

SOME RHODIUM(I) AND RHODIUM(III) COMPLEXES WITH THE TRIPOD-LIKE LIGANDS $\text{RC}(\text{CH}_2\text{PPh}_2)_3$ (R = Me: triphos; R = Et: triphos-I) AND THE X-RAY CRYSTAL STRUCTURE OF $[\text{RhH}_3(\text{triphos-I})]$

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Summary

The syntheses of $[\text{RhH}_3(\text{triphos})]$ (**8**, triphos = $\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3$) and the related compound $[\text{RhH}_3(\text{triphos-I})]$ (triphos-I = $\text{EtC}(\text{CH}_2\text{PPh}_2)_3$) are described, and the X-ray crystal structure of the latter is reported. The crystals are monoclinic space group $P2_1/a$, a 15.985(6), b 19.683(7), c 11.900(4) Å, β 103.73(6)°, Z = 4. The structure was solved by the heavy atom method and refined by full-matrix least-squares to the conventional R factor value of 0.057 for 2649 observed reflections. The metal atom is octahedrally coordinated by three phosphorus atoms and by three hydrogen atoms, each *trans* to one phosphorus.

Complex **8** has been shown to react with CO to give $[\text{RhH}(\text{CO})(\text{triphos})]$ (**2**). Compound **2** reacts with $\text{CH}_2=\text{CHCO}_2\text{Me}$ to give only the branched insertion product $[\text{Rh}(\text{CH}(\text{CH}_3)\text{CO}_2\text{Me})(\text{CO})(\text{triphos})]$. The complex $[\text{RhCl}(\text{CO})(\text{triphos})]$ has been re-investigated and was obtained in a single isomeric form which has been assigned a five-coordinate structure. The five-coordinate compounds $[\text{RhX}(\text{CO})(\text{triphos})]$ ($X = \text{Br}$ and I) are also described.

Introduction

Rhodium hydride complexes have acquired great importance in homogeneous catalysis largely because of their hydrogenating properties, especially their effectiveness to stereospecific hydrogenation of prochiral substrates [1]. Rhodium hydride complexes have also been extensively used as hydroformylation catalysts [2]. In both cases, phosphinerhodium complexes are among the most active species [1b,2].

While iridium(III) readily forms stable trihydrides, e.g., *fac*- and *mer*- $[\text{IrH}_3(\text{PPh}_3)_3]$ [3], the corresponding rhodium(III) complexes do not seem to have

been reported. As the ligands $\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3$, triphos, and $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_2\text{PPh}_2)_3$, triphos-I, show the tendency to facilitate the formation of six-coordinate hydrido complexes of d^6 -metal centers, e.g., iron(II) [4], their rhodium coordination chemistry [5,6] was re-investigated. We report here the preparation and reactions of the first, stable rhodium(III) trihydrido complexes $[\text{RhH}_3(\text{triphos})]$ (**8**) and its triphos-I analogue, **9**. The X-ray crystal structure of **9** is reported.

Results and discussion

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

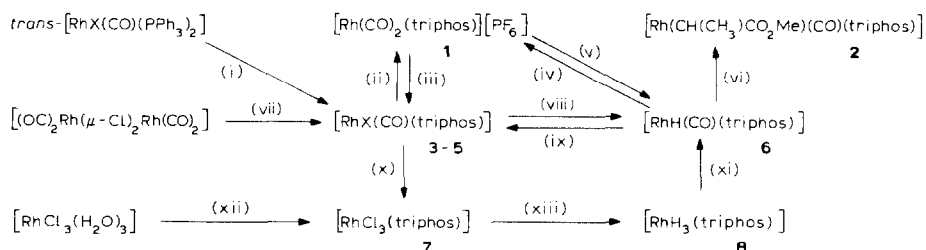
$[\text{RhCl}_3(\text{triphos})]$ (**7**) reacts with NaBH_4 in acetonitrile/water, to give $[\text{RhH}_3(\text{triphos})]$ (**8**) in good yield. This colourless compound is air-stable as a solid but decomposes slowly in solution, even in the absence of air.

Hydride **8** reacts with CO, in anhydrous aprotic solvents, to give $[\text{RhH}(\text{CO})(\text{triphos})]$ (**6**), presumably by the pathway shown in Scheme 2. It is noteworthy that when this reaction is carried out in moist solvents small amounts of $[\text{Rh}(\text{CO})_2(\text{triphos})]^+$ (**1**) are formed. The formation of **1** is quantitative when this reaction is carried out in the presence of a protonic acid. The postulated reaction mechanism is shown in Scheme 3.

