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Complexes of Iridium(I) and Rhodium(I) with Polydentate Phosphines¹

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Iridium(I) and rhodium(I) complexes of $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$ (triphos), $(C_6H_5)_2PCH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)_2$ (tetraphos-1), and $P[CH_2CH_2P(C_6H_5)_2]_3$ (tetraphos-2) are described. The reactions of $M(CO)Cl(PPh_3)_2$ ($M =$ iridium(I), rhodium(I)) with triphos, tetraphos-1, and tetraphos-2 in boiling benzene gave respectively the complexes $[M(\text{triphos})(CO)]Cl$, $[M(\text{tetraphos-1})]Cl$, and $[M(\text{tetraphos-2})(CO)]Cl$. The iridium(I) and rhodium(I) complexes thus prepared undergo oxidative addition reactions with molecular hydrogen, hydrogen chloride, and methyl iodide. Reaction with molecular oxygen gave the corresponding dioxygen complexes with $[M(\text{tetraphos-1})]Cl$ and $[M(\text{tetraphos-2})(CO)]Cl$. The complexes $[M(\text{triphos})(CO)]Cl$ undergo oxidation of coordinated carbonyl to the carbonato group by molecular oxygen.

Introduction

In recent years a number of multidentate phosphine ligands and their complexes has been studied. The ligands $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$ (triphos), $(C_6H_5)_2PCH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)_2$ (tetraphos-1) and $P[CH_2CH_2P(C_6H_5)_2]_3$ (tetraphos-2) were first synthesized by King and Kapoor² and their complexes with several metal ions have been reported.³ The isomeric ligands tetraphos-1 and tetraphos-2 contain respectively linear P-P-P and tripod P-P₃ arrangements of the donor phosphorus atoms. Siegel, *et al.*,⁴ have reported the iridium(I) and rhodium(I) complexes of the tripod ligand 1,1,1-tris(diphenylphosphinomethyl)ethane (TDPME). Several complexes of TDPME and closely related ligands were studied by Venanzi and coworkers.⁵ Complexes of the tripod tetradentate ligands $[(CH_3)_2AsCH_2CH_2CH_2]_3As$ were reported by Barclay and Barnard⁶ and by Benner and Meek.⁷ The complexes of $[(CH_3)_2AsCH_2CH_2]_3P$ were investigated by Benner, *et al.*⁸

As a part of a general investigation by the authors on the activation of small molecules by metal ions in homogeneous catalysis, it was considered important to study the complexes formed by the polydentate ligands triphos, tetraphos-1, and tetraphos-2 with iridium(I) and rhodium(I). A special advantage of the terdentate or tetradentate character of these polyphosphine ligands is the attainment of stereochemistries and specific geometries of metal complexes not possible with the corresponding monophosphine (unidentate) ligands. Such stereochemical requirements may result in interesting changes in the reactivity pattern of the phosphine complexes of iridium(I) and rhodium(I). The synthesis of some new complexes formed by treatment of $IrCl(CO)(PPh_3)_2$ and $RhCl(CO)(PPh_3)_2$ with triphos, tetraphos-1, and tetraphos-2 and reactions of the resulting complexes with small molecules are reported in this paper.

Experimental Section

The ligands triphos, tetraphos-1, and tetraphos-2 were purchased from Pressure Chemical Corp., Inc. Rhodium(III) chloride and iri-

um(III) chloride were obtained from Alfa Inorganics. Microanalyses were performed by Chemalytics, Tempe, Ariz., and Australian Micro-analytical Service, CSIRO, Canberra, Australia. Infrared spectra in Nujol mull were recorded on a Beckman IR-12 and the far-infrared spectra were measured in Nujol mull pressed between polyethylene plates with a Perkin-Elmer FIS-3 spectrophotometer. The nmr spectra of the solution of the samples in deuterated chloroform were recorded with a Varian T-60 spectrometer. The conductivity measurements were done on an Elico conductivity bridge in dimethylformamide solution on complexes 1-6 of Table I at 30°. All reactions were carried out in a glove box under a purified nitrogen atmosphere. The nitrogen led into the glove box was freed from oxygen and moisture by passing through a vanadium(II) sulfate solution and finally through Ascarite. All solvents were purged with purified nitrogen prior to their use. The complexes $IrCl(CO)(PPh_3)_2$ ⁹ and $RhCl(CO)(PPh_3)_2$ ¹⁰ were prepared by standard procedures.

Synthesis of Complexes. The six complexes of Table I were synthesized by a general synthetic scheme that involves the addition of 0.010 mol of $MCl(CO)(PPh_3)_2$ ($M = Ir, Rh$) to about 50 ml of dry benzene in a Schlenk tube. To the yellow solution was added 0.015 mol of triphos, 0.010 mol of tetraphos-1, or 0.010 mol of tetraphos-2 and the solution was heated for 2 hr at 80-90°. In the case of iridium(I), when heated, the solution turned greenish yellow for triphos and yellow for tetraphos-1 and tetraphos-2 complexes, respectively. For rhodium(I) however, on heating, the solution acquired an orange-red color for triphos, yellow for tetraphos-1, and orange for tetraphos-2 complexes, respectively. The solutions in all cases were cooled to room temperature and about 50 ml of hexane was then added. The products $[M(\text{triphos})(CO)]Cl$ (I), $[M(\text{tetraphos-1})]Cl$ (II), and $[M(\text{tetraphos-2})(CO)]Cl$ (III) were collected by filtration, washed with hexane, and dried under vacuum. Yields, analytical data, and colors of the products are tabulated in Table I. The samples were heated at 50° under vacuum before carrying out elementary analyses. Table II presents the analytical data on the stable solid products obtained by the reaction of complexes 1-6 of Table I with CO , O_2 , HCl , and CH_3I . The discrepancies between the analyses and the compositions deduced from the spectroscopic data may be due to incomplete removal of the solvent on drying or the presence of a small amount of occluded reactant. The possibility of decomposition of these complexes precluded further purification by recrystallization.

