounds [IrH(CO)(triphos)] (**2**) and $[IrH_nCl_{3-n}(triphos)]$ ($n = 1, 2, 3$) have also been obtained from **1** and **5**, respectively, by treating them with a variety of hydride sources.

Introduction

The ligand $CH_3C(CH_2PPh_2)_3$ (triphos) has produced a rich and interesting coordination chemistry [1]. Thus fragments such as "P_3" have been stabilized in complexes containing triphos [2], and rhodium(III) has been shown to form stable trihydrides such as $[RhH_3(triphos)]$ [3]. Furthermore, it has been shown that this trihydride readily forms unusual heterometallic hydrido-bridged complexes, e.g., $[Ag_3Rh_3H_9(triphos)_3]^{3+}$ [4].

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* Dedicated to Professor Lamberto Malatesta in recognition of his important contributions to organometallic chemistry.

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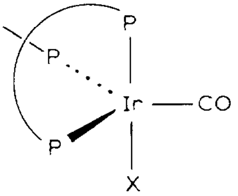
As it has been reported [5] that iridium readily forms complexes containing triphos, these were re-examined in order to compare their properties with those of the corresponding rhodium compounds.

Results and discussion

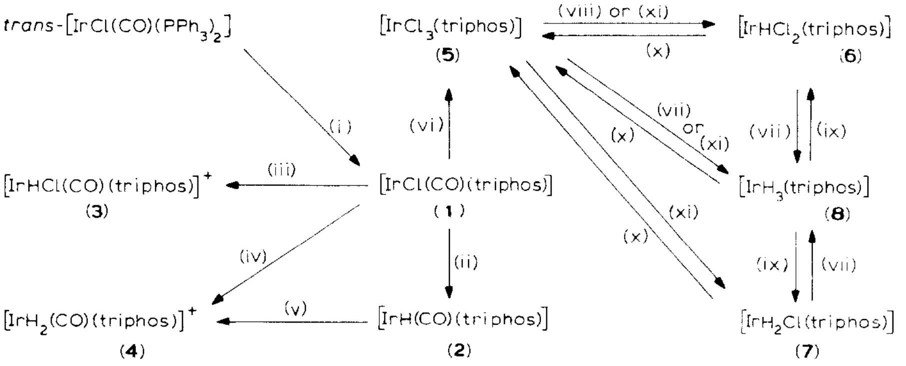
Synthetic studies

The reactions of the triphos complexes which were investigated are summarized in Scheme 1.

The chlorocarbonyl complex [IrCl(CO)(triphos)] (**1**), was prepared by the method of Siegl et al. [5], and its X-ray crystal structure (vide infra) shows that it has the coordination geometry shown schematically below. It reacts with $[NMe_4][BH_4]$ in CH_3CN/H_2O to give the corresponding hydride [IrH(CO)(triphos)] (**2**), in good yield. This yellow compound is very air sensitive and the solid decomposes spontaneously during several days even when kept in an inert atmosphere. The trigonal bipyramidal structure **2** is assigned to this compound on the basis of its low temperature ^1H and ^{31}P NMR spectra (vide infra).



(**1**; X = Cl;
2; X = H)



SCHEME 1. Syntheses and reactions of iridium triphos complexes. (i) triphos/benzene; see [5]. (ii) $[NMe_4][BH_4]/CH_3CN/H_2O$. (iii) Isolated as its $[PF_6]$ salt. HCl/CH_2Cl_2 or CF_3SO_3H/CH_2Cl_2 followed by $NH_4[PF_6]/MeOH$. (iv) Isolated as its $[PF_6]$ salt. $H_2/MeOH$ followed by $NH_4[PF_6]/MeOH$. (v) HCl/CH_2Cl_2 or $CF_3SO_3H/MeOH$ followed by $NH_4[PF_6]/MeOH$. (vi) Cl_2/CH_2Cl_2, see [5]. (vii) $LiAlH_4/THF$. (viii) $H_2/MeOH$ (this reaction is incomplete). (ix) HCl/CH_2Cl_2 (a mixture of **7** and **6** is produced). (x) Cl_2/CH_2Cl_2. (xi) $Na[BH_4]/THF$ (mixtures of **7** and **6** or **7** and **8** are obtained depending on reaction time).

The chlorocarbonyl complex **1** also reacts quantitatively with HCl or CF_3SO_3H in CH_2Cl_2 giving the cation $[IrHCl(CO)(triphos)]^+$ (**3**) which was isolated as its $[PF_6]^-$ salt.

A methanolic solution of the chlorocarbonyl complex **1** reacts with H_2 to give $[IrH_2(CO)(triphos)]^+$, which was isolated as its $[PF_6]^-$ salt. This cation can also be obtained by adding a methanolic solution of CF_3SO_3H to [IrH(CO)(triphos)] (**2**). However, when HCl is used as a proton source one obtains **4**, contaminated with significant amounts of $[IrH_2Cl(triphos)]$ (**7**) and $[IrCl_3(triphos)]$ (**5**).

The trichloro complex $[IrCl_3(triphos)]$ (**5**), which is easily prepared by the method of Siegl et al. [5], reacts with a variety of hydride sources to give several products. Thus, its reaction with H_2 in methanol gives $[IrHCl_2(triphos)]$ (**6**). Addition of NaOMe to the above solution leads to the formation of $[IrH_2Cl(triphos)]$ (**7**) and $[IrH_3(triphos)]$ (**8**).

The observation that the trichloro-complex, **5**, suspended in methanol, reacts with molecular hydrogen at room temperature to give the mono-hydrido complex, **6**, is indicative of the formation of a solvento complex followed by heterolytic H_2-activation. The conventional pathway through alkoxide formation followed by β-H-elimination [6] can be excluded, as the starting material is recovered unchanged if N_2 is used instead of H_2.