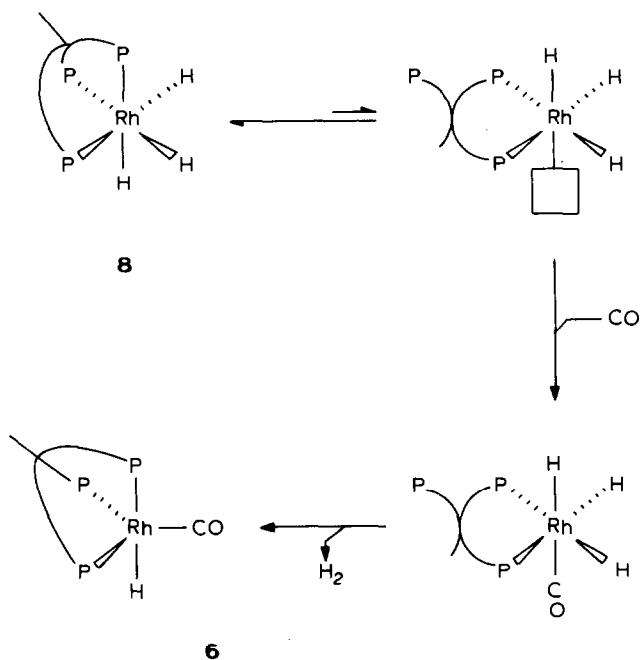
The halocarbonyl complexes $[\text{RhX}(\text{CO})(\text{triphos})]$ (**3–5**) were obtained from the reaction of triphos with *trans*- $[\text{RhX}(\text{CO})(\text{PPh}_3)_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) in benzene. The products which separated from the solution showed only one carbonyl band in the infrared spectrum (see Table 1). Given the geometry of the triphos ligand and the ^{31}P NMR spectra of the complexes (see later) we assign a five-coordinate structure to them. The $\nu(\text{CO})$ infrared stretch of **3** corresponds to the main band reported by Siegl et al. [5]. However, when hexane was added to the mother liquor to complete precipitation, the mixture of products they described was obtained.

Solutions of halocarbonyls **3–5** were also obtained by treating the hydrido-carbonyl complex **6** with halocarbons such as $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$, $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ and CH_3I or by reaction of $[\text{Rh}(\text{CO})_2(\text{triphos})][\text{PF}_6]$ (**1**) with the corresponding halide in the form of its $[\text{Bu}_4\text{N}]$ salt.

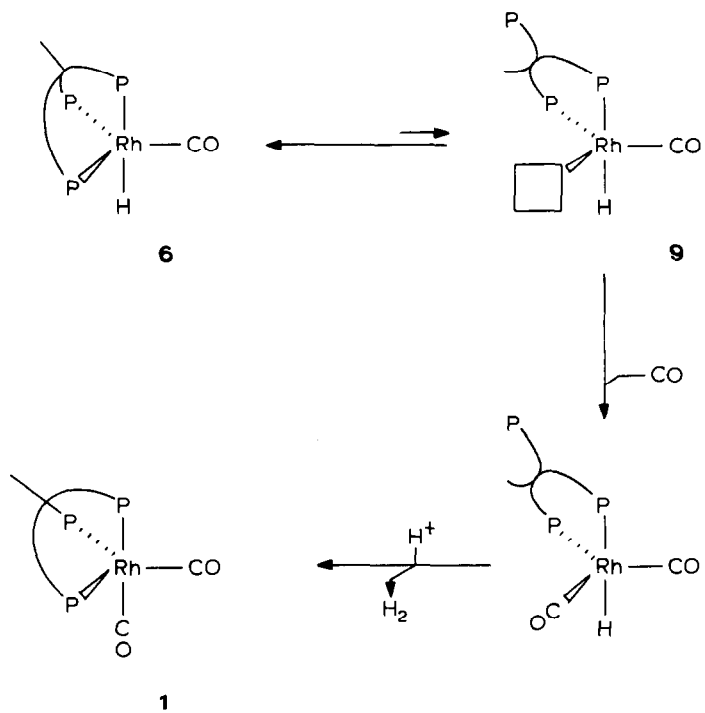
The hydrido carbonyl complex **6** reacts with activated olefins, e.g., $\text{CH}_2=$



SCHEME 1. Syntheses and reactions of rhodium triphos complexes. (**3**: $\text{X} = \text{Cl}$; **4**: $\text{X} = \text{Br}$; **5**: $\text{X} = \text{I}$). (i) triphos, [5]. (ii) CO; for $\text{X} = \text{Cl}$ see [5]. (iii) X^- ; for $\text{X} = \text{Cl}$ see [5]. (iv) $\text{CO} + \text{H}^+$. (v) $\text{Na}[\text{BH}_4]/\text{MeOH}$ or $\text{Li}[\text{BH}_4\text{Et}_3]/\text{THF}$. (vi) $\text{CH}_2=\text{CHCO}_2\text{Me}$. (vii) triphos [5]. (viii) $\text{Na}[\text{BH}_4]/\text{MeOH}$. (ix) PhCH_2Cl for $\text{X} = \text{Cl}$, PhCH_2Br for $\text{X} = \text{Br}$ and MeI for $\text{X} = \text{I}$. (x) Cl_2 [5]. (xi) CO. (xii) triphos. (xiii) $\text{Na}[\text{BH}_4]/\text{MeCN}/\text{H}_2\text{O}$.



SCHEME 2. A postulated mechanism for the reaction of $[\text{RhH}_3(\text{triphos})]$ with CO.



SCHEME 3. A postulated reaction pathway for the formation of $[\text{Rh}(\text{CO})_2(\text{triphos})]^+$ from $[\text{RhH}(\text{CO})(\text{triphos})]$.

