

ture. In addition, it shows that there are five oxygen/molecule and four oxygen/molecule, which would have a theoretical oxygen analysis of 9.9% rather than the 12.2%, and thus gives further support to the Ti(IV) assignment rather than to a Ti(II) oxidation state.

TiOMPIXDME in chloroform has a typical metalloporphyrin visible spectrum: 407 (5.60), 500 (small shoulder), 536 (2.35), and 574 m $\mu$  (2.46) (log  $\epsilon$  values are given in parentheses). The Ti(IV) species is stable in solution. The shoulder at 500 m $\mu$  is also present in the vanadyl mesoporphyrin and thus may be due to a perturbation on the porphyrin system by the doubly bound oxygen.

The organo-transition metal method of metal insertion would probably be applicable for the preparation of the molybdenum, tungsten, and other metalloporphyrins which cannot be prepared easily by any existing methods.

The successful preparation of the chromium and tita-

um porphyrins may be explained by the concept of hard and soft acids and bases.<sup>34</sup> Porphyrins are soft bases due to their ability to  $\pi$  bond with the metal. The acid softness of the metals increases with decreasing oxidation state and Cr(II) and Ti(II) are considered to be soft acids. Metal insertion is thereby favorable since soft acids are reacting with a soft base. The low 2+ oxidation state of the chromium would be stabilized by synergistic  $\pi$  bonding with the porphyrin. The titanium is not stabilized in the 2+ oxidation state, probably due to unfilled electronic orbitals of the metal atom<sup>15</sup> which facilitate oxidation by a strong base such as oxygen. Electron density is supplied by the doubly bound oxygen, and the stable effective atomic number of 36 is approached.

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(34) R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963).

## The Reaction of Rhodium Halides with Tri-*o*-tolylphosphine and Related Ligands. Complexes of Divalent Rhodium and Chelate Complexes Containing Rhodium-Carbon $\sigma$ and $\mu$ Bonds<sup>1</sup>

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**Abstract:** Reaction of tri-*o*-tolylphosphine, (*o*-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P, with ethanolic rhodium(III) chloride at 25° gives blue-green RhCl<sub>2</sub>{(*o*-tol)<sub>3</sub>P}<sub>2</sub> ( $\mu_{eff} = 2.27 \pm 0.03$  BM at 25°), which is one of the few examples of a divalent rhodium complex having one unpaired electron. A purple modification ( $\mu_{eff} = 2.0 \pm 0.05$  BM) can also be made. The blue-green form has a *trans*-planar configuration, as shown by comparison of far-infrared spectra with the isomorphous palladium(II) and platinum(II) complexes. In high-boiling alcohols, tri-*o*-tolylphosphine reacts with rhodium(III) chloride to give initially a trimeric complex of apparent formula [RhCl<sub>2</sub>{(*o*-tol)<sub>3</sub>P}]<sub>3</sub> and finally a monomeric complex of apparent formula RhCl{(*o*-tol)<sub>3</sub>P}<sub>2</sub>. In some solvents the carbonyl complex RhCl(CO){(*o*-tol)<sub>3</sub>P}<sub>2</sub> is also formed. The trimer reacts with a number of monodentate and bidentate ligands (*e.g.*, CO, tertiary phosphines, tertiary arsines, pyridine) to give octahedral chelate complexes of rhodium(III) which are shown by nmr spectroscopy to contain a metal-carbon  $\sigma$  bond, *e.g.*, RhCl<sub>2</sub>(py)<sub>2</sub>{(*o*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>-)(*o*-tol)<sub>2</sub>P}. The trimeric complex also contains the chelate group (*o*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>-)(*o*-tol)<sub>2</sub>P formed by deprotonation of the ligand, and possible structures are discussed. The far-infrared spectra of the complexes are reported; bands due to Rh-Cl stretching are identified and used where possible to derive the stereochemistry of the complexes. The second complex, "RhCl{(*o*-tol)<sub>3</sub>P}<sub>2</sub>," is shown by infrared and nmr spectroscopy to contain the new ligand, *trans*-2,2'-(di-*o*-tolylphosphino)stilbene, (*o*-tol)<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>P(*o*-tol)<sub>2</sub>, which is coordinated as a tridentate ligand *via* the double bond and two *trans*-phosphorus atoms. The free ligand, which can be isolated by heating the rhodium complex with sodium cyanide, is derived by coupling two molecules of tri-*o*-tolylphosphine through adjacent methyl groups with the loss of four hydrogen atoms. It is suggested that this proceeds *via* a three-coordinate rhodium(I) complex, RhCl{(*o*-tol)<sub>3</sub>P}<sub>2</sub>, formed by disproportionation of the rhodium(II) complex. The reactions of phenyldi-*o*-tolylphosphine, (C<sub>6</sub>H<sub>5</sub>)(*o*-CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>P, and diphenyl-*o*-tolylphosphine, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(*o*-CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)P, with alcoholic rhodium(III) chloride have also been studied. The first gives a red divalent rhodium complex ( $\mu_{eff} \sim 1.0$  BM) which may contain Rh-Rh bonds; the second gives an ill-defined rhodium(I) complex, possibly containing some Rh(II) impurity. At higher temperatures, deprotonation of the ligands, decarbonylation of the solvent, and oxidative coupling of the ligand methyl groups all occur as with tri-*o*-tolylphosphine, the last reaction being favored as the number of *o*-tolyl groups increases.