The nature of the product obtained from the reaction of the trichloro complex, **5**, with $Na[BH_4]$ in THF depends on the reaction time. After ca. 30 min the mixture contains unreacted starting material and the monohydride species $[IrHCl_2(triphos)]$ (**6**), while after ca. 5 h both **6** and the dihydride $[IrH_2Cl(triphos)]$ (**7**), are present. Longer reaction times lead to the formation of a mixture of di-, **7**, and trihydride $[IrH_3(triphos)]$ (**8**), but the latter is not formed quantitatively. However, pure **8** can be prepared by treating the trichloro-complex, **5**, with $Li[AlH_4]$ in THF.

The reaction of trihydride **8** with equimolecular amounts of HCl in CH_2Cl_2 gives a mixture of products, i.e., **5**, **6**, **7** and **8**. Thus, because of the above mentioned synthetic difficulties the mixed hydridochloro complex **7** could not be obtained pure, but it was characterized in solution by ^1H and ^{31}P NMR spectroscopy (vide infra).

^{31}P NMR spectra

The relevant parameters are listed in Table 1.

The room temperature spectra of the iridium(I) species, **1** and **2**, appear as singlets at -16.1 and -13.5 ppm, respectively, indicating rapid equilibration of the chemical environment of these atoms. However, a spectrum corresponding to that expected for the static structure is obtained upon cooling a solution of **1** to ca. 170 K; two signals at $+1.1$ and -21.2 ppm are then seen, with integrals in the ratio 2/1. These remain broad even at lower temperatures and thus no P,P-coupling can be observed.

In the case of the hydrido-complex **2** a spectrum corresponding to that of the static structure is observed more easily. Thus two signals (a broad signal at -9.9 and a sharper signal at -15.8 ppm of relative intensity 1/2) are observable at 193 K, while a triplet at -10.1 and a doublet at -15.8 ppm are clearly recognized at 163 K. The more dynamic nature of the P-atom in *trans*-position to the H-atom is expected on the basis of the high *trans*-effect of the latter ligand [7].

The spectra of the six-coordinate complexes $[IrX_3(triphos)]$ (X = Cl, **5**; X = H, **8**)

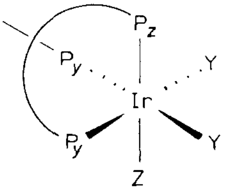
TABLE 1

NMR DATA FOR IRIDIUM TRIPHOS COMPLEXES

	^1H NMR [a]			^{31}P NMR [b]
	$\delta(CH_2)$(ppm) [c]	$\delta(CH_3)$(ppm) [d]	δ(Ir–H)(ppm)	δ(P)(ppm)
triphos	2.55	1.05	–	−26
[IrCl(CO)(triphos)]	2.44	1.52	–	−16.1 [e]
[IrH(CO)(triphos)]	2.22	1.45	−10.18 [f]	−13.5 [e,g]
[IrHCl(CO)(triphos)][PF_6] [h]	3.35–2.47 [i]	1.96	−8.35	−38.5/−27.0/−10.4 [j]
[IrH_2(CO)(triphos)][PF_6] [h]	2.61	1.85	−10.15	−21.7/−11.9 [k]
[$IrCl_3$(triphos)]	2.67	1.53	–	−35.2
[$IrHCl_2$(triphos)]	(1)	1.56	−7.9	−44.2/−13.3 [k]
[IrH_2Cl(triphos)]	2.40	1.49	−8.3 [m]	−23.8/+1.8 [k]
[IrH_3(triphos)]	2.22	1.45	−10.6 [m]	−8.0

[a] Unless otherwise specified the spectra were measured in CD_2Cl_2. [b] Measured in CH_2Cl_2 using an acetone-d_6 capillary tube. [c] Unless otherwise specified these resonances appear as complex spin systems with virtual couplings; therefore only the centers of the resonances are listed. [d] These resonances appear as quartets with ^4J(H, P) values in the range 2.5–3 Hz. [e] Low temperature spectrum measured in $CD_2Cl_2/CH_2Cl_2/CHCl_3$ 5/2/3 see text. [f] Low temperature spectrum measured in $CD_2Cl_2/CDCl_3$ 7/3 see text and Fig. 1. [g] The signal appears at room temperature as a quartet with a coupling constant of 20.7 Hz. [h] Measured in $CDCl_3$. [i] Broad multiplet; see text. [j] The signal at −27.0 ppm is tentatively assigned to the phosphorus *trans* to chloride on the basis of the magnitude of the *cis* effect of chloride in complexes **6** and **7**. [k] The resonances for the phosphorus atoms *trans* to the hydride could be assigned to the numbers first listed on the basis of hydride coupled off-resonance ^{31}P NMR spectra. [l] The CH_2 groups are not equivalent. One group appears as a doublet at 2.61 ppm with ^2J(H, P) 8 Hz. The other two groups are equivalent but show inequivalent protons. The δ values of the two CH_2 protons are 2.42 and 2.54 ppm with ^2J(H, H) 14 Hz. [m] Higher order spectrum; see text.

show singlets at −35.2 and −8.0 ppm. The spectra of [$IrHCl_2$(triphos)] (**6**) and [IrH_2Cl(triphos)] (**7**) can be assigned on the basis of an AX_2 spin-system, i.e., the P_y-atoms appear as doublet and the P_z-atoms as triplets. However, in **6** the doublet appears at lower field than the triplet, while in **7** the converse is the case.



(**6**: Y = Cl, Z = H;
7: Y = H, Z = Cl)

The spectrum of [IrH_2(CO)(triphos)]$^+$ (**4**) is also of the above type, the doublet appearing at higher field than the triplet. It is noteworthy that the values of the ^2J(P, P) coupling constants in this complex (27 Hz) are significantly larger than those in **6** and **7** (10 Hz).

The spectrum of [IrHCl(CO)(triphos)]$^+$ (**3**) is assignable on the basis of an AMX spin-system [8] with three non-equivalent phosphorus atoms with J(A, M) 25, J(A, X) 10 and J(M, X) 26 Hz.

^1H NMR spectra

The relevant data are summarized in Table 1.