TABLE 1
NMR AND IR DATA FOR RHODIUM TRIPHOS AND TRIPHOS-I COMPLEXES

	¹ H NMR		³¹ P NMR		IR ν(CO) (cm ⁻¹)
	δ(CH ₂) (ppm) ^a	δ(CH ₃) (ppm) ^b	δ(P) (ppm)	¹ J(Rh, P) (Hz)	
triphos ^c	2.55	1.05	-26		
triphos-I ^d	2.5 ^e	0.65	-25.7		
[RhCl ₃ (triphos)] ^d	2.6	1.6	9.5	103	
[RhCl ₃ (triphos-I)] ^d	2.45 ^f	0.9	8.0	104	
[RhCl(CO)(triphos)] ^g	2.2	1.1	3.0	107	1920
[RhBr(CO)(triphos)] ^g	2.15	1.05	1.6	109	1920
[RhI(CO)(triphos)] ^g	2.15	1.05	-0.5	116	1915
[RhH(CO)(triphos)] ^{d,h}	2.15 ^c	1.45	16	116	1885 ⁱ
[RhR(CO)(triphos)] ^j	^k	1.5	6.5	107	1900
[Rh(CO) ₂ (triphos)]PF ₆ ^l	2.9	1.95	7.8	98.5	2060, 1980
[RhH ₃ (triphos)] ^{d,m}	2.2	1.5	24.5	90	
[RhH ₃ (triphos-I)] ^{d,n}	2.15 ^o	1.1	23.2	87	

^a Unless otherwise specified these groups are those bonded to phosphorus. Their resonances appear as doublets with ²J(P,H) values in the range 2–10 Hz. ^b These resonances appear as quartets with ⁴J(P,H) in the range 2–4 Hz in the triphos complexes, and as triplets with ³J(H,H) in the range 7–7.5 Hz in the triphos-I derivatives. ^c Measured in CDCl₃. ^d Measured in CD₂Cl₂. ^e The CH₂ of the ethyl group appears as a quartet centered at 1.6 ppm with ³J(H,H) 7.5 Hz. There is an additional coupling with the phosphorus which complicates the shape of the signal. This is more evident in the triphos-I complexes. ^f The CH₂ of the ethyl group appears as a broad multiplet centered at 1.70 ppm. ^g Measured in C₆D₆. ^h δ(H_{hydride}) -8.2 ppm (dxq, ¹J(Rh,H) 14 Hz, ²J(P,H) 35 Hz). ⁱ ν(Rh-H) 1930 cm⁻¹. ^j R = CH(CH₃)CO₂Me. ^k The CH₂ protons are not equivalent. Their δ values are 2.1 and 2.45 ppm with a ²J(H,H) 15 Hz. ^l Measured in acetone-*d*₆. ^m δ(H_{hydride}) -8.3 ppm (²J(P,H)+2²J(P,H'))=132 Hz. ¹J(Rh,H) 20 Hz. ⁿ δ(H_{hydride}) -8.25 ppm (²J(P,H)+2²J(P,H'))=133 Hz. ¹J(Rh,H) 20 Hz. ^o The CH₂ of the ethyl group appears as a broad multiplet centered at 1.70 ppm.

CHCO₂Me, to give the carbyl complex **2**; only the branched isomer was detected. It is conceivable that complex **2** results from coordination of the acrylate to the coordinatively unsaturated intermediate **9** (see Scheme 3) followed by a migratory insertion step [7].

The ¹H and ³¹P NMR parameters recorded for complexes **1** to **9** are listed in Table 1.

¹H NMR spectra. That of [RhH(CO)(triphos)] (**6**) in the hydride region, (see Table 1) appears as a doublet of quartets as expected from the ¹⁰³Rh, ¹H and ³¹P, ¹H coupling assuming dynamic equivalence of the phosphorus atoms.

The spectra of [RhH₃(triphos)] (**8**) (see Fig. 1) and [RhH₃(triphos-I)] (**9**) are not first order but similar to those found for *fac*-[IrH₃(PEt₂Ph)₃] [8]. Irradiation at the phosphorus frequency allows the determination of the value of ¹J(¹⁰³Rh, ¹H). We were unable to simulate these spectra.

³¹P NMR spectra. Those of the six-coordinate complexes [RhX₃(triphos)] (**7**, X = Cl; **8**, X = H) appear as doublets (see Table 1) and are first order.

The spectra for the five-coordinate species **1** to **6** show a single doublet consistent with chemically equivalent phosphorus atoms coupled to ¹⁰³Rh. However, X-ray crystal structure determinations of related five-coordinate complexes, e.g., [Co(BH₄)(triphos)] [9], show that in the solid state the three phosphorus atoms are not structurally equivalent. Thus, the solution data must be interpreted in terms of a

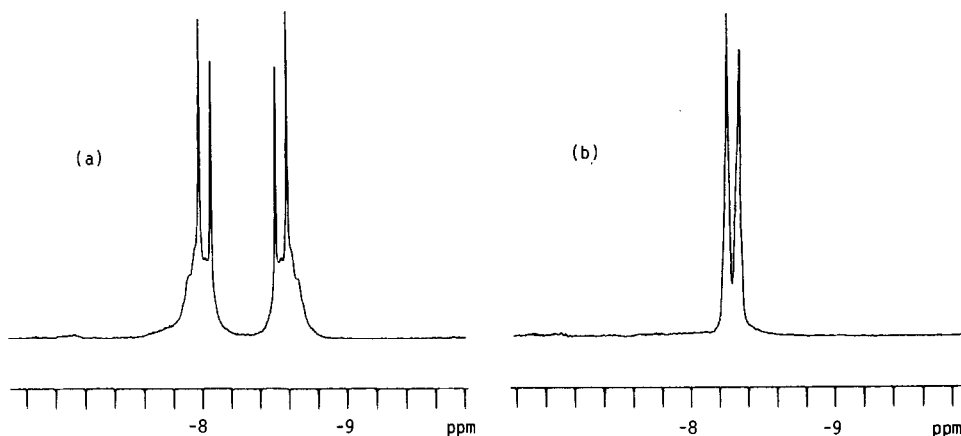


Fig. 1. The 250 MHz ^1H NMR spectrum of $[\text{RhH}_3(\text{triphos})]$ (**8**) (hydride region): (a) normal spectrum; (b) $\{^{31}\text{P}\}^1\text{H}$ spectrum.