Carbonylation of $[M(\text{triphos})(CO)]Cl$, $[M(\text{tetraphos-1})]Cl$, and $[M(\text{tetraphos-2})(CO)]Cl$. About 0.010 mol of I, II, or III was dissolved in dry chloroform in a Schlenk tube and a stream of carbon monoxide was passed through the solution till there was no further color change. Addition of cyclohexane precipitated out the carbonyls which were filtered and dried under vacuum. The complexes $[M(\text{triphos})(CO)]Cl$ gave a bright yellow (iridium(I)) and chocolate-colored (rhodium(I)) dicarbonyl, respectively. In the case of $[M(\text{tetraphos-1})]Cl$ yellow carbonyls of the composition $[M(\text{tetraphos-1})(CO)]Cl$ were obtained. For the $[M(\text{tetraphos-2})(CO)]Cl$, however, there was no indication of reaction with carbon monoxide.

Oxygenation of the Complexes. About 0.010 mol of each of six complexes of Table I was dissolved in benzene and a stream of

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(2) R. B. King and P. N. Kapoor, *J. Amer. Chem. Soc.*, **93**, 4158 (1971).

(3) (a) R. B. King, P. N. Kapoor, and R. N. Kapoor, *Inorg. Chem.*, **10**, 1841 (1971); (b) R. B. King, R. N. Kapoor, M. S. Saran, and P. N. Kapoor, *Inorg. Chem.*, **10**, 1851 (1971).

(4) W. O. Siegel, S. J. Lapporte, and J. P. Collman, *Inorg. Chem.*, **10**, 2158 (1971).

(5) L. M. Venanzi, *Angew. Chem.*, **76**, 621 (1964).

(6) G. A. Barclay and A. K. Barnard, *J. Chem. Soc.*, 4269 (1961).

(7) G. S. Benner and D. W. Meek, *Inorg. Chem.*, **6**, 1399 (1967).

(8) G. A. Benner, W. E. Hatfield, and D. W. Meek, *Inorg. Chem.*, **3**, 1544 (1964).

(9) D. Evans, J. A. Osborn, and G. Wilkinson, *Inorg. Syn.*, **11**, 99 (1968).

(10) J. P. Collman, C. T. Sears, Jr., and M. Kuboles, *Inorg. Syn.*, **11**, 101 (1968).

Table I. Analytical Data for the Iridium(I) and Rhodium(I) Complexes of Polydentate Phosphines^a

Entry	Compd	Color	Analysis, %								Yield, %
			C		H		Cl		P		
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
1	[Ir(triphos)(CO)]Cl	Greenish yellow	53.28	54.70	4.36	4.54	4.50	5.31	11.82	11.27	95
2	[Rh(triphos)(CO)]Cl	Beige	58.58	57.20	4.65	4.48	5.10	5.25	12.42	11.63	95
3	[Ir(tetraphos-1)]Cl	Yellow	55.82	54.13	4.60	4.63	4.00	4.80	13.81	12.21	85
4	[Rh(tetraphos-1)]Cl	Yellow	62.30	60.73	5.20	5.16	4.41	4.56	15.31	13.56	80
5	[Ir(tetraphos-2)(CO)]Cl	Yellow	54.61	54.80	4.51	4.56	3.81	5.32	13.41	12.55	80
6	[Rh(tetraphos-2)(CO)]Cl	Orange	60.32	58.90	5.01	5.09	4.21	5.57	14.81	13.46	80

^a Conductivities in units of $M^{-1} \text{ cm}^2 \text{ ohm}^{-1}$: 1, 78; 2, 72; 3, 85; 4, 82; 5, 90; 6, 86.

Table II. Analytical Data for the Reactions of Iridium(I) and Rhodium(I) Complexes of Polyphosphines with Small Molecules

Entry	Compd	Analysis, %							
		C		H		Cl		P	
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
1	[Ir(triphos)(CO) ₂]Cl	52.64	52.24	4.04	4.02	4.34	4.01	11.38	10.88
2	[Rh(triphos)(CO) ₂]Cl	59.30	58.84	4.53	4.50	4.98	5.24	12.65	13.12
3	[Ir(tetraphos-1)(CO)]Cl	55.76	56.24	4.57	4.60	3.84	5.02	13.40	12.66
4	[Rh(tetraphos-1)(CO)]Cl	61.67	60.98	5.02	5.06	4.24	4.80	14.82	13.50
5	[Ir(triphos)(CO) ₂]Cl	52.59	53.28	4.01	4.03	4.42	4.85	11.32	11.63
6	[Rh(triphos)(CO) ₂]Cl	58.98	48.28	4.51	4.54	4.85	4.25	12.70	12.24
7	[Ir(tetraphos-2)(CO)(O ₂)]Cl	53.76	53.26	4.34	4.32	3.71	4.02	12.95	13.24
8	[Rh(tetraphos-2)(CO)(O ₂)]Cl	59.40	60.01	4.84	4.82	4.08	4.38	14.28	14.70
9	Ir(triphos)Cl ₃	49.01	49.72	3.96	3.94	12.79	13.00	11.17	11.84
10	Rh(triphos)Cl ₃	54.83	55.34	4.44	4.41	14.31	13.42	12.51	12.02
11	Ir(tetraphos-2)Cl ₃	52.04	52.44	4.34	4.31	11.00	11.42	12.80	12.44
12	Rh(tetraphos-2)Cl ₃	57.31	58.21	4.78	4.76	12.10	12.72	14.10	14.92
13	Rh(tetraphos-1)Cl ₃	57.31	57.92	4.78	4.74	12.10	12.62	14.10	14.72
14	[Ir(triphos)(CO)(CH ₃)]Cl	46.38	46.78	3.87	3.85	3.81	3.95	9.98	10.22
15	[Rh(triphos)(CO)(CH ₃)]Cl	51.28	51.78	4.27	4.24	4.21	4.61	11.04	11.44
16	[Ir(tetraphos-1)(CH ₃)]Cl	49.78	49.48	4.33	4.31	3.42	3.62	11.93	12.23
17	[Rh(tetraphos-1)(CH ₃)]Cl	54.29	55.00	4.73	4.71	3.82	4.00	13.05	13.62
18	[Ir(tetraphos-2)(CH ₃)(CO)]Cl	53.96	54.22	4.60	4.58	3.63	3.93	12.68	13.42
19	[Ir(tetraphos-2)(CH ₃)(CO)]Cl	49.48	50.01	4.23	4.20	3.32	3.42	11.62	12.00

molecular oxygen was passed through the solution. In the case of [M(tetraphos-1)]Cl and [M(tetraphos-2)(CO)]Cl the dioxygen complexes were precipitated as brown solids by adding hexane to the solution. In the case of [M(triphos)(CO)]Cl molecular oxygen oxidized the coordinated carbonyl to form the carbonate complexes [M(triphos)(CO₃)]Cl.