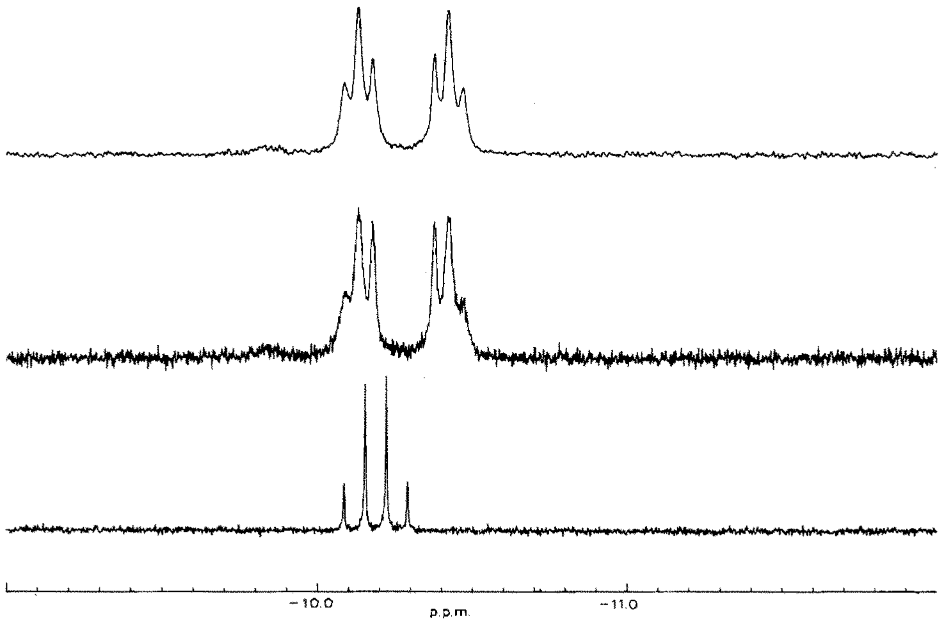


Fig. 1. The temperature-dependence of the ^{1}H NMR spectrum of [IrH(CO)(triphos)] (**2**) the temperatures being 298, 183 and 173 K, respectively.

Hydride region. The hydride signal of [IrH(CO)(triphos)] (**2**) at room temperature appears as a quartet (^2J(P, H) 20.7 Hz), as expected from the dynamic behaviour of this five-coordinate species. The low-temperature spectrum 173 K (see Fig. 1) appears as a doublet of triplets centered at −10.28 ppm. The two ^2J(P, H) coupling constants are 88 and 14 Hz. This spectrum is consistent with a trigonal bipyramidal structure in which CO occupies an equatorial and H and axial position, as predicted by Rossi and Hoffmann [9] on the basis of the σ-donor and π-acceptor capacities of these ligands. The large value of ^2J(P, H) for H *trans* to P is attributable to the high *trans*-geometry of these spins [10].

The spectrum of [IrHCl$_2$(triphos)] (**6**) shows a doublet of triplets centered at −7.9 ppm, and is first-order ^1J(H, P) 187.5 and 9.8 Hz *trans* and *cis* respectively.

The spectrum of [IrH$_2$Cl(triphos)] (**7**) can be simulated as the X-part of an AA′MXX′ spin-system using the following parameters: $\delta(\mathrm{H_X})$ $\delta(\mathrm{H_{X'}})$ −8.3 ppm; $^2J(\mathrm{P_A}, \mathrm{H_X}) = {}^2J(\mathrm{P_{A'}}, \mathrm{H_{X'}}) = 164$ Hz; $^2J(\mathrm{P_{A'}}, \mathrm{H_X}) = {}^2J(\mathrm{P_A}, \mathrm{H_{X'}}) = -10$ Hz; $^2J(\mathrm{P_M}, \mathrm{H_X}) = {}^2J(\mathrm{P_M}, \mathrm{H_{X'}}) = 13$ Hz; $^2J(\mathrm{H_X}, \mathrm{H_{X'}}) = 5$ Hz; $^2J(\mathrm{P_A}, \mathrm{P_{A'}}) = {}^2J(\mathrm{P_A}, \mathrm{P_M}) = {}^2J(\mathrm{P_{A'}}, \mathrm{P_M}) = 10$ Hz. However, the spectrum must be affected by other couplings, e.g., those of the CH$_2$-ligand protons, as the line-widths in the experimental spectrum are larger than those in the simulation.

The spectrum of the dihydride **4** is similar to that of dihydride **7**, but in this case no simulation studies were carried out. The signals are centered at ca. −10.15 ppm and the $^2J(\mathrm{P, H})_{trans}$ coupling constant is estimated to be ca. 110 Hz.

The spectrum of **8** can be simulated as the X-part of an AA′A″XX′X″ spin system using the following parameters: δ(H) −10.63 ppm; $^2J(\mathrm{P, H})_{trans}$ 119.5 Hz; $^2J(\mathrm{P, H})_{cis}$ −12.0 Hz; ^2J(H, H) 6 Hz and ^2J(P, P) −5.5 Hz. A similar spectrum and its simulation have been reported by Jesson [11] for *fac*-[IrH$_3$(PEt$_2$Ph)$_3$].

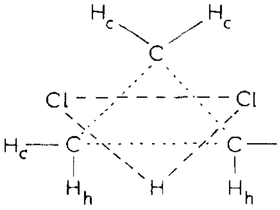
The spectrum of [IrHCl(CO)(triphos)] (**3**) appears as a doublet of triplets centered at −8.35 ppm with the coupling constants $^2J(\mathrm{P,H})_{trans}$ 134.5 Hz and $^2J(\mathrm{P,H})_{cis}$ 10 Hz.

Organic ligand. The methyl group invariably appears as a quartet since it is coupled to the three phosphorus atoms. The values of J(P, H) are in the range 2.5–3 Hz. The signals due to the phenyl groups appear as broad multiplets and will not be discussed further.

The spectra arising from the methylene groups are complex because of the occurrence of "virtual coupling" as normally found for *trans* complexes of phosphines with methyl and ethyl substituents [12]. This type of coupling has also been reported in complexes of rhodium and iridium with methyl- and ethyl-substituted phosphines [13]. Therefore, the CH_2 resonances of only two complexes will be discussed in detail, viz., those of **6** and **3**.