rapid averaging of environments, on the NMR time-scale. This must be a low activation energy process as in the compounds $[\text{RhH}(\text{CO})(\text{triphos})]$ (**6**), and $[\text{Rh}(\text{CO})_2(\text{triphos})]^+$ (**1**), no line-broadening is observed on cooling their solutions down to -80°C . This behaviour appears to be typical for five-coordinate organometallic species [10].

The ^{31}P NMR spectra of the mixtures of chloro- or bromo-carbonyl compounds, obtained by the method of Siegl et al. [5] show that the second species are dynamic on the NMR time-scale. Their spectra are indicative of complex sets of equilibria which will be described elsewhere [11]. It should also be noted that the ^{31}P NMR spectra of our $[\text{RhX}(\text{CO})(\text{triphos})]$ compounds are strongly solvent-dependent and that use of solvents such as dichloromethane and acetonitrile results in the formation of $[\text{Rh}(\text{CO})_2(\text{triphos})]^+$.

The molecular structure of **9** consists of discrete mononuclear $[\text{RhH}_3(\text{CH}_3\text{CH}_2\text{C}(\text{CH}_2\text{PPh}_2)_3)]$ species. Figure 2 shows a perspective view of the molecule and Table 2 lists a selection of bond distances and angles. The metal atom is coordinated to the three phosphorus atoms of the triphos-I ligand and by three hydrogen atoms in a slightly distorted octahedral geometry. Owing to the requirement of the ligand, which does not allow the P-Rh-P angles to be significantly different from 90° , the complex attains a facial configuration, each of the three hydrogen ligands being *trans* to one phosphorus atom. Moreover, due to the rigidity of the coordinated ligand and to the moderate steric hindrance of the hydrogen atoms, the metal atom displays an almost regular octahedral geometry, the *trans*- P-Rh-H angles and the *cis*- P-Rh-P , $-\text{P-Rh-H}$, and $-\text{H-Rh-H}$ angles being very close to the idealized values of 180° and 90° , respectively.

The Rh-P values range from 2.296(3) to 2.316(3) Å, with an average of 2.304(6) Å. These values may be compared with those of 2.302(2) and 2.321(2) Å in $[\text{RhH}_2(\text{O}_2\text{COH})(\text{P}(\text{i-Pr})_3)_2]$ [12] and with those of 2.319(1) and 2.338(1) Å in $[(\text{PPh}_3)_2\text{HClRh}(\mu\text{-SH})_2\text{RhClH}(\text{PPh}_3)_2]$ [13]. Moreover, these distances agree with the sum of the covalent radii (2.31 Å) and are shorter than those expected on the basis of the *trans* influence of the hydride ligand [14]. It is possible that the

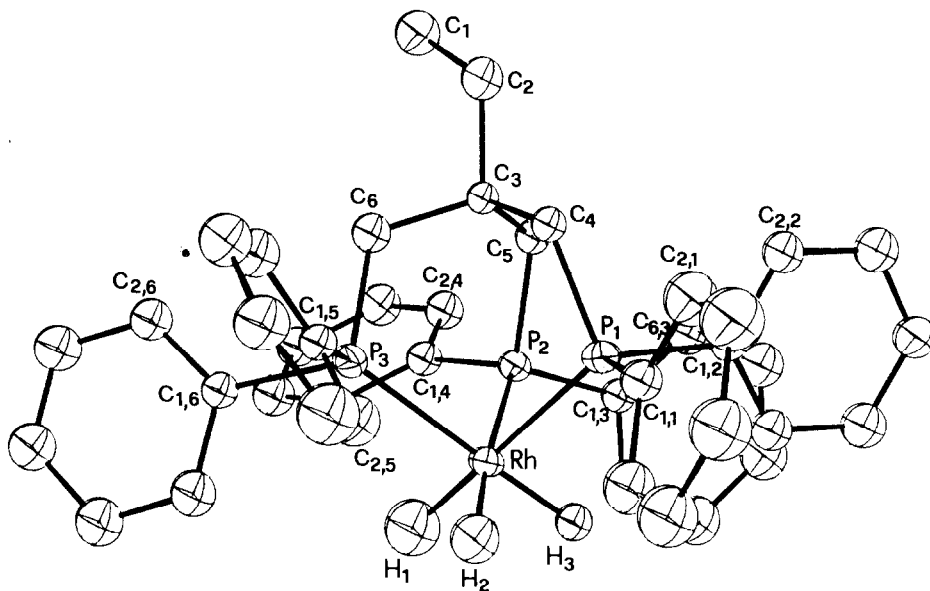


Fig. 2. An ORTEP view of the molecule $[\text{RhH}_3(\text{triphos})]$ (**8**) (30% probability ellipsoids).

lengthening expected on the basis of the *trans* influence may be balanced by the small steric requirements of the hydride ligands, which allow a closer approach of the phosphorus to the metal.