Hydrogenation of the Complexes. Molecular hydrogen was bubbled through a 0.010 *M* benzene solution of the complexes [M(triphos)(CO)]Cl, [M(tetraphos-1)]Cl, and [M(tetraphos-2)(CO)]Cl for about 1–2 hr. The infrared spectra of the resulting complexes were recorded in benzene solution in a KRS-5 cell. In all the cases, *cis*-dihydrides were formed by the oxidative addition of hydrogen. The hydrides were very labile and could not be isolated in the solid state.

Reaction of the Complexes with Hydrochloric Acid. The reaction of the complexes [M(triphos)(CO)]Cl, [M(tetraphos-1)]Cl, and [M(tetraphos-2)(CO)]Cl with hydrochloric acid was conducted in a Schlenk tube by mixing 10 ml of a 0.010 *M* solution of the complex in methanol with 2 ml of 10% methanolic hydrochloric acid and heating the solution at reflux for about 1 hr. The complexes [M(triphos)(CO)]Cl, [Rh(tetraphos-1)]Cl, and [M(tetraphos-2)(CO)]Cl gave the corresponding trichlorides, M(triphos)Cl₃, Rh(tetraphos-1)Cl₃, and M(tetraphos-2)Cl₃, the first and third with the loss of coordinated carbon monoxide. Reaction of [Ir(tetraphos-1)]Cl with hydrochloric acid, on the other hand, gave pale yellow crystals of [Ir(tetraphos-1)(H)(Cl)]Cl.

Reaction of the Complexes with Methyl Iodide. To about 10 ml of a 0.030 *M* solution of [M(triphos)(CO)]Cl, [M(tetraphos-1)]Cl, and [M(tetraphos-2)(CO)]Cl in dry methanol was added 0.20 ml of a 1.0 *M* solution of methyl iodide in methanol. The solution was heated at reflux in a Schlenk tube for about 1 hr and the product was precipitated with dry hexane.

Results

Table III presents the infrared spectra of the six main complexes (no. 1–6) and their reaction products with carbon monoxide (no. 7–10), molecular oxygen (no. 11–16), molecular hydrogen (no. 17–22), and hydrochloric acid (no. 23–28). Assignments of the carbonyl (C–O stretch), metal-

hydride, metal-dioxygen, and metal-halide frequencies were based on comparisons with known spectra of related compounds.^{3a,4} The assignment of the metal-phosphorus bands in the range 340–550 cm^{-1} must be regarded as tentative until more quantitative data become available on these compounds. Table IV presents the proton magnetic resonance spectra of the six main compounds (no. 1–6) and their oxidative addition products with methyl iodide (no. 7–12). Attempts to obtain the nmr spectra of the hydrides in the high-field metal-hydride region failed due to the instability of the hydrides in the several solvents investigated.

Carbonylation of the Complexes. Carbonylation of the complexes [M(triphos)(CO)]Cl and [M(tetraphos-1)]Cl resulted in the formation of the compounds [M(triphos)(CO)₂]Cl and [M(tetraphos-1)(CO)]Cl, respectively. The dicarbonyl compounds (entries 7 and 8, Table III) were confirmed by a strong peak around 1940 cm^{-1} and a shoulder at 1950 cm^{-1} (iridium) and at 1975 cm^{-1} (rhodium), characteristic of *cis*-dicarbonyls.⁶ The compounds [Ir(tetraphos-1)(CO)]Cl and [Rh(tetraphos-1)(CO)]Cl (entries 9 and 10, Table III) were confirmed by the appearance of peaks at 1925 and 1935 cm^{-1} , respectively, characteristic of metal-carbonyl stretch. In the case of [M(tetraphos-2)(CO)]Cl complexes, the infrared spectra of the solution of the complexes through which carbon monoxide was passed were identical with the spectra of the parent compounds in the 1920–2100- cm^{-1} spectral range. This indicated that no further carbonylation of the compounds had taken place.

Oxygenation of the Complexes. Oxygenation of [M(triphos)(CO)]Cl resulted in the disappearance of the characteristic carbonyl peaks at 1940 and 1935 cm^{-1} respectively of the iridium(I) and rhodium(I) complexes and appearance of new peaks at 1645 (m) and 1620 cm^{-1} (s) in the iridium-

Table III. Infrared Spectra of the Poly(tertiary phosphine) Complexes of Iridium(I) and Rhodium(I) and the Reaction Products with Carbon Monoxide, Molecular Oxygen, Hydrogen, and Hydrogen Chloride^a