The spectrum of [IrHCl$_2$(triphos)] (**6**) shows the presence of non-equivalent methylene groups. One of them appears as a doublet centered at 2.61 ppm with a ^2J(H, P) coupling of 8 Hz. The other two CH_2 units are equivalent, but each of them shows inequivalent protons with δ-values of 2.42 and 2.54 respectively with a value of the geminal coupling ^2J(H, H) 14 Hz. Each of these doublets is further split into a doublet by phosphorus with ^2J(P, H) 8Hz. This assignment has been confirmed by heteronuclear ^{31}P decoupling.

This pattern is expected on the basis of the structural scheme **A**.



(A)

A similar pattern of resonances is observed in the spectrum of [IrHCl(CO)(triphos)]$^+$ (**3**). However, the multiplet observed between 2.47 and 3.35 ppm was not analysed by heteronuclear decoupling.

IR spectra

The IR spectra of triphos complexes have been extensively discussed by Siegl et al. [5] and by Davis and Fergusson [14]. Only some characteristic bands will be mentioned here.

The CO-stretch in [IrH(CO)(triphos)] (**2**) (1870 cm^{-1}) is in accordance with the low values usually found in five-coordinate complexes [5,15]. As expected, the CO-stretching vibrations of the cationic complexes **3** and **4** occur at higher frequencies, 2085 and 2050 cm^{-1}, respectively.

The Ir–H stretches appear over a wide frequency range and show the following trends: (a) the iridium(I) complex [IrH(CO)(triphos)] (**2**) shows a lower stretching vibration (2040 cm^{-1} with a shoulder at 2065 cm^{-1}) than the iridium(III) complexes, with the exception of the trihydride, **8**, (2020 and 2004 cm^{-1}); (b) the values of ν(Ir–H) increase with an increase in the number of coordinated chloride ligands;

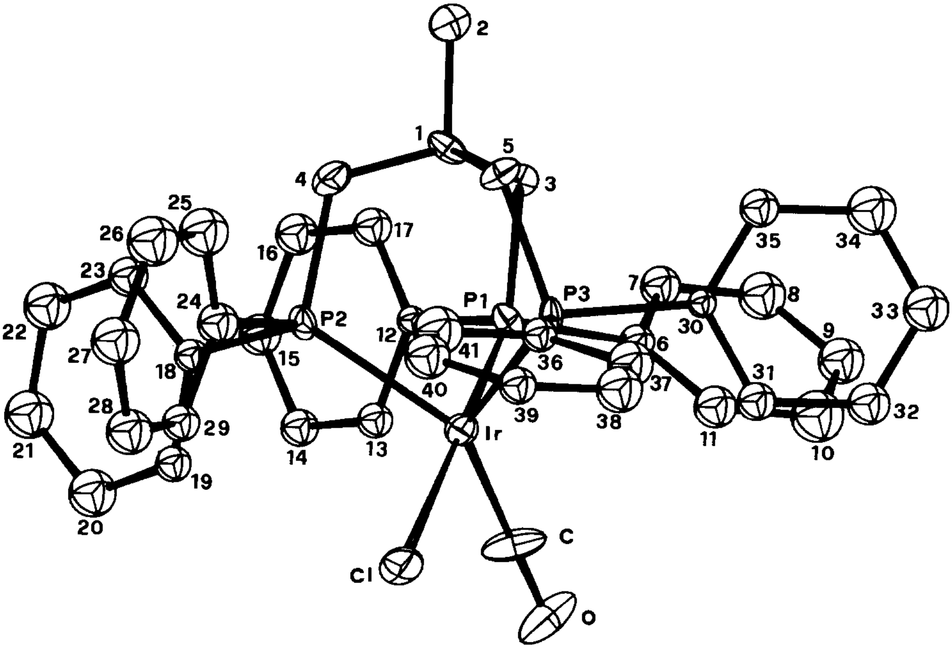


Fig. 2. Perspective view of the complex [IrCl(CO)(triphos)] (**1**). The ellipsoids represent 30% probability.

(c) the cationic complexes $[IrH_2(CO)(triphos)]^+$ (**4**) and $[IrHCl(CO)(triphos)]^+$ (**3**) are found at high frequencies (2085 and 2125 cm^{-1} respectively).

Crystal structure

The crystal structure consists of discrete molecules of the complex [IrCl(CO)(triphos)] (**1**). Perspective views of the complex are shown in Fig. 2 and 3. Table 2 lists a selection of intramolecular distances and angles with their standard deviations.

The coordination geometry at the iridium atom is trigonal bipyramidal with the axial sites occupied by one phosphorus atom of triphos, P(1), and Cl, while the three equatorial positions are taken up by the other two phosphorus atoms, P(2), P(3) and by the carbon atom of CO. The iridium atom is coplanar with the atoms in the equatorial coordination plane, i.e., P(2), P(3) and C, and there is no distortion towards a square pyramidal geometry.

Angles within the coordination sphere are somewhat distorted from the idealized D_{3h} symmetry. Thus the angles involving the chlorine atom (Cl–Ir–C 86.0(6)°, Cl–Ir–P(2) 95.2(1)°, Cl–Ir–P(3) 97.2(2)°, with Cl–Ir–P(1) 172.2(2)° are indicative of strong steric interactions between the halogen and the triphos ligand relative to the halogen–carbonyl interactions. On the other hand, the angles from the axial P(1) to the equatorial atoms are close to the ideal values (P(1)–Ir–P(3) 90.5(1)°, P(1)–Ir–C 88.3(6)°) except P(1)–Ir–P(2), which is unusually small (85.7(1)°) for a coordination angle of the triphos ligand [16–18]. This brings P(1) to a closer distance to P(2) (P(1)–P(2) 3.15 Å, P(1)–P(3) 3.29 Å, P(2)–P(3) 3.38 Å). Angular distorsions within the trigonal plane are significantly greater, with the P(2)–Ir–C angle of 130.5(8)°, the P(3)–Ir–C angle of 138.8(8)° and the P(2)–Ir–P(3) angle of 90.3(1)°. The small