An outstanding feature of the complex RhCl(Ph<sub>3</sub>P)<sub>3</sub><sup>3</sup> is the ease with which one molecule of triphenylphosphine is lost.<sup>4,5</sup> Oxidative additions to the com-

(1) Preliminary communication: M. A. Bennett, R. Bramley, and P. A. Longstaff, *Chem. Commun.*, 806 (1966); presented in part at the

plex often yield complexes containing formally five-co-

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ordinate rhodium(III),<sup>6</sup> although a solvent molecule may occupy the sixth coordination position. Molecular weight measurements on solutions of  $\text{RhX}(\text{Ph}_3\text{P})_3$  ( $\text{X} = \text{Cl}, \text{Br}, \text{and I}$ )<sup>4,5</sup> apparently indicate that one molecule of triphenylphosphine is completely dissociated to give a formally three-coordinate species  $\text{RhX}(\text{Ph}_3\text{P})_2$ , but a recent <sup>31</sup>P nmr study<sup>7</sup> suggests that the extent of dissociation is <5% at concentrations greater than  $10^{-2} \text{ M}$ . Despite this discrepancy, there is little doubt that one coordination position of  $\text{RhCl}(\text{Ph}_3\text{P})_3$  is readily vacated, a fact which is of key importance in the use of the complex as a catalyst for the homogeneous hydrogenation of unsaturated organic molecules.<sup>5</sup> Although species of formula  $\text{RhX}(\text{Ph}_3\text{P})_2$  can be isolated by heating solutions of  $\text{RhX}(\text{Ph}_3\text{P})_3$ ,<sup>4,5</sup> these are dimeric and probably contain bridging halogens. The work reported in this paper was started with the idea that by using a sterically hindered triarylphosphine, such as tri-*o*-tolylphosphine, (*o*- $\text{CH}_3\text{C}_6\text{H}_4$ )<sub>3</sub>P (abbreviated (*o*-tol)<sub>3</sub>P), it might be possible to prepare a complex containing three-coordinate rhodium(I). The complexes which have been isolated in this work are listed in Table I with pertinent analytical and molecular weight data.