Entry	Compd	$\nu(\text{CO}), \text{cm}^{-1}$	$\nu(\text{M}-\text{O}_2), \text{cm}^{-1}$	$\nu(\text{M}-\text{H}), \text{cm}^{-1}$	Other bands, 250–600 cm^{-1}
1	[Ir(triphos)(CO)]Cl	1940 s			420 w, 487 m, 525 m, 540 m
2	[Rh(triphos)(CO)]Cl	1935 s			425 w, 485 w, 525 m, 550 m
3	[Ir(tetraphos-1)]Cl				425 w, 487 w, 532 s
4	[Rh(tetraphos-1)]Cl				420 w, 485 w, 530 s
5	[Ir(tetraphos-2)(CO)]Cl	1945 s			337 s, 360 sh, 420 s, 487 s
6	[Rh(tetraphos-2)(CO)]Cl	1950 s			340 s, 362 sh, w, 412 s, 480 s, 525 s
7	[Ir(triphos)(CO) ₂]Cl	1935 s, 1950 m			420 w, 520 m, 540 m
8	[Rh(triphos)(CO) ₂]Cl	1940 s, 1975 br			420 w, 515 m, 550 m
9	[Ir(tetraphos-1)(CO)]Cl	1925 m			420 w, 480 w, 530 m
10	[Rh(tetraphos-1)(CO)]Cl	1935 m			420 w, 480 w, 532 m
11	[Ir(triphos)(CO) ₂]Cl				1645 m, 1620 s, 415 w, 480 w, 520 m
12	[Rh(triphos)(CO) ₂]Cl				1755 m, 1625 s, 420 w, 480 w, 520 m
13	[Ir(tetraphos-1)(O ₂)]Cl		870 s		425 w, 487 w, 530 s
14	[Rh(tetraphos-1)(O ₂)]Cl		850 s		420 w, 485 w, 530 s
15	[Ir(tetraphos-2)(CO)(O ₂)]Cl	1945 s	875 s		335 s, 415 s, 480 s, 520 s, 500 br
16	[Rh(tetraphos-2)(CO)(O ₂)]Cl	1950 s	845 s		335 s, 415 s, 480 s, 520 s, 550 m
17	[Ir(triphos)(CO)(H) ₂]Cl	1940 m		1980 br, 2020 sh	415 w, 480 m, 520 m
18	[Rh(triphos)(CO)(H) ₂]Cl	1935 m		1985 br, 2020 sh	420 w, 480 m, 522 m
19	[Ir(tetraphos-1)(H) ₂]Cl			1970 br, 2100 sh	420 w, 480 w, 530 s
20	[Rh(tetraphos-1)(H) ₂]Cl			1975 br, 2100 sh	415 w, 480 w, 520 s
21	[Ir(tetraphos-2)(CO)(H) ₂]Cl	1938 s		1970 br, 2050 sh	330 s, 415 s, 480 s, 520 s, 550 s
22	[Rh(tetraphos-2)(CO)(H) ₂]Cl	1942 s		1975 br, 2050 sh	335 s, 412 s, 480 s, 520 s, 550 s
23	Ir(triphos)Cl ₃				220–240 br, 480 m, 520 m
24	Rh(triphos)Cl ₃				230–250 br, 480 m, 520 m
25	Ir(tetraphos-2)Cl ₃				220–260 br, 335 s, 415 s, 480 s, 520–550 br
26	Rh(tetraphos-2)Cl ₃				220–260 br, 335 s, 415 s, 480 s, 520–550 br
27	[Ir(tetraphos-1)(H)(Cl)]Cl			1930 s	220–250 br, 487 w, 530 s
28	Rh(tetraphos-1)Cl ₃				220–250 br, 485 w, 530 s

^a Key: s, strong; m, medium; w, weak; br, broad; sh, shoulder.

Table IV. Proton Nmr Spectra of Iridium(I) and Rhodium(I) Complexes of Poly(tertiary phosphines)^a

Entry	Compd	Chem shifts, τ	
		Phenyl protons	Methylene protons
1	[Ir(triphos)(CO)]Cl	2.7 d	8.4 d
2	[Rh(triphos)(CO)]Cl	2.2 d	7.8 d
3	[Ir(tetraphos-1)]Cl	2.6 t	7.8 s
4	[Rh(tetraphos-1)]Cl	2.1 t	7.7 s
5	[Ir(tetraphos-2)(CO)]Cl	2.5 m	7.0 m
6	[Rh(tetraphos-2)(CO)]Cl	2.3 m	7.0 m
7	[Ir(triphos)(CO)(CH ₃)I]Cl	2.7 d	7.0–8.6 br, m
8	[Rh(triphos)(CO)(CH ₃)I]Cl	2.2 d	7.0–8.5 br, m
9	[Ir(tetraphos-1)(CH ₃)I]Cl	2.6 t	8.0–9.0 br, m
10	[Rh(tetraphos-1)(CH ₃)I]Cl	2.1 t	8.0–9.0 br, m
11	[Ir(tetraphos-2)(CO)(CH ₃)I]Cl	2.5 d	7.2–8.5 br, m
12	[Rh(tetraphos-2)(CO)(CH ₃)I]Cl	2.8 d	7.2–8.5 br, m

^a Key: d, doublet; s, singlet; t, triplet; m, multiplet; br, broad.

(III) complex and at 1655 (m) and 1625 cm^{-1} (s) for the rhodium(III) complex (entries 11 and 12, Table III), indicating the formation of carbonate complexes⁴ by the oxidation of the coordinated carbonyl group. The carbonate complexes decomposed slowly in solution to form products that were not characterized.

Well-defined dioxygen complexes of the composition [M-(tetraphos-1)(O₂)]Cl (entries 13 and 14, Table III) and [M-(tetraphos-2)(CO)(O₂)]Cl (entries 15 and 16, Table III) were obtained by the oxygenation of [M(tetraphos-1)]Cl and [M(tetraphos-2)(CO)]Cl, respectively. In the case of [M-(tetraphos-2)(CO)]Cl, the formation of the dioxygen complexes took place without the oxidation of the coordinated carbonyl group, as evidenced by the existence of the carbonyl peaks at 1945 cm^{-1} (iridium) and 1950 cm^{-1} (rhodium) in the spectra of the oxygenated complexes. The dioxygen complexes (entries 13–16, Table III) were confirmed by the appearance of an intense peak at 845–870 cm^{-1} , characteristic of the M–O₂ group, and also by the reaction of

the dioxygen complexes with sulfur dioxide to form the sulfato complexes.⁴

Hydrogenation of the Complexes. Hydrogenation of the complexes took place readily in benzene solution to form the *cis*-dihydrides (entries 17–22, Table III) in solution. The *cis*-dihydrides were confirmed by the appearance of a broad peak around 1970–1980 cm^{-1} and a shoulder around 2000–2110 cm^{-1} . The *cis*-dihydrides were stable only in solution.