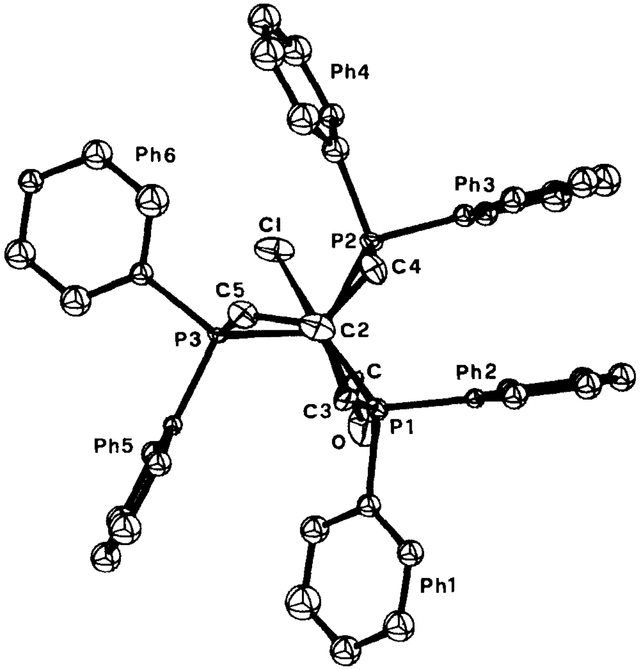


Fig. 3. Perspective view of the complex [IrCl(CO)(triphos)] (**1**), along the pseudo C_3 axis. The ellipsoids represent 30% probability.

P–Ir–P angle reflects the spanning limitations of the triphos ligand.

The Ir–CO bond length (1.86(4) Å) falls within the range 1.81–2.08 Å observed for second and third row transition-metal carbonyls [19–21]. Also the C–O bond distance (1.18(2) Å) shows the expected value [19–21]. The Ir–Cl bond length (2.468(5) Å) is about 0.07 Å longer than those generally found in other five-coordinated iridium compounds [15,21]. The two equatorial Ir–P bond lengths are equivalent (2.383(4) and 2.378(4) Å) and are similar to those found in other phosphine complexes. On the other hand, the axial Ir–P is significantly shorter than the other two (2.248(4) Å) and from those generally observed [22].

TABLE 2

SELECTED BOND LENGTHS (Å) AND ANGLES (°)

Ir–P(1)	2.248(4)	P(1)–Ir–P(2)	85.7(1)
Ir–P(2)	2.383(4)	P(1)–Ir–P(3)	90.5(1)
Ir–P(3)	2.378(4)	P(1)–Ir–Cl	172.2(2)
Ir–Cl	2.468(5)	P(1)–Ir–C	88.6(3)
Ir–C	1.863(16)	P(2)–Ir–P(3)	90.3(1)
C–O	1.177(23)	P(2)–Ir–Cl	95.2(1)
		P(2)–Ir–C	138.8(5)
		P(3)–Ir–Cl	97.2(2)
		P(3)–Ir–C	130.4(5)
		Cl–Ir–C	86.0(6)
		Ir–C–O	178.6(14)

Dimensions in the triphos ligand are normal, with small deviations from the ideal geometry, as is generally found in triphos complexes [16–18]. The angles at the phosphorus atoms can be divided in four sets: the Ir–P–C_{aryl} angles with an average of 188.0°, the Ir–P–C_{alkyl} angles with an average of 111.1°, the C_{aryl}–P–C_{alkyl} angles with an average of 103.8° and the C_{aryl}–P–C_{aryl} angles with an average of 100.1°. These values show the extent to which the phenyl groups are bent away from the coordination sites not occupied by the triphos ligand.

The relative orientations of the phenyl groups are shown in Fig. 3. The phenyl rings Ph(2)(C(12)–C(17)) and Ph(3)(C(18)–C(23)) face each other (the dihedral angle between their planes is 9°) and, pushed closer by the short P(1)–P(2) distance, give rise to C—C and C—H contacts in the range 3.4–3.6 Å. Non-bonded intramolecular C—H contacts between phenyl rings are considered to be important in increasing the stability of organic molecules [23–24], and have been observed in a very strained Pt complex cis[$PtCl_2$(L)], where L is the bidentate ligand 2,11-bis(diphenylphosphynomethyl)benzo[c]phenanthrene [25].

Finally, it should be noticed that there are several non-bonded distances between hydrogen atoms and either chlorine or oxygen atoms which are shorter than the sums of the corresponding Van der Waals radii [26]; i.e., Cl...H(29)C(29) = 2.75 Å, Cl...H(17)C(15) $[x-1/2,\ y,\ 1/2-z] = 2.85$ Å, O...H(34)C(35) $[x,\ 1/2-y,\ 1/2+z] = 2.55$ Å.

Experimental

The infrared spectra were recorded on samples in CsI discs on a Beckman, Model 4250 spectrometer. The ^{31}P NMR spectra were recorded with solutions contained in 10 mm sample tubes, on a Bruker HX 90 spectrometer operating at 36.43 MHz. A positive sign of the chemical shift denotes a resonance to low field of the reference (external H_3PO_4). The ^1H NMR spectra were recorded with either a Bruker WM 250 or an HX 90 spectrometer.

The manipulations involved in the syntheses and reactions of iridium(I) compounds were carried out under nitrogen using standard Schlenk techniques [27].

All solvents were dried by standard procedures [28] and were distilled under nitrogen before use. The ligand triphos was prepared by a published procedure [29]; its IR and NMR spectra have been reported elsewhere [14]. Complexes [IrCl(CO)$(PPh_3)_2$] [30], [IrCl(CO)(triphos)] [5], and [$IrCl_3$(triphos)] [5] were also prepared by published procedures.