## Results and Discussion

**Reaction between Rhodium Halides and *o*-Tolylphosphines at Room Temperature.** Hydrated rhodium(III) chloride reacts with tri-*o*-tolylphosphine (>four-fold molar excess) in ethanol at room temperature to give a blue-green solid of formula  $\text{RhCl}_2\{(\text{o-tol})_3\text{P}\}_2$  (**1a**) in ~50% yield. The complex is paramagnetic ( $\mu_{\text{eff}}$  at 25° =  $2.27 \pm 0.03 \text{ BM}$ ), and is isomorphous with the corresponding palladium(II) (**2**) and platinum(II) (**4**) complexes, as judged by visual comparison of their X-ray powder patterns. The infrared spectrum shows no bands attributable to  $\nu(\text{Rh-H})$  or  $\nu(\text{CO})$ . This suggests that complex **1a** contains square-planar, divalent rhodium ( $d^7$ , one unpaired electron). In agreement with this, the far-infrared spectra of the rhodium and palladium complexes show a single intense band at 352 and 351  $\text{cm}^{-1}$ , respectively, which is absent from the spectrum of  $\text{PdBr}_2\{(\text{o-tol})_3\text{P}\}_2$  (**3**), and can be assigned to a metal-chlorine stretching vibration [ $\nu(\text{M-Cl})$ ] (Table II). The corresponding band in **4** appears at 337  $\text{cm}^{-1}$ . These values are typical of square-planar complexes of palladium(II) and platinum(II) having *trans* chlorines,<sup>8</sup> and the near-identity of  $\nu(\text{Rh-Cl})$  and  $\nu(\text{Pd-Cl})$  is good evidence for the presence of divalent rhodium. By contrast, the value of  $\nu(\text{Rh-Cl})$  in the rhodium(I) complex  $\text{RhCl}(\text{CO})\{(\text{o-tol})_3\text{P}\}_2$  (**7**) appears at a considerably lower value of 304  $\text{cm}^{-1}$ .

Surprisingly, the X-ray powder patterns of  $\text{MCl}_2\{(\text{o-tol})_3\text{P}\}_2$  ( $\text{M} = \text{Rh}, \text{Pd}, \text{and Pt}$ ) are also very similar to that of  $\text{RhCl}(\text{CO})\{(\text{o-tol})_3\text{P}\}_2$ . The values of  $\nu(\text{CO})$  and  $\nu(\text{Rh-Cl})$  for **7** are almost identical with those of  $\text{RhCl}(\text{CO})(\text{Ph}_3\text{P})_2$ , for which X-ray studies<sup>9</sup> and dipole

moment measurements<sup>10</sup> indicate a *trans*-planar configuration. Ibers<sup>11</sup> has reported that the carbonyl groups and chlorine atoms of  $\text{IrO}_2\text{Cl}(\text{CO})(\text{Ph}_3\text{P})_2$  are indistinguishable by X-rays owing to disorder in the crystal, and partial isomorphous replacement of CO by Cl has been shown to occur in solid  $\text{IrCl}_{1.07}(\text{CO})_{2.93}$  (" $\text{IrCl}(\text{CO})_3$ ").<sup>12</sup>

When the reaction between rhodium(III) chloride and (*o*-tol)<sub>3</sub>P in ethanol is carried out below 0°, a mauve form of  $\text{RhCl}_2\{(\text{o-tol})_3\text{P}\}_2$  (**1b**) is obtained which is not isomorphous with the blue-green form. Its magnetic moment at room temperature is  $2.0 \pm 0.05 \text{ BM}$ , and the far-infrared spectrum shows a strong band at 350  $\text{cm}^{-1}$  with a shoulder at 328  $\text{cm}^{-1}$ . These could be assigned to the two  $\nu(\text{M-Cl})$  modes expected for *cis*- $\text{RhCl}_2\{(\text{o-tol})_3\text{P}\}_2$ , but since in general, the  $\nu(\text{M-Cl})$  frequencies for *cis* isomers of  $\text{MCl}_2\text{L}_2$  ( $\text{M} = \text{Pd}, \text{Pt}$ ) are considerably lower than the single  $\nu(\text{M-Cl})$  frequency for the corresponding *trans* isomer,<sup>8</sup> we believe that the mauve form is a different crystalline modification of *trans*- $\text{RhCl}_2\{(\text{o-tol})_3\text{P}\}_2$ . In the absence of air, both modifications are insoluble in most organic solvents and slightly soluble in dichloromethane. The purple solution so obtained is stable at -78° in the absence of air, but slowly decomposes at room temperature; decomposition is instantaneous in the presence of air. Rapid evaporation of dichloromethane *in vacuo* leaves **1b** which, on trituration with acetone, reverts to **1a**. All attempts to prepare the corresponding bromo-, iodo- and thiocyanato-rhodium(II) complexes have been unsuccessful.

As reported previously,<sup>1</sup> both forms show esr spectra, but so far we have been unable to obtain single crystals suitable for esr work. The spectrum of the powdered mauve form at room temperature shows a resonance corresponding to  $g(\text{rms}) = 2.03$ , and the blue form shows a very broad resonance, the range of  $g$  being 4 to *ca.* 2. There is no improvement in resolution when spectra are recorded in the powder form at 77°K, or when the spectrum of the mauve modification is measured in a dichloromethane glass.