Reaction of the Complexes with Hydrogen Chloride. Reaction of [M(triphos)(CO)]Cl and [M(tetraphos-2)(CO)]Cl with hydrochloric acid resulted in the loss of coordinated carbon monoxide and formation of the trivalent yellow chlorides (entries 23–26, Table III). The presence of coordinated chloride in these compounds (no. 23–26) was confirmed by the presence of a broad band in 220–260 cm^{-1} in the far-infrared spectra of the complexes. The formation of Ir(tetraphos-1)(H)Cl₂ (entry 27, Table III) was confirmed by the presence of a sharp peak at 1930 cm^{-1} , characteristic of M–H stretch. The complex [Rh(tetraphos-1)]Cl reacted with hydrochloric acid to give Rh(tetraphos-1)Cl₃, confirmed by the appearance of a broad band in the 220–260 cm^{-1} region.

Reaction of the Complexes with Methyl Iodide. Oxidative addition of methyl iodide to complexes 1–6, Table III, proceeded quite readily in methanol solution to form the corresponding complexes of iridium(III) and rhodium(III) (entries 7–12, Table IV). The nmr spectra of the methyl iodide oxidative addition products show a complicated splitting pattern in the range τ 7.0–9.0 of the ligand methylene protons and the protons of the coordinated methyl group.

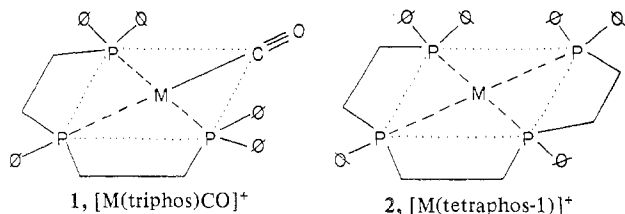
Discussion

The displacement of the coordinated unidentate phosphine ligands from IrCl(CO)(PPh₃)₂ and RhCl(CO)(PPh₃)₂ in benzene solution by the poly(tertiary phosphine) ligands triphos,

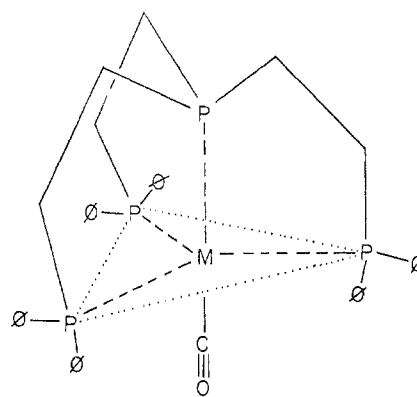
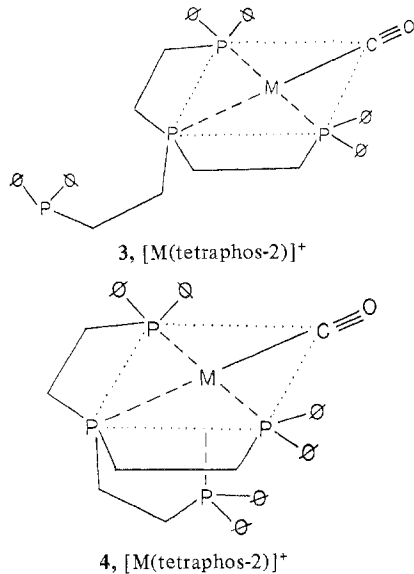
tetraphos-1, and tetraphos-2 and precipitation of the complexes by petroleum ether afford the most convenient method for the preparation of the poly(tertiary phosphine) complexes of iridium(I) and rhodium(I). The method gave a quantitative yield of the compounds with no possibility of the dimerization or polymerization which sometimes occur when IrCl_3 or RhCl_3 in hydrochloric acid are used as starting materials.

The structures I, II, and III, assigned to the three main groups of complexes $[\text{M}(\text{triphos})(\text{CO})\text{Cl}]$, $[\text{M}(\text{tetraphos-1})\text{Cl}]$, and $[\text{M}(\text{tetraphos-2})(\text{CO})\text{Cl}]$ are based on infrared and nmr spectra (Tables III and IV). The absence of coordinated chloride in complexes 1-6 of Table III is confirmed by the absence of peaks in the $220\text{--}270\text{-cm}^{-1}$ range in the far-infrared spectra² and also by facile conversion of the compounds to the corresponding tetraphenylborates which gave spectra identical with those tabulated for compounds 1-6 in Table III. Conductivity of complexes 1-6 in dimethylformamide (Table I) was in the range $72\text{--}90\text{ M}^{-1}\text{ cm}^2\text{ ohm}^{-1}$ as expected¹¹ for a 1:1 electrolyte in this solvent.

For the $[\text{M}(\text{triphos})(\text{CO})\text{Cl}]$ complexes nmr evidence (phenyl doublet at $\tau 2.7$ and methylene doublet at $\tau 8.4$) indicates probable coordination of triphos in three coordination positions in the plane of the metal ion with the carbonyl occupying the fourth position (formula 1). Complexes of the type $[\text{M}(\text{tetraphos-1})\text{Cl}]$ may have the tetradentate ligand tetraphos-1 coordinated to all the four positions in the plane of the metal ion (formula 2). This is confirmed by

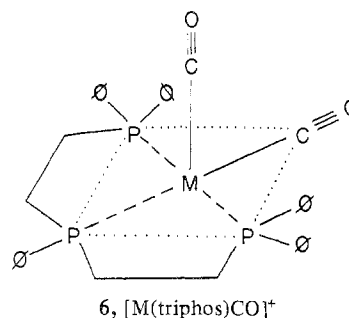


the appearance of a phenyl triplet at $\tau 2.6$ and a single methylene resonance peak at about $\tau 7.8$. The tripod ligand tetraphos-2 may be coordinated to three of four positions on the metal ion in the complexes $[\text{M}(\text{tetraphos-2})(\text{CO})\text{Cl}]$ to form respectively a planar four-coordinate complex (formula 3), a five-coordinate square-pyramidal arrangement (formula 4), or a trigonal-bipyramidal complex (formula 5).

5, $[\text{M}(\text{tetraphos-2})]^+$

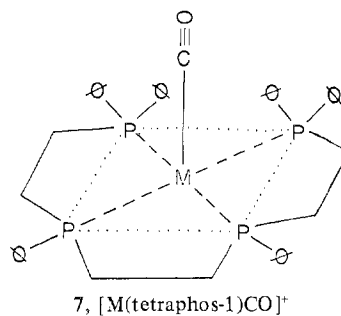
There is not enough evidence based on ^{31}P resonance spectra to favor any one of these over the other configurations. The proton nmr spectra of $[\text{M}(\text{tetraphos-2})(\text{CO})\text{Cl}]$ with a multiplet at $\tau 2.5$ (phenyl protons) and another at $\tau 7.0$ (methylene protons) are in agreement with any one of 3, 4, and 5.