The Rh–H bond distances range from 1.42(9) to 1.60(9) Å, and the mean value of 1.52(5) Å may be compared with the average value of 1.57(8) Å reported by Bau and Teller [15].

Experimental

The infrared spectra were recorded on samples in KBr discs, on a Beckman Model 4250 spectrophotometer. The ^{31}P NMR spectra were recorded using 10 mm sample tubes on a Bruker HX 90 spectrometer. A positive sign of the chemical shift denotes a resonance to low field of the reference. The ^1H NMR spectra were obtained using either a Bruker WM 250 or a HX 90 spectrometer.

The compounds marked with an asterisk (★) were prepared under nitrogen. The ligand triphos was prepared as described by Hewertson and Watson [16]. The ligand triphos-I was prepared analogously starting from $\text{EtC}(\text{CH}_2\text{Cl})_3$ [17].

$[\text{Rh}(\text{CO})_2(\text{triphos})][\text{PF}_6]$ (**1**)

This was prepared by the method of Siegl et al. [5]. It was also obtained from $[\text{RhH}(\text{CO})(\text{triphos})]$ (**6**) as follows:

A solution of 0.5 ml hexafluorophosphoric acid (~75% in water) in 10 ml methanol was saturated with carbon monoxide. Solid $[\text{RhH}(\text{CO})(\text{triphos})]$ (**6**) (151 mg, 0.2 mmol) was then added while CO was bubbled through the solution for ca. 30 min. Yellow microcrystals gradually precipitated out when the solution was kept at -10°C for ca. 8 h. They were filtered off, washed three times with 5 ml of ether, and

TABLE 2

SELECTED BOND DISTANCES (Å) AND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS

Rh-P(1)	2.316(3)	P(2)-C(1,3)	1.831(8)
Rh-P(2)	2.296(3)	P(2)-C(1,4)	1.837(7)
Rh-P(3)	2.299(3)	P(3)-C(6)	1.838(9)
Rh-H(1)	1.60(9)	P(3)-C(1,5)	1.855(8)
Rh-H(2)	1.53(9)	P(3)-C(1,6)	1.853(7)
Rh-H(3)	1.42(9)	C(1)-C(2)	1.54(1)
P(1)-C(4)	1.830(9)	C(2)-C(3)	1.56(1)
P(1)-C(1,1)	1.829(9)	C(3)-C(4)	1.55(1)
P(1)-C(1,2)	1.857(9)	C(3)-C(5)	1.55(1)
P(2)-C(5)	1.845(9)	C(3)-C(6)	1.54(1)
P(1)-Rh-P(2)	87.0(1)	Rh-P(2)-C(1,3)	117.0(2)
P(1)-Rh-P(3)	90.5(1)	Rh-P(2)-C(1,4)	120.1(2)
P(1)-Rh-H(1)	175(3)	C(5)-P(2)-C(1,3)	104.6(4)
P(1)-Rh-H(2)	92(3)	C(5)-P(2)-C(1,4)	101.9(4)
P(1)-Rh-H(3)	84(3)	C(1,3)-P(2)-C(1,4)	100.2(3)
P(2)-Rh-P(3)	91.8(1)	Rh-P(3)-C(6)	109.5(3)
P(2)-Rh-H(1)	88(3)	Rh-P(3)-C(1,5)	118.1(2)
P(2)-Rh-H(2)	175(3)	Rh-P(3)-C(1,6)	120.7(2)
P(2)-Rh-H(3)	91(3)	C(6)-P(3)-C(1,5)	104.5(4)
P(3)-Rh-H(1)	90(3)	C(6)-P(3)-C(1,6)	102.8(4)
P(3)-Rh-H(2)	93(3)	C(1,5)-P(3)-C(1,6)	99.0(3)
P(3)-Rh-H(3)	174(3)	C(1)-C(2)-C(3)	118.4(9)
H(1)-Rh-H(2)	92(4)	C(2)-C(3)-C(4)	106.3(7)
H(1)-Rh-H(3)	96(5)	C(2)-C(3)-C(5)	106.3(7)
H(2)-Rh-H(3)	84(4)	C(2)-C(3)-C(6)	107.5(8)
Rh-P(1)-C(4)	109.0(3)	C(4)-C(3)-C(5)	111.0(7)
Rh-P(1)-C(1,1)	120.5(2)	C(4)-C(3)-C(6)	113.3(8)
Rh-P(1)-C(1,2)	116.7(2)	C(5)-C(3)-C(6)	111.9(8)
C(4)-P(1)-C(1,1)	103.5(4)	P(1)-C(4)-C(3)	116.4(6)
C(4)-P(1)-C(1,2)	104.5(3)	P(2)-C(5)-C(3)	115.5(6)
C(1,1)-P(1)-C(1,2)	100.9(3)	P(3)-C(6)-C(3)	115.7(7)
Rh-P(2)-C(5)	111.1(3)		

dried under high-vacuum. More product could be precipitated by adding 5 ml of water to the mother liquor. This solid was also purified as described above. Yield 82%. Found: C, 55.66; H, 4.34; $C_{43}H_{39}P_4O_2F_6Rh$ calcd.: C, 55.62; H, 4.23%.