[IrH(CO)(triphos)] (2)

Solid tetramethylammonium tetrahydroborate (0.2 mmol, 17.8 mg) was added to a suspension of [IrCl(CO)(triphos)] (**1**) (0.1 mmol, 88 mg) in 8 ml of acetonitrile containing 3 drops of water. The suspension was boiled under reflux for 30 minutes. The bright yellow precipitate was then filtered off, washed three times with 3 ml of methanol, and dried under high vacuum. Yield 85%, Recrystallisation from methylene chloride and a mixture of methanol/pentane (1/1) yielded bright yellow microcrystals. Its infrared spectrum showed a split strong band at 1870 cm^{-1} and a medium strong band at 2040 cm^{-1} with a shoulder at 2065 cm^{-1}. Found: C, 58.61; H, 4.66; $C_{42}H_{40}IrOP_3$ calcd.: C, 59.64; H, 4.77%.

[IrHCl(CO)(triphos)][PF$_6$] (3)

Gaseous hydrochloric acid (0.1 mmol, 2.24 ml (NTP)) was introduced from a syringe into a solution of [IrCl(CO)(triphos)] (**1**) (0.1 mmol, 88 mg) in 3 ml of methylene chloride. The orange-red solution immediately turned pale yellow. Stirring was continued for 1 h and the solvent was then evaporated off to about 1 ml. A solution of ammonium hexafluorophosphate (ca. 200 mg) in 1 ml of methanol was then added and the mixture was stored at ca. +8°C. for 1 h. The pale yellow precipitate was then filtered off and washed with pentane. Yield 53%. Found: C, 49.45; H, 4.02; Cl, 3.10; $C_{42}H_{40}ClF_6IrOP_4$ calcd.: C, 49.15; H, 3.93; Cl, 3.87%.

This compound was also obtained by the following method: CF_3SO_3H (0.03 mmol, 2.6 μl) was added to a solution of [IrCl(CO)(triphos)] (**1**) (0.03 mmol, 26.4 mg) in 2 ml of methylene chloride. The orange-red solution immediately turned pale yellow. Its ^{31}P NMR spectrum showed that it contained about 95% of cation **3**, together with small amounts of other unidentified species.

[IrH$_2$(CO)(triphos)][PF$_6$] (4)

A suspension of [IrCl(CO)(triphos)] (**1**) (0.1 mmol, 88 mg) in 5 ml of methanol was heated to reflux. Hydrogen was bubbled through the suspension until all solid had dissolved (15 min). The resulting pale yellow solution was then concentrated to about 1 ml and a solution of ammonium hexafluorophosphate (200 mg) in 1 ml of methanol was added. The pale yellow precipitate which gradually deposited was filtered off and washed with methanol. Yield 56%. Found: C, 50.37; H, 4.32; $C_{42}H_{41}F_6IrOP_4$ calcd.: C, 50.86; H, 4.17%.

Reaction of [IrH(CO)(triphos)] (2) with hydrochloric acid

Gaseous hydrogen chloride (0.1 mmol, 2.24 ml (NTP)) was introduced from a syringe into a solution of [IrH(CO)(triphos)] (**2**) (0.1 mmol, 84.6 mg) in 3 ml of methylene chloride. The yellow solution turned immediately pale yellow and was stirred for 1 h at room temperature. Its ^{31}P NMR spectrum showed the presence of the cation $[IrH_2(CO)(triphos)]^+$ (**4**) contaminated with some $[IrCl_3(triphos)]$ (**5**) and $[IrH_2Cl(triphos)]$ (**7**).

Pure $[IrH_2(CO)(triphos)]^+$ (**4**) was prepared as above using methanol as solvent and CF_3SO_3H (0.1 mmol, 8.8 μl) as the acid.

[IrH$_3$(triphos)] (8)

A solution of 10 g of lithium aluminium hydride in 150 ml of ether was prepared and 0.2 ml (0.2 mmol) of this solution were added to a suspension of $[IrCl_3(triphos)]$ (**5**) (0.1 mmol, 92.3 mg) in 10 ml of THF. The solid dissolved immediately and the solution turned pale yellow. After 1 h stirring 0.1 ml of water was carefully added followed by another 10 ml portion. Sodium hydroxide (5 pellets) was then added and the mixture was stirred for 20 min and 10 ml CH_2Cl_2 added. The organic layer was then removed and the aqueous layer extracted with two 10 ml portions of methylene chloride. The organic layers were combined and dried over $MgSO_4$. Evaporation of the solvent gave a white powder. Yield 80–85%. Found: C, 60.20; H, 5.21; $C_{41}H_{42}IrP_3$ calcd.: C, 60.06; H, 5.16%. Recrystallisation from CH_2Cl_2/hexane yielded white needles.

Reaction of [IrCl$_3$(triphos)] (5) with hydrogen

A suspension of $[IrCl_3(triphos)]$ (**5**) (0.1 mmol, 92.3 mg) in 5 ml of methanol was purged with hydrogen at room temperature for 5 h. The solution was markedly acidic and the precipitate consisted of about 90% of monohydride [IrHCl$_2$(triphos)] (**6**) and 10% of starting material **5** as indicated by its ^{31}P NMR spectrum. An attempt to lower the acidity with sodium methoxide yielded a mixture of dihydride **7** and trihydride **8**. However, small amounts of [IrHCl$_2$(triphos)] (**6**) could be obtained by fractional recrystallisation from chloroform of the mixture obtained above (yield 5%).

Reaction of [IrCl$_3$(triphos)] (5) with Na[BH$_4$]

Na[BH$_4$] (2.65 mmol, 100 mg) was added to a suspension of [IrCl$_3$(triphos)] (**5**) (0.1 mmol, 92.3 mg) in 5 ml of THF. After 30 min stirring at room temperature the precipitates consisted of monohydride **6** and starting material **5**. After 4 h the ^{31}P NMR spectrum showed complete conversion of the starting material **5** into monohydride **6** and dihydride **7**. The suspension was then heated to reflux and boiled for 12 h. The resulting precipitate consisted of a 1/1 mixture of dihydride **7** and trihydride **8**. No further reaction was observed.