In the carbonylation of $[\text{M}(\text{triphos})(\text{CO})\text{Cl}]$ a five-coordinate *cis*-dicarbonyl complex 6 was formed by the addition



of another carbonyl group in the axial position of 1. Formation of *cis*-dicarbonyls was also observed⁴ in the reaction of the iridium(I) and rhodium(I) complexes $\text{M}(\text{TDPME})(\text{CO})\text{Cl}$ of the tripod ligand TDPME. The carbonyl frequencies at $1935\text{--}1940$ and $1950\text{--}1970\text{ cm}^{-1}$ in $[\text{M}(\text{triphos})(\text{CO})_2]\text{Cl}$ are those expected⁴ for five-coordinate iridium(I) or rhodium(I) complexes with three coordinated phosphine groups.

Complexes of the type $[\text{M}(\text{tetraphos-1})\text{Cl}]$ that have the tetradentate ligand tetraphos-1 coordinated to all the four positions in the plane of the metal ion added one molecule of carbon monoxide at the fifth position to give the carbonyl species $[\text{M}(\text{tetraphos-1})\text{CO}]\text{Cl}$; see formula 7. Further

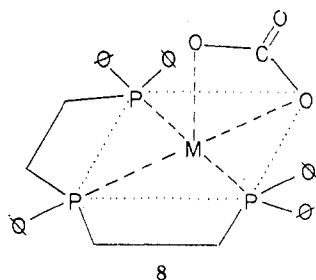


carbonylation of $[\text{M}(\text{tetraphos-1})\text{CO}]\text{Cl}$ did not take place.

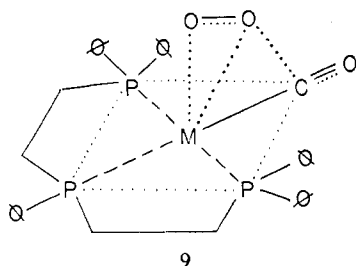
The carbonylation of $[\text{M}(\text{tetraphos-2})\text{CO}]\text{Cl}$ did not result in the formation of the *cis*-dicarbonyl as was the case for the $[\text{M}(\text{triphos})\text{CO}]\text{Cl}$ complexes. This strongly suggests that a fifth coordination position is already occupied in the

complexes by tetraphos-2 in structures of the types 4 and 5 so that further addition of 1 mol of carbon monoxide was not possible as it would give rise to a six-coordinate rhodium(I) or iridium(I) species.

Oxidation of the coordinated carbonyl group in the complexes $[M(\text{triphos})(\text{CO})]\text{Cl}$ to a carbonato complex 8 might

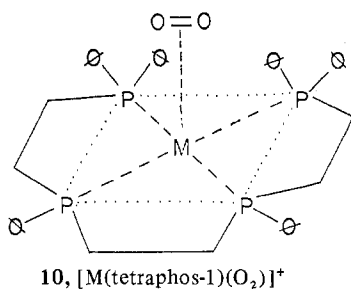


have proceeded through the formation of an intermediate dioxygen complex which then attacks the cis carbonyl group as in 9. The formation of the carbonato complex might



have proceeded through the formation of an intermediate peroxy carbonate.^{12,13} Formation of unstable carbonato complexes by the oxygenation of $\text{Ir}(\text{TDPME})(\text{CO})\text{Cl}$ was also reported by Siegel, *et al.*⁴

Oxygenation of the complexes $[M(\text{tetraphos-1})]\text{Cl}$ and $[M(\text{tetraphos-2})(\text{CO})]\text{Cl}$ gave rise to stable dioxygen complexes of the type $[M(\text{tetraphos-1})(\text{O}_2)]\text{Cl}$ (see 10) and $[M$

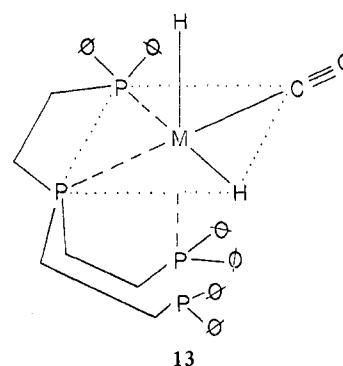
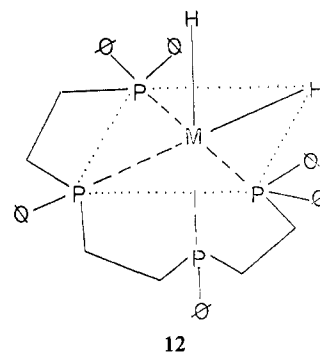
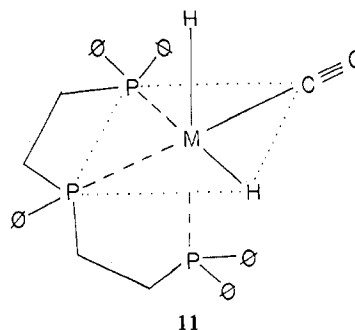


(tetraphos-2)(CO)(O₂)]Cl, respectively. Oxygenation of the cationic rhodium(I) complexes $[\text{RhL}_4]^+$ ($L = \text{P}(\text{C}_6\text{H}_5)(\text{CH}_3)_2, \text{P}(\text{OCH}_3)_3, \text{P}(\text{OC}_2\text{H}_5)_3$) to stable $[\text{RhL}_4(\text{O}_2)]^+$ was reported by Haines.¹⁴ The coordinated carbonyl group in $[M(\text{tetraphos-2})(\text{CO})]\text{Cl}$ seems to be more strongly coordinated than the carbonyl group in $[M(\text{triphos})(\text{CO})]\text{Cl}$ as the former complexes were not oxidized to the carbonato complexes by molecular oxygen.