*[RhCl(CO)(triphos)]**, (3)

This was prepared from $[RhCl(CO)(PPh_3)_2]$ by the following modification of the method of Siegl et al. [5]: To a mixture of $[RhCl(CO)(PPh_3)_2]$ (345 mg, 0.5 mmol) and triphos (312 mg, 0.5 mmol) 5 ml benzene were added. A red brown solution formed, and after a few minutes a red brown solid separated. This was filtered off, washed with small amounts of benzene, and dried under high-vacuum. Yield 73%. Its infrared spectrum (in Nujol) showed only one carbonyl band, at 1920 cm^{-1} . Found: C, 63.41; H, 4.97, Cl, 4.178. $C_{42}H_{39}P_3ORhCl$ calcd.: C, 63.77; H, 4.97; Cl, 4.48%. Addition of 10 ml hexane to the filtrate caused precipitation of a brown solid. Its infrared spectrum showed a strong band at 1920 cm^{-1} and a medium band at 2005 cm^{-1} , i.e., it gave the mixture of products obtained by Siegl et al. [5].

*[RhBr(CO)(triphos)]** (4)

This was prepared as described for the corresponding chloride **3**, starting from [RhBr(CO)(PPh₃)₂]. Yield 60%. Found: C, 60.94; H, 4.92; Br, 8.94. C₄₂H₃₉P₃ORhBr calcd.: C, 60.38; H, 4.71; Br, 9.56%.

*[RhI(CO)(triphos)]** (5)

This was prepared as described for the corresponding chloride **3**, starting from [RhI(CO)(PPh₃)₂]. Yield 52%. Found: C, 55.24; H, 4.49; I, 14.19. C₄₂H₃₉P₃ORhI calcd.: C, 57.16; H, 4.45; I, 14.38%.

Reaction of [RhH(CO)(triphos)] (6) with methyl iodide

[RhH(CO)(triphos)] (**6**) (151 mg, 0.2 mmol) was added to a solution of methyl iodide (142 mg, 1 mmol) in 5 ml benzene. After stirring for 2 h at 50°C the resulting red-brown solution contained only [RhI(CO)(triphos)] (**5**) as indicated by its ³¹P NMR spectrum.

Solutions of the complexes [RhBr(CO)(triphos)] (**4**) and [RhCl(CO)(triphos)] (**3**) were obtained by the same procedure using C₆H₅CH₂Br or C₆H₅CH₂Cl instead of CH₃I.

*Reaction of [Rh(CO)₂(triphos)][PF₆], **1**, with tetrabutylammonium iodide*

[Rh(CO)₂(triphos)][PF₆], **1**, (93 mg, 0.1 mmol) was added to a solution of tetrabutylammonium iodide (160 mg, 0.5 mmol) in 3 ml THF. After stirring for 30 min at 50°C the resulting red-brown solution contained only [RhI(CO)(triphos)] (**5**) as indicated by its ³¹P NMR spectrum. The complexes [RhBr(CO)(triphos)] (**4**) and [RhCl(CO)(triphos)] (**3**) were obtained by the same procedure using [Bu₄N]Br or [Bu₄N]Cl instead of [Bu₄N]I.

[RhCl₃(triphos-I)]

A solution of RhCl₃ · 3H₂O (263 mg, 1 mmol) in warm (50°C) ethanol was added to a solution of the ligand (624 mg, 1 mmol) in boiling ethanol. From the resulting solution crystals of [RhCl₃(triphos-I)] rapidly separated. They were filtered off, washed successively with ethanol, benzene, and light petroleum, and dried in vacuo. Yield 87%.

[RhCl₃(triphos)] (7)

This was prepared as described above. Found: C, 59.05; H, 4.71; Cl, 12.75. C₄₁H₃₉P₃Cl₃Rh calcd.: C, 59.14; H, 4.77; Cl, 12.44%.

*[RhH₃(triphos-I)]** (9)

Sodium tetrahydroborate (227 mg, 6 mmol) was added to a suspension of [RhCl₃(triphos)] (834 mg, 1 mmol) in ethanol. The resulting mixture was moderately heated (50°C) and colorless crystals of [RhH₃(triphos)] formed. After ca. 1 h all the starting compound had disappeared. The crystals were filtered off, washed with absolute ethanol, water, and ethanol again, then with light petroleum, and dried in current of nitrogen. Yield 83%.

Suitable crystals for X-ray diffraction were prepared by the following method: the ligand (624 mg, 1 mmol), dissolved in THF, was added to a solution of RhCl₃ · 3H₂O (263 mg, 1 mmol) in ethanol (10 ml). A solution of sodium tetrahydroborate (6

mmol) in ethanol was added, and the mixture was kept at ca. 50°C. Crystals of $[\text{RhH}_3(\text{triphos-I})]$ separated upon slow evaporation of THF from the warm solution under a current of nitrogen.

$[\text{RhH}_3(\text{triphos})]^*$ (8)

This was prepared as described for 9, but with 10/1 acetonitrile/ H_2O as solvent. Yield 60%. Found: C, 67.36; H, 5.86. $\text{C}_{41}\text{H}_{42}\text{P}_3\text{Rh}$ calcd.: C, 67.40; H, 5.79%.