Reaction of [IrH$_3$(triphos)] (8) with hydrochloric acid

Gaseous hydrogen chloride (0.1 mmol, 2.24 ml) was introduced from a syringe into a solution of [IrH$_3$(triphos)] (**8**) (0.1 mmol, 82 mg) in 8 ml of methylene chloride. The resulting pale yellow solution contained the four species [IrH$_3$(triphos)] (**8**) (ca. 50%), [IrH$_2$Cl(triphos)] (**7**) [IrHCl$_2$(triphos)] (**6**) and [IrCl$_3$(triphos)] (**5**) as indicated by its ^{31}P NMR spectrum.

X-Ray crystal structure

Single crystals of [IrCl(CO)(triphos)] (**1**), suitable for diffraction analysis, were obtained by dissolving the solid in CH$_2$Cl$_2$, adding a second layer of pentane, and leaving the mixture at room temperature under argon.

Crystal data

$C_{42}H_{39}OP_3ClIr$, $M = 880.3$. Orthorhombic, a 18.941(6), b 22.193(8), c 17.501(7) Å, $V = 7357$ Å^3, $Z = 8$, D_c 1.589 g cm^{-3}, $F(000) = 2393.8$, space group *Pbca* (D_{2h}^{15}, No. 61). Mo-K_α radiation, λ 0.71069 Å, μ(Mo-K_α) 19.24 cm^{-1}.

Measurements

A preliminary photographic study allowed deviation of the space group from the systematically absent reflections. A single crystal of approximate dimensions 0.25 × 0.25 × 0.90 mm was selected and used for all measurements. The cell constants were determined from the setting angles of 15 reflections centered on a Nicolet R3 computer controlled diffractometer equipped with a graphite monochromator. The intensities of 13190 reflections with $1.5° \geqslant \theta \geqslant 28°$ were measured by ω-scan technique. The intensities of three standard reflections, periodically remeasured, remained constant throughout the data collection. The reflections were processed as described elsewhere [31], using an ignorance factor $p = 0.018$, and were corrected for shape anisotropy. Only 6462 independent reflections met the condition $I \geqslant 3\sigma(I)$, and were used in the subsequent calculations.

TABLE 3

FINAL POSITIONAL AND THERMAL PARAMETERS OF THE NONHYDROGEN ATOMS, FRACTIONAL COORDINATES AND ISOTROPIC THERMAL PARAMETERS

Atom	x	y	z	B_{iso}
Ir	0.22836(3)	0.14431(3)	0.14353(3)	
P(1)	0.3066(2)	0.2203(2)	0.1370(2)	
P(2)	0.3095(2)	0.0900(1)	0.0654(2)	
P(3)	0.1699(2)	0.1811(1)	0.0327(2)	
Cl	0.1501(3)	0.0574(2)	0.1673(3)	
O	0.2054(8)	0.1745(9)	0.3111(9)	
C	0.2152(8)	0.1630(9)	0.2463(9)	
C(1)	0.3121(7)	0.1966(6)	−0.0237(8)	
C(2)	0.3460(9)	0.2241(9)	−0.0964(9)	
C(3)	0.3215(7)	0.2455(6)	0.0382(8)	
C(4)	0.3531(7)	0.1405(6)	−0.0059(9)	
C(5)	0.2358(7)	0.1909(6)	−0.0471(8)	
C(6)	0.2874(6)	0.2920(7)	0.1861(9)	3.7(3)
C(7)	0.3391(6)	0.3365(7)	0.1928(9)	4.6(4)
C(8)	0.3220(6)	0.3925(7)	0.2238(9)	6.4(6)
C(9)	0.2532(6)	0.4041(7)	0.2480(9)	6.2(6)
C(10)	0.2015(6)	0.3596(7)	0.2413(9)	8.2(8)
C(11)	0.2186(6)	0.3036(7)	0.2103(9)	5.3(5)
C(12)	0.3948(5)	0.2020(6)	0.1756(6)	2.4(2)
C(13)	0.3957(5)	0.1720(6)	0.2456(6)	3.7(3)
C(14)	0.4599(5)	0.1547(6)	0.2780(6)	4.2(4)
C(15)	0.5231(5)	0.1673(6)	0.2403(6)	5.1(4)
C(16)	0.5221(5)	0.1974(6)	0.1703(6)	5.2(5)
C(17)	0.4580(5)	0.2147(6)	0.1379(6)	4.5(4)
C(18)	0.3846(6)	0.0534(6)	0.1152(7)	3.3(3)
C(19)	0.3714(6)	0.0277(6)	0.1866(7)	3.7(3)
C(20)	0.4262(6)	0.0008(6)	0.2273(7)	6.7(6)
C(21)	0.4942(6)	−0.0005(6)	0.1968(7)	7.0(6)
C(22)	0.5074(6)	0.0251(6)	0.1254(7)	6.4(6)
C(23)	0.4526(6)	0.0521(6)	0.0846(7)	4.5(4)
C(24)	0.2818(9)	0.0220(8)	0.0113(9)	4.9(4)
C(25)	0.2822(9)	0.0196(8)	−0.0684(9)	7.1(7)
C(26)	0.2513(9)	−0.0291(8)	−0.1060(9)	7.7(7)
C(27)	0.2200(9)	−0.0754(8)	−0.0640(9)	6.9(6)
C(28)	0.2197(9)	−0.0730(8)	0.0156(9)	6.3(6)
C(29)	0.2506(9)	−0.0242(8)	0.0533(9)	4.2(3)
C(30)	0.1290(7)	0.2580(5)	0.0442(6)	2.3(2)
C(31)	0.0814(7)	0.2623(5)	0.1047(6)	4.4(4)
C(32)	0.0472(7)	0.3168(5)	0.1194(6)	5.3(5)
C(33)	0.0606(7)	0.3669(5)	0.0736(6)	6.0(6)
C(34)	0.1082(7)	0.3626(5)	0.0130(6)	7.1(7)
C(35)	0.1424(7)	0.3081(5)	−0.0017(6)	4.4(4)
C(36)	0.0996(9)	0.1372(9)	−0.0148(9)	3.5(3)
C(37)	0.0305(9)	0.1592(9)	−0.0157(9)	6.2(11)
C(38)	−0.0239(9)	0.1236(9)	−0.0449(9)	6.2(11)
C(39)	−0.0093(9)	0.0662(9)	−0.0732(9)	4.0(7)
C(40)	0.0597(9)	0.0443(9)	−0.0723(9)	6.0(11)
C(41)	0.1141(9)	0.0798(9)	−0.0431(9)	7.3(14)

Structure determination and refinement

The structure was solved by heavy atom method and refined by least-squares procedures. The isotropic refinement converged at $R = 0.092$.