A study of the variation with temperature of the magnetic susceptibility of **1a** has been carried out by Mr. R. B. Bentley and Professor J. Lewis at Manchester University, as part of their examination of the magnetic behavior of planar  $d^7$  metal complexes. The results are in Table III. The effective magnetic moment is independent of field strength in the range 2000–6670 Oe. A plot of  $1/\chi_m$  vs.  $T$  shows slight downward curvature at higher temperatures, indicative of a contribution from temperature-independent paramagnetism (t.i.p.).<sup>13</sup> This is estimated as  $400 \times 10^{-6}$  cgsu from a plot of  $\chi_m'$  vs.  $1/T$  (value at  $1/T = 0$ ), giving a value for the corrected magnetic moment of  $2.07 \pm 0.02 \text{ BM}$ . The fact that this value is somewhat higher than the spin-only value of 1.73 BM provides further evidence in support of planar coordination about Rh(II), since square-planar cobalt(II) complexes usually have unexpectedly high moments in the range 2.2–2.9 BM.<sup>14</sup>

(3) For convenience, the following abbreviations are used throughout this paper: Ph =  $\text{C}_6\text{H}_5$ ; *o*-, *m*-, or *p*-tol = *o*-, *m*- or *p*- $\text{CH}_3\text{C}_6\text{H}_4$ .

(4) M. A. Bennett and P. A. Longstaff, *Chem. Ind.* (London), 846 (1965).

(5) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc., A*, 1711 (1966).

(6) M. C. Baird, J. T. Mague, J. A. Osborn, and G. Wilkinson, *ibid.*, 1347 (1967).

(7) D. R. Eaton and S. R. Stuart, *J. Am. Chem. Soc.*, **90**, 4170 (1968).

(8) G. E. Coates and C. E. Parkin, *J. Chem. Soc.*, 421 (1963).

(9) S. F. Watkins, J. Obi, and L. F. Dahl, unpublished results cited by

J. L. de Boer, D. Rogers, A. C. Skapski, and P. G. H. Troughton, *Chem. Commun.*, 756 (1966).

(10) L. Vallarino, *J. Chem. Soc.*, 2287 (1957).

(11) S. J. LaPlaca and J. A. Ibers, *J. Am. Chem. Soc.*, **87**, 2581 (1965).

(12) K. Krogmann, W. Binder, and H. D. Hausen, *Angew. Chem. Intern. Ed. Engl.*, **7**, 812 (1968).

(13) A. Earnshaw, "Introduction to Magnetochemistry," Academic Press, New York, N. Y., 1968, pp 101–102.

(14) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 192 (1964).

Table I. Analytical Data, Melting Points, and Colors of Metal Complexes of Tolyphosphines