$[\text{RhH}(\text{CO})(\text{triphos})]^*$ (6)

A solution of $[\text{RhCl}_3(\text{triphos})]$ (7) (250 mg, 0.3 mmol) in 20 ml acetonitrile/methanol (1/1) was saturated with CO. Tetramethylammonium tetrahydroborate (250 mg, 3 mmol) was added while CO was bubbled through the solution. After 20 min the yellow microcrystals which separated from the solution were filtered off, washed three times with 3 ml of methanol, and dried under high-vacuum. Yield 82%. Found: C, 65.76; H, 5.43. $\text{C}_{42}\text{H}_{40}\text{P}_3\text{ORh}$ calcd.: C, 66.68; H, 5.33%.

This compound was also obtained as follows: (a) $[\text{RhH}_3(\text{triphos})]$ (8) (73 mg, 0.1 mmol) was suspended in 5 ml dry benzene and CO was bubbled through the stirred suspension for 45 min. The resulting yellow solution contained only $[\text{RhH}(\text{CO})(\text{triphos})]$ as shown by its ^{31}P NMR spectrum.

(b) A solution of $\text{Li}[\text{HBEt}_3]$ in THF (0.3 ml of 1 M solution) was added to a solution of $[\text{Rh}(\text{CO})_2(\text{triphos})][\text{PF}_6]$ (1) (88 mg, 0.1 mmol) in 5 ml THF. The mixture was stirred for 15 min and then the solvent was evaporated to 2 ml. The product was precipitated by adding 10 ml of ether, filtered off, washed with methanol, and dried under high-vacuum. Yield 70%.

(c) Sodium borohydride (38 mg, 1 mmol) was added to a solution of $[\text{Rh}(\text{CO})_2(\text{triphos})][\text{PF}_6]$ (1) (88 mg, 0.1 mmol) in 5 ml methanol. The solution was stirred for 15 min and yellow microcrystals gradually separated. These were filtered off, washed with methanol and dried under high-vacuum. Yield 80%.

$[\text{Rh}(\text{CH}(\text{CH}_3)\text{CO}_2\text{Me})(\text{CO})(\text{triphos})]^*$ (2)

$[\text{RhH}(\text{CO})(\text{triphos})]$ (6) (227 mg, 0.3 mmol) was added to a solution of methyl acrylate (1 ml, 11 mmol) in 5 ml dichloromethane. After stirring for 1 h, 20 ml hexane were added to the orange solution, causing precipitation of the product as a yellow powder. This was filtered off, washed three times with 3 ml of hexane, and dried under high-vacuum. Yield 85%. Found: C, 64.04; H, 5.60. $\text{C}_{46}\text{H}_{46}\text{O}_3\text{RhP}_3$ calcd.: C, 65.56; H, 5.50%.

^{13}C NMR: $\delta(\text{COOR})$ 186 ppm; $\delta(\text{OCH}_3)$ 49 ppm; $\delta(\text{CH}_3$ of methyl acrylate) 26 ppm; $\delta(\text{Rh}-\text{CH})$ 17 ppm. This assignment is supported (a) by the corresponding off-resonance-spectra and (b) by the DEPT spectra.

^1H NMR: $\delta(\text{OCH}_3)$ 3.4 ppm; $\delta(\text{CH}_3$ of methyl acrylate) 1.35 ppm; $\delta(\text{Rh}-\text{CH})$ 2.5 ppm; $\delta(\text{CH}_3$ of triphos) 1.5 ppm; $\delta(\text{CH}_2$ of triphos): the geminal protons are inequivalent: (3 H_a) 2.45 ppm, (3 $\text{H}(6)$) 2.1 ppm; $^2J(\text{H},\text{H})$ 15 Hz.

X-Ray data collection

Data collection was carried out on a Philips PW 1100 automatic diffractometer. Unit cell parameters were determined by the refinement of the setting angles of 25 carefully centered reflections. The crystals belong to the monoclinic system, with extinctions $h0l$ for $h = 2n + 1$ and $0k0$ for $k = 2n + 1$, characteristic of the space

TABLE 3
CRYSTAL DATA AND DATA COLLECTION DETAILS FOR [RhH₃(triphos)]

formula	C ₄₂ H ₄₄ P ₃ Rh
mol wt	744.6
<i>a</i> (Å)	15.985(6)
<i>b</i> (Å)	19.683(7)
<i>c</i> (Å)	11.900(4)
β (deg)	103.73(6)
<i>V</i> (Å ³)	3637.1
space group	<i>P</i> 2 ₁ / <i>a</i>
<i>Z</i>	4
<i>d</i> _{calcd} (g cm ⁻³)	1.359
habit	regular prism
dimensions (mm)	0.08 × 0.12 × 0.40
linear abs coeff (cm ⁻¹)	6.19
transmission factors	0.93–0.97
radiation (Å)	Mo- <i>K</i> _α λ = 0.7107
monochromator	graphite crystal
method	ω–2θ scan
scan speed (deg/s)	0.05
scan width (deg)	0.7 + 0.3 tan θ
background time	half the scan time
standards	3 every 120 min
maximum deviation of standards (%)	2
2θ limits (deg)	5 ≤ 2θ ≤ 50
number of data with <i>I</i> ≥ 3σ(<i>I</i>)	2649
final number of variables	148

group *P*2₁/*a*. Details of crystal data and data collection are given in Table 3, and selected bond distances and angles in Table 2. The intensities *I* were corrected for background and assigned standard deviations σ(*I*) calculated by using the value of 0.03 for the instability factor *p* [18]. Intensity data were corrected for Lorentz and polarization effects and for absorption [19].