The complexes $[M(\text{tetraphos-1})(\text{O}_2)]\text{Cl}$ and $[M(\text{tetraphos-2})(\text{CO})(\text{O}_2)]\text{Cl}$ underwent facile addition reactions with sulfur dioxide to form the corresponding sulfato complexes. The infrared spectra of the sulfato complexes gave peaks around 1250, 1135, 1000, and 890 cm^{-1} , that are charac-

teristic of a bidentate sulfate.^{13,15} The coordinated dioxygen in the complexes $[M(\text{tetraphos-1})(\text{O}_2)]\text{Cl}$ and $[M(\text{tetraphos-2})(\text{CO})(\text{O}_2)]\text{Cl}$ was quite labile and was readily liberated to regenerate the parent compounds. In this regard the chelated phosphine dioxygen complexes were different from those of the monodentate phosphine complexes where the coordinated dioxygen is more stable.^{14,16-18}

The hydrogenation of $[M(\text{triphos})(\text{CO})]\text{Cl}$, $[M(\text{tetraphos-1})]\text{Cl}$, and $[M(\text{tetraphos-2})(\text{CO})]\text{Cl}$ proceeded quite readily through oxidative addition to form dihydrido complexes of iridium(III) and rhodium(III). In order to form the *cis*-dihydride, the coordinated phosphine groups might have undergone rearrangement in the hydrido complexes. Probable structures of $[M(\text{triphos})(\text{CO})(\text{H})_2]\text{Cl}$, $[M(\text{tetraphos-1})(\text{H})_2]\text{Cl}$, and $[M(\text{tetraphos-2})(\text{H})_2(\text{CO})]\text{Cl}$ are shown in formulas 11, 12, and 13, respectively. The hydrides could not



be characterized further due to their lability in solution.

Reaction of the complexes $[M(\text{triphos})(\text{CO})]\text{Cl}$, $[M(\text{tetraphos-2})(\text{CO})]\text{Cl}$, and $[\text{Rh}(\text{tetraphos-1})]\text{Cl}$ with hydrogen chloride resulted in the "oxidative" addition to form the corresponding trichlorides (entries 23-26 and 28, Table III).

(15) R. W. Horn, E. Weinberger, and J. P. Collman, *Inorg. Chem.*, **9**, 2367 (1970).

(16) L. Vaska, *Science*, **140**, 809 (1963).

(17) J. J. Davison and S. D. Robinson, *J. Chem. Soc. A*, 762 (1971).

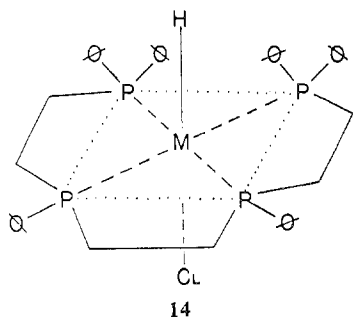
(18) A. Nakamura, Y. Tatsuno, M. Yamamoto, and S. Otsuka, *J. Amer. Chem. Soc.*, **93**, 6052 (1971).

(12) P. J. Hayward, D. M. Blake, G. Wilkinson, and C. J. Nyman, *J. Amer. Chem. Soc.*, **92**, 5873 (1970).

(13) J. Valentine, D. Valentine, Jr., and J. P. Collman, *Inorg. Chem.*, **10**, 219 (1971).

(14) L. M. Haines, *Inorg. Chem.*, **10**, 1685 (1971).

The reaction of $[\text{Ir}(\text{tetraphos-1})]\text{Cl}$ with hydrogen chloride, however, resulted in the formation of *trans*- $[\text{Ir}(\text{tetraphos-1})\text{(H)}(\text{Cl})]\text{Cl}$ (see 14) with a metal hydride stretching frequen-



cy at 1930 cm^{-1} . The formation of stable hydrides by the oxidative addition reaction of iridium(I) complexes with hydrochloric acid is quite well known.^{19,20} Iridium(III) hydrido complexes in general are more stable than the corresponding rhodium(III) complexes.

Oxidative addition of methyl iodide to $[\text{M}(\text{triphos})(\text{CO})]\text{Cl}$, $[\text{M}(\text{tetraphos-1})]\text{Cl}$, and $[\text{M}(\text{tetraphos-2})(\text{CO})]\text{Cl}$ resulted in the formation of methyl iodide adducts. Oxidative addition of cationic rhodium complexes of the type $[\text{RhL}_4]^+$ ($\text{L} = \text{P}(\text{C}_6\text{H}_5)(\text{CH}_3)_2$, $\text{P}(\text{OCH}_3)_3$) with methyl iodide was reported by Haines.²¹ The adducts obtained in the present investigation were methyl iodide adducts and not the diiodides, as verified by the elemental analysis (Table II). The metal- CH_3 peak in the $400\text{--}500\text{ cm}^{-1}$ region could not be identified in

(19) J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1625 (1964).

(20) J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc. A*, 604 (1962).

(21) L. M. Haines, *Inorg. Chem.*, 10, 1971 (1971).

the ir because of the overlap with the ligational peaks of the polyphosphines. The broad multiplet in the range $\tau\ 7.0\text{--}8.5$ in the nmr spectra of complexes 7-12 of Table IV may be due to the coupling of the coordinated methyl group with the phosphorus atoms in the plane of the metal ion and the methylene groups in a complicated splitting pattern. There was, however, no change in the nmr spectrum of the phenyl protons of the methyl iodide adducts as compared to the original complexes.

As mentioned in the earlier part of the Discussion, iridium(I) and rhodium(I) complexes of poly(tertiary phosphines) form labile adducts with molecular hydrogen and oxygen and as such are possible catalysts in homogeneous hydrogenation and oxygenation reactions. Investigations of catalytic properties of the metal complexes described in this paper are in progress.