Afterwards the phenyl groups of the triphos ligand were constrained to $6/mmm$ symmetry, d(C–C) 1.395 Å but the carbon atoms were assigned individual isotropic thermal parameters. All the hydrogen contributions were taken into account. All the non group, non hydrogen atoms were allowed to vibrate anisotropically.

The refinement converged at $R = 0.074$ and $R_w = 0.096$. A final electron density map did not reveal residual peaks. The refinement was carried out by full matrix and the function minimized was $\Sigma w(|F_0| - |F_c|)^2$ with $w = 1/[\sigma^2(F_0) + b|F_0|^2]$. Scattering factors and anomalous dispersion terms were taken from the International Tables for X-ray Crystallography [32]. The calculations were carried out on the HP21 MX minicomputer of the NRC Research Area of Rome, using local programs and on the Data General Eclipse MV 8000II computer using the SHELX system (G.M. Sheldrick, 1980).

The final positional parameters are listed in Table 3. A table of thermal atomic parameters and lists of observed and calculated structure factors are available from the authors upon request.

References

1 L. Sacconi and F. Mani, 3rd Metal Complexes with Tripodal Polytertiary Phosphines and Arsines, in G.A. Melson and B.N. Figgis (Eds.), Transition Metal Chemistry, Marcel Decker, New York, 8 (1982) 179 and ref. quoted therein.
2 M. Di Vaira and L. Sacconi, Angew. Chem., 94 (1982) 338.
3 J. Ott, L.M. Venanzi, C.A. Ghilardi, S. Midollini and A. Orlandini, J. Organomet. Chem., 291 (1985) 89.
4 F. Bachechi, J. Ott, and L.M. Venanzi, J. Am. Chem. Soc., 107 (1985) 1760.
5 W.O. Siegl, S.J. Lapporte and J.P. Collman, Inorg. Chem., 10 (1971) 2158.
6 H.D. Kaesz and R.B. Saillant, Chem. Revs., 72 (1972) 231 and ref. quoted therein.
7 J.K. Burdett, Inorg. Chem., 16 (1977) 3013 and ref. quoted therein.
8 F.A. Bovey, Nuclear Magnetic Resonances Spectroscopy, Academic Press, New York, 1969, p. 103.
9 A.R. Rossi and R. Hoffmann, Inorg. Chem., 14 (1975) 365.
10 E.M. Shustorovich, M.A. Porai-Koshits and Y.A. Buslaev, Coord. Chem. Rev., 17 (1975) 1 and ref. quoted therein.
11 J.P. Jesson, Stereochemistry and Stereochemical Nonrigidity in Transition Metal Hydrides in E.L. Muetterties (Ed.), Transition Metal Hydrides, Marcel Dekker, New York, 1971, p. 75.
12 R.K. Harris, Canad. J. Chem., 42 (1964) 2275.
13 B.L. Shaw, R.M. Slade and R.E. Steinbank, J. Chem. Soc., A, (1971) 1826.
14 R. Davis and J.E. Ferguson, Inorg. Chim. Acta, 4 (1970) 17.
15 J.Y. Chen, J. Halpern and J. Molin-Case, J. Coord. Chem., 2 (1973) 239.
16 P. Dapporto, S. Midollini, A. Orlandini and L. Sacconi, Inorg. Chem., 15 (1976) 2768.
17 C. Benelli, M. Di Vaira, G. Noccioli and L. Sacconi, Inorg. Chem., 16 (1977) 182.
18 C. Bianchini, A. Meli and A. Orlandini, Inorg. Chem., 24 (1982) 4166.
19 J.S. Fields and P.J. Wheathley, J. Chem. Soc. Dalton, (1972) 2269.
20 M. Ciechanowicz, A.C. Skapski and P.G.H. Troughton, Acta Cryst. B, 32 (1976) 1673.
21 M.S. Weininger, E.A.H. Griffith, C.T. Sears and E.L. Amma, Inorg. Chim. Acta, 60 (1982) 67.
22 M.R. Churchill and S.A. Bezman, Inorg. Chem., 13 (1974) 1418.
23 D.E. Williams, J. Chem. Phys., 45 (1966) 3770.
24 G. Casalone, C. Mariani, A. Mugnoli and M. Simonetta, Mol. Phys., 15 (1968) 339.
25 G. Bracher, D.M. Grove, L.M. Venanzi, F. Bachechi, P. Mura and L. Zambonelli, Helv. Chim. Acta, 63 (1980) 2519.

26 L. Pauling, "The Nature of the Chemical Bond", Cornell Univ. Press, Ithaca, N.Y., 1960, p. 260.
27 D.F. Shriver, The Manipulation of Air-Sensitive Compounds, McGraw-Hill, New York, 1969.
28 D.D. Perren, W.L.F. Armarego and D.R. Perrin, Purification of Laboratory Chenicals, Pergamon Press, Oxford, 1980.
29 W. Hewertson and H.R. Watson, J. Chem. Soc., (1962) 1940.
30 K. Vrieze, Inorg. Syntheses, 11 (1961) 101.
31 F. Bachechi, L. Zambonelli and G. Marcotrigiano, J. Cryst. Mol. Struct., 7 (1977) 11.
32 International Tables for X-Ray Crystallography, Vol. IV, Kynoch Press, Birmingham, 1974.