Solution and refinement of the structure

All the calculations were carried out on a SEL 32/77 computer by using the SHELX-76 [19] and ORTEP [20] programs. Atomic scattering factors for the neutral atoms were taken from ref. 21 for the non-hydrogen atoms and from ref. 22 for hydrogen atoms. Both the Δ*f*' and Δ*f*'' components of anomalous dispersion were included for all non-hydrogen atoms [23]. The refinement was based on *F*₀, the function minimized being Σ*w*(|*F*₀ – |*F*_c||)², where *w* = 1/σ²(*F*₀). The structure was solved by the heavy atom method and a few Fourier maps revealed all the non-hydrogen atoms. Full-matrix least-squares refinements were carried out assigning anisotropic thermal parameters to the rhodium and phosphorus atoms and isotropic ones to the carbon atoms. The phenyl rings of the ligand were treated as rigid groups, each carbon atom being assigned an individual thermal parameter. A difference Fourier map calculated at the *R* factor value of 0.064 using the reflections having sin δ ≤ 0.2, clearly showed three peaks at 1.4–1.6 from the metal, each *trans* to the phosphorus atoms, which were attributed to the hydride ligands. The reliability of their position parameters was confirmed by a *F*₀ Fourier map [24],

TABLE 4
POSITIONAL PARAMETERS ($\times 10^4$)

Atom	x	y	z	Atom	x	y	z
Rh	2282(1)	2270(1)	1076(1)	C(4,3)	723(4)	1094(3)	-3558(6)
P(1)	990(2)	2844(1)	867(2)	C(5,3)	71(4)	1056(3)	-2963(6)
P(2)	1479(2)	1321(1)	416(2)	C(6,3)	270(4)	1117(3)	-1761(6)
P(3)	2289(2)	2017(1)	2965(2)	C(1,4)	1922(4)	471(4)	826(5)
C(1)	-307(7)	712(6)	2915(10)	C(2,4)	1443(4)	-102(4)	385(5)
C(2)	-287(60)	1452(5)	2512(9)	C(3,4)	1772(4)	-750(4)	697(5)
C(3)	510(6)	1697(5)	2070(8)	C(4,4)	2581(4)	-824(4)	1451(5)
C(4)	386(6)	2468(4)	1840(8)	C(5,4)	3060(4)	-251(4)	1892(5)
C(5)	478(6)	1304(5)	931(8)	C(6,4)	2731(4)	397(4)	1580(5)
C(6)	1321(6)	1524(5)	3010(8)	C(1,5)	2289(4)	2732(4)	3979(5)
C(1,1)	979(4)	3753(4)	1183(7)	C(2,5)	2599(4)	3357(4)	3701(5)
C(2,1)	246(4)	4064(4)	1392(7)	C(3,5)	2642(4)	3908(4)	4451(5)
C(3,1)	235(4)	4764(4)	1565(7)	C(4,5)	2376(4)	3833(4)	5479(5)
C(4,1)	957(4)	5154(4)	1529(7)	C(5,5)	2066(4)	3208(4)	5757(5)
C(5,1)	1690(4)	4844(4)	1320(7)	C(6,5)	2022(4)	2658(4)	5007(5)
C(6,1)	1701(4)	4143(4)	1147(7)	C(1,6)	3168(4)	1502(4)	3866(6)
C(1,2)	235(4)	2811(4)	-583(5)	C(2,6)	3044(4)	1006(4)	4648(6)
C(2,2)	-655(4)	2748(4)	-745(5)	C(3,6)	3748(4)	652(4)	5304(6)
C(3,2)	-1184(4)	2738(4)	-1861(5)	C(4,6)	4576(4)	793(4)	5178(6)
C(4,2)	-822(4)	2792(4)	-2816(5)	C(5,6)	4700(4)	1289(4)	4396(6)
C(5,2)	68(4)	2856(4)	-2654(5)	C(6,6)	3996(4)	1643(4)	3740(6)
C(6,2)	596(4)	2866(4)	-1537(5)	H(1)	3126(63)	1816(48)	1184(87)
C(1,3)	1122(4)	1217(3)	-1154(6)	H(2)	2808(55)	2918(44)	1408(76)
C(2,3)	1774(4)	1256(3)	-1749(6)	H(3)	2227(52)	2485(42)	-75(78)
C(3,3)	1575(4)	1194(3)	-2951(6)				

which also showed the hydride atoms. The positional parameters as well as the isotropic thermal factors of these hydrogen atoms were included in the least-squares process and successfully refined. The hydrogen atoms of the triphos-I ligand were introduced in calculated positions but not refined. The refinements converged at the R and R_w factors values of 0.057 and 0.052 respectively. R and R_w are defined as $\Sigma \|F_o| - |F_c| \| / \Sigma |F_o|$ and $[\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$ respectively. Final positional parameters are listed in Table 4. Lists of thermal parameters and structure factors are available from the authors on request.

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