Compd no.	Compound	Color	Mp, °C	Calcd, %				Found, %				Mol wt		Solvent	Molarity	
				C	H	Halogen	P	C	H	Halogen	P	Calcd	Found			
1a	RhCl <sub>2</sub> {(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> P} <sub>2</sub>	Blue-green	330-335	64.5	5.4	9.1	7.9	63.5	5.4	8.9	7.7					
1b	RhCl <sub>2</sub> {(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> P} <sub>2</sub>	Mauve	185-190	64.5	5.4	9.1	7.9	63.5	5.2	9.7	8.2					
2	PdCl <sub>2</sub> {(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> P} <sub>2</sub>	Yellow	285-295 dec	64.1	5.4	9.0	7.9	63.3	5.7	9.0	8.2					
3	PdBr <sub>2</sub> {(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> P} <sub>2</sub> · 0.8(toluene)	Orange	294	60.3	4.5	16.8	6.5	60.6	5.4	17.6	7.3					
4	PtCl <sub>2</sub> {(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> P} <sub>2</sub> · 0.2CHCl <sub>3</sub>	White	290 dec	56.4	4.7	10.3	6.9	56.5	4.3	10.5	7.4					
5	RhCl <sub>2</sub> {(C <sub>6</sub> H <sub>5</sub> )(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> P} <sub>2</sub>	Red	190-195 dec	63.6	5.1	9.4	8.2	62.0	5.2	9.8	8.4					
6	PdCl <sub>2</sub> {(C <sub>6</sub> H <sub>5</sub> )(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> P} <sub>2</sub>	Pale yellow	278-282 dec	63.3	5.1	9.4	8.2	63.7	5.8	9.5	8.7					
7	RhCl(CO){(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> P} <sub>2</sub> · 0.2CHCl <sub>3</sub>	Yellow	230	64.9	5.3	7.1	7.7	64.7	5.7	7.1	7.6 <sup>a</sup>	775	725	CHCl <sub>3</sub>	0.006	
8	RhCl(CO){(C <sub>6</sub> H <sub>5</sub> )(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> P} <sub>2</sub>	Yellow	280 dec	65.9	5.1	4.7	8.3	66.1	5.9	4.3	8.7	747	735	CHCl <sub>3</sub>	0.008	
9	RhCl(CO){(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> )P} <sub>2</sub>	Yellow	250-255	65.1	4.8	4.9	8.6	65.4	4.9	4.6	8.4	719	725	CHCl <sub>3</sub>	0.015	
10	RhCl(CO){(m-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> P} <sub>2</sub>	Yellow	164	66.6	5.5	4.6		66.6	5.6	4.4		775	785	C <sub>6</sub> H <sub>6</sub>	0.021	
11	RhCl(CO){(p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> P} <sub>2</sub> · 0.2CH <sub>2</sub> Cl <sub>2</sub>	Yellow	200-210	65.4	5.4	6.3	7.8	65.3	5.4	6.1	7.6	775	740	C <sub>6</sub> H <sub>6</sub>	0.022	
12	[RhCl <sub>2</sub> {(o-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> -)(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> P} <sub>3</sub> ]	Yellow	264-268	52.9	4.2	14.8	6.5	52.7	4.1	15.6	6.4	1431	1510	Acetone	0.0065	
								51.9	4.3	15.4	6.6		1280	C <sub>6</sub> H <sub>6</sub>	0.0073	
												1350	CHCl <sub>3</sub>	0.0059		
												1290	CHCl <sub>3</sub>	0.0052		
13	[RhBr <sub>2</sub> {(o-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> -)(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> P} <sub>3</sub> ]	Yellow-orange	Not recorded	44.5	3.6	28.2	5.5	44.4	3.7	28.5	5.8	1698	1530	CHCl <sub>3</sub>	0.0097	
												1640	CHCl <sub>3</sub>	0.011		
14a	RhCl <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> N) <sub>2</sub> {(o-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> -)(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> P} (isomer A)	Pale yellow	240-242 dec	58.6	4.8	11.2	4.4 (N)	59.1	5.2	10.7	4.4 (N)	637	615	CHCl <sub>3</sub>	0.019	
14b	RhCl <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> N) <sub>2</sub> {(o-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> -)(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> P} (isomer B)	Straw	222	58.6	4.8	11.2	4.4 (N)	56.7	4.6	11.7	4.7 (N)	637	645	CHCl <sub>3</sub>	0.0086	
15	RhCl <sub>2</sub> (p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub> ){(o-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> -)(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> P}	Off-white	290 dec	57.4	5.0	12.2	5.3	57.6	5.2	11.2	4.6					
							2.4 (N)				2.9 (N)					
16	[RhCl <sub>2</sub> {(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P}{(o-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> -)(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> P}] <sub>2</sub>	Pale yellow	265-270 dec	63.3	4.8	9.6	8.4	62.0	4.6	8.8	8.1	1480	1490	CHCl <sub>3</sub>	0.005	
								61.6	4.7	9.0	7.9		1210	CHCl <sub>3</sub>	0.004	
17	RhCl <sub>2</sub> {(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> }{(o-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> -)(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> P}	Yellow	205-215	64.4	5.1	8.1	10.6	63.3	5.1	8.3	10.6	876	830	CHCl <sub>3</sub>	0.0082	
18	RhCl <sub>2</sub> {(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> AsCH <sub>2</sub> CH <sub>2</sub> As(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> }{(o-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> -)(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> P}	Pale yellow	235	58.6	4.6	7.4	3.2	58.1	4.8	7.4	3.5	963	970	CHCl <sub>3</sub>	0.013	
												920	CHCl <sub>3</sub>	0.006		
19a	RhCl <sub>2</sub> (C <sub>5</sub> H <sub>4</sub> N) <sub>2</sub> {(o-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> -)(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> P} · 0.3C <sub>6</sub> H <sub>6</sub> (C <sub>5</sub> H <sub>4</sub> N) <sub>2</sub> = 2,2'-bipyridyl	Straw	314-322 dec	60.2	4.6	10.7	4.2 (N)	60.2	4.4	10.6	4.4 (N)	633	625	CHCl <sub>3</sub>	0.0066	
19b	RhCl <sub>2</sub> (C <sub>5</sub> H <sub>4</sub> N) <sub>2</sub> {(o-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> -)(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> P} · 0.75CHCl <sub>3</sub> [(C <sub>5</sub> H <sub>4</sub> N) <sub>2</sub> = 2,2'-bipyridyl]	Straw	314-322 dec	52.7	4.3	20.9	3.9 (N)	53.2	4.3	22.8	4.2 (N)					
20	RhBr <sub>2</sub> (p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub> ){(o-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> -)(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> P}	Yellow	280 dec	49.8	4.3	23.8	4.6	50.1	4.2	22.8	3.9					
							2.1 (N)				2.5 (N)					
21	RhCl <sub>2</sub> (CO){(o-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> -)(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> P}	White	285-290 dec	52.2	4.2	14.0	6.1	51.9	3.9	14.5	6.8					
								52.6	4.3	13.8	6.4					
22	RhBr <sub>2</sub> (CO){(o-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> -)(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> P}	Cream	260-270 dec	44.4	3.6	26.9	5.2	44.5	4.1	26.8	5.2					
23	RhCl <sub>2</sub> (CO){(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P}{(o-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> -)(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> P}	Pale yellow	228-232	62.5	4.7	9.2	8.1	62.3	4.7	8.9	8.1	763	775	CHCl <sub>3</sub>	0.0068	
												745	CHCl <sub>3</sub>	0.0093		
24	RhCl <sub>2</sub> (CO){(m-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> P}{(o-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> -)(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> P}	White	212-216	63.6	5.2	8.8	7.7	63.3	5.1	8.7	7.7	810	830	CHCl <sub>3</sub>	0.021	
25	RhI <sub>2</sub> (CO){(m-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> P}{(o-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> -)(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> P}	Yellow	160-165 dec	52.0	4.2	25.6	6.2	54.3	4.6	25.6	6.2	993	960	C <sub>6</sub> H <sub>6</sub>	0.0097	
26	RhCl <sub>2</sub> (CO){(p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> P}{(o-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> -)(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> P}	White	212-215	63.6	5.2	8.8		62.2	5.2	8.7		810	805	CHCl <sub>3</sub>	0.015	
												770	CHCl <sub>3</sub>	0.006		