Registry No. $[\text{Ir}(\text{triphos})(\text{CO})]\text{Cl}$, 52175-33-4; $[\text{Rh}(\text{triphos})(\text{CO})]\text{Cl}$, 52175-34-5; $[\text{Ir}(\text{tetraphos-1})]\text{Cl}$, 52225-40-8; $[\text{Rh}(\text{tetraphos-1})]\text{Cl}$, 52224-99-4; $[\text{Ir}(\text{tetraphos-2})(\text{CO})]\text{Cl}$, 52216-72-5; $[\text{Rh}(\text{tetraphos-2})(\text{CO})]\text{Cl}$, 52216-74-7; $[\text{Ir}(\text{triphos})(\text{CO})_2]\text{Cl}$, 52175-35-6; $[\text{Rh}(\text{triphos})(\text{CO})_2]\text{Cl}$, 52175-37-8; $[\text{Ir}(\text{tetraphos-1})(\text{CO})]\text{Cl}$, 52175-36-7; $[\text{Rh}(\text{tetraphos-1})(\text{CO})]\text{Cl}$, 52175-38-9; $[\text{Ir}(\text{triphos})(\text{CO})_2]\text{Cl}$, 52175-40-3; $[\text{Rh}(\text{triphos})(\text{CO})_2]\text{Cl}$, 52175-39-0; $[\text{Ir}(\text{tetraphos-1})(\text{O}_2)]\text{Cl}$, 52175-42-5; $[\text{Rh}(\text{tetraphos-1})(\text{O}_2)]\text{Cl}$, 52175-41-4; $[\text{Ir}(\text{tetraphos-2})(\text{CO})(\text{O}_2)]\text{Cl}$, 52216-73-6; $[\text{Rh}(\text{tetraphos-2})(\text{CO})(\text{O}_2)]\text{Cl}$, 52216-75-8; $[\text{Ir}(\text{triphos})(\text{CO})(\text{H})_2]\text{Cl}$, 52175-43-6; $[\text{Rh}(\text{triphos})(\text{CO})(\text{H})_2]\text{Cl}$, 52175-44-7; $[\text{Ir}(\text{tetraphos-1})(\text{H})_2]\text{Cl}$, 52175-45-8; $[\text{Rh}(\text{tetraphos-1})(\text{H})_2]\text{Cl}$, 52175-46-9; $[\text{Ir}(\text{tetraphos-2})(\text{CO})(\text{H})_2]\text{Cl}$, 52216-76-9; $[\text{Rh}(\text{tetraphos-2})(\text{CO})(\text{H})_2]\text{Cl}$, 52216-77-0; $\text{Ir}(\text{triphos})\text{Cl}_3$, 33847-54-0; $\text{Rh}(\text{triphos})\text{Cl}_3$, 52225-00-0; $\text{Ir}(\text{tetraphos-2})\text{Cl}_3$, 52216-70-3; $\text{Rh}(\text{tetraphos-2})\text{Cl}_3$, 52216-71-4; $[\text{Ir}(\text{tetraphos-1})(\text{H})(\text{Cl})]\text{Cl}$, 52175-59-4; $\text{Rh}(\text{tetraphos-1})\text{Cl}_3$, 52225-01-1; $[\text{Ir}(\text{triphos})(\text{CO})(\text{CH}_3)]\text{I}\text{Cl}$, 52175-58-3; $[\text{Rh}(\text{triphos})(\text{CO})(\text{CH}_3)]\text{I}\text{Cl}$, 52225-41-9; $[\text{Ir}(\text{tetraphos-1})(\text{CH}_3)]\text{I}\text{Cl}$, 52175-57-2; $[\text{Rh}(\text{tetraphos-1})(\text{CH}_3)]\text{I}\text{Cl}$, 52175-56-1; $[\text{Ir}(\text{tetraphos-2})(\text{CO})(\text{CH}_3)]\text{I}\text{Cl}$, 52216-78-1; $[\text{Rh}(\text{tetraphos-2})(\text{CO})(\text{CH}_3)]\text{I}\text{Cl}$, 52216-79-2; $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$, 14871-41-1; $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$, 13938-94-8; H_2 , 1333-74-0; HCl , 7647-01-0; MeI , 74-88-4.

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Mixed-Ligand Complexes of Terpyridinecobalt(II). New Low-pH Oxygen Carriers¹

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Two new mixed-ligand oxygen-carrying cobalt(II) species are reported, $\text{Co}(\text{terpy})(\text{LL})^{2+}$, where terpy is terpyridine and LL is 1,10-phenanthroline or 2,2'-bipyridine. These complexes are unique in that they combine with oxygen reversibly in strongly acid solutions, the oxygen uptake being essentially complete at pH 3.0. Equilibrium constants for these oxygen complexes were calculated from both kinetic and potentiometric data. These complexes are also unique in the second-order dependence of the rate of formation of $[\text{Co}(\text{terpy})(\text{LL})_2]\text{O}_2$ on the concentration of $\text{Co}(\text{terpy})(\text{LL})^{2+}$. Agreement between kinetic and potentiometric determination of equilibrium constants, second-order dependence on the mixed-ligand complex for oxygen uptake, and the esr of the corresponding superoxide all support a binuclear structure for the oxygen complex.

Introduction

Of the many transition metal complexes that have the ability to absorb oxygen,³ perhaps the most outstanding are those of cobalt(II).⁴ Over the past decade there has been

a resurgence in the study of cobalt(II) complexes, and many studies related to oxygen absorption on the structure, composition, kinetics, and equilibria of these species have been reported.⁵⁻⁸ The most widely studied, because of their

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(3) For reviews in this area see L. Vaska, *Accounts Chem. Res.*, 1, 335 (1968); J. P. Collman, *ibid.*, 1, 136 (1968); H. Taube, *J. Gen. Physiol.*, 49, 29 (1965).

(4) R. G. Wilkins, *Advan. Chem. Ser.*, No. 100 (1971);

L. H. Vogt, H. M. Faigenbaum, and S. E. Wiberley, *Chem. Rev.*, 63, 269 (1963).

(5) (a) R. Nakon and A. E. Martell, *Inorg. Chem.*, 11, 1002 (1972); (b) *J. Inorg. Nucl. Chem.*, 34, 1365 (1972); (c) *J. Amer. Chem. Soc.*, 94, 3026 (1972).

(6) F. Miller and R. G. Wilkins, *J. Amer. Chem. Soc.*, 92, 2687 (1970).

(7) M. S. Michailidis and R. B. Martin, *J. Amer. Chem. Soc.*, 91, 4683 (1969).

(8) F. Miller, J. Simplicio, and R. G. Wilkins, *J. Amer. Chem. Soc.*, 91, 1962 (1969).