27	RhCl <sub>3</sub> (CO){(o-FC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> P}·	White	204-207	58.4	3.9	8.6	6.9 (F)	58.3	4.1	9.0	7.6 (F)	822	830	CHCl <sub>3</sub>	0.0098
28	{(o-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> )(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> P}	Cream	199	62.9	4.9	9.1	7.9	62.7	5.1	8.6	7.9	782	720	CHCl <sub>3</sub>	0.0057
29	{(o-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> )(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> P}	White	>350	55.5	4.5	12.1	5.3	57.6	4.5	11.1	5.7				
30	{(o-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> )(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> P}	Pale yellow	192-196	50.1	3.9		2.4 (N)	51.3	4.1		2.3 (N)				
31	{(o-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> )(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> P}·0.4C <sub>6</sub> H <sub>6</sub>	White	229-233	56.9	4.9	11.6	2.3 (N)	57.0	5.1	10.9	2.7 (N)	701	700	CHCl <sub>3</sub>	0.012
32	{(o-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> )(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> P}	Pale yellow	208	49.6	4.2		2.0 (N)	50.2	4.2		2.3 (N)	903	890	CHCl <sub>3</sub>	0.0059
33	{(o-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> )(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> P}	Pale yellow	200-205	63.8	4.9	7.9	10.3	63.6	4.9	8.2	10.4	743	950	CHCl <sub>3</sub>	0.0081
34a	RhCl <sub>3</sub> (CO){(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> }	Yellow	>350	70.1	5.4	4.3	7.6	69.2	5.4	4.4	7.3				
34b	RhCl <sub>3</sub> (CO){(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> ·C <sub>6</sub> H <sub>6</sub>	Yellow	>350	66.5	5.1	6.8	8.1	66.6	5.2	6.8	8.0				
35	RhCl <sub>3</sub> (CO){(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> ·0.15CHCl <sub>3</sub>	Yellow	>350	64.1	4.9	10.1	7.9	65.5	4.7	11.5	8.4				
36	Rh(NCS){(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> ·½	Orange	300-308	67.4	5.0	1.8 (N)	8.1	67.9	5.1	2.3 (N)	8.6	826	785	C <sub>6</sub> H <sub>6</sub>	0.024
37a	RhCl <sub>3</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> ·½	Yellow	330-335	67.0	5.1	4.9	8.6	66.7	5.4	5.2	8.6	715	704	C <sub>6</sub> H <sub>6</sub>	0.021
37b	RhCl <sub>3</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> ·½	Yellow	290 dec	67.0	5.1	4.9	8.6	66.8	4.9	4.8	8.1	715	685	C <sub>6</sub> H <sub>6</sub>	0.011
38	RhCl <sub>3</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> ·½	Yellow	300 dec	66.4	4.4	5.2	9.0	65.8	4.6	4.9	9.1	687	700	C <sub>6</sub> H <sub>6</sub>	0.014
													663	C <sub>6</sub> H <sub>6</sub>	0.0079

<sup>a</sup> Calcd Cl:P:Rh, 1.6:2:1. Found: 1.6:1.9:1.

**Table II.** Absorption Frequencies (cm<sup>-1</sup>) of Tollyphosphine Complexes of Rhodium(II), Rhodium(III), Palladium(II), and Platinum(II) in the Range 460-200 cm<sup>-1</sup> <sup>a</sup>

Compd no.	$\nu$ (M-Cl)	Other bands
1a	352 vs	455 vs, 430 sh, 388 w, 274 m br, 266 sh, 222 w br
1b	350 vs, 328 sh	448 vs, 430 sh, 388 w, 274 s br, 266 sh, 222 m br
2	351 vs	450 vs, 427 sh, 389 w, 361 w, 275 s br, 222 w br
3		450 vs, 426 vs, 386 m, 368 m, 329 m, 274 vs br, 222 m br
4	337 vs	450 vs, 431 sh, 388 w, 370 w, 275 s br, 266 sh, 222 w br
5	357 sh, 345 vs, 335 sh	448 vs, 412 m, 275 s br, 267 sh, 247 m br, 222 m br
6	350 vs	450 vs, 417 m, 376 w, 272 s, 266 sh, 247 m br, 222 m br
7	304 vs	448 vs, 427 s, 384 m, 368 m, 274 vs br, 243 w, 221 m
8	303 vs	440 s, 411 s, 377 w, 272 s, 251 s, 242 s, 222 s
9	303 s	448 s, 411 s, 275 m, 265 m, 244 s, 222 s
12	331 vs, 247 m br <sup>b</sup>	450 vs, 392 w, 278 vs br, 267 sh, 224 w
13		450 vs, 390 m, 270 s br, 250 sh, 236 w
14a	320 vs	444 s, 386 m, 363 w, 286 vs br, 247 w, 234 w br, 229 w br
14b	318 vs	435 vs br, 392 sh, 278 vs br, 243 s br, 222 s br
15	315 sh, 308 vs	426 m, 387 m, 282 vs, 267 vs, 222 vs br
20		444 s, 425 s, 386 m, 310 m, 280 s
16	339 sh, 325 vs	435 s, 394 w, 275 vs, 239 s
17	339 vs	450 vs, 408 m, 377 m, 326 m, 282 m, 262 m, 256 m, 231 m, 229 m
18	335 sh <sup>c</sup>	442 s, 383 s, 313 vs br, 300 sh, 234 m br
19a	333 vs	422 s, 389 w, 278 s br, 234 s br
21	314 vs	448 vs, 388 w, 286 vs, 270 vs, 253 sh, 228 s
22		444 vs, 420 sh, 387 w, 278 vs, 252 vs, 247 sh, 226 s
23	301 s, 268 vs, 231 s <sup>d</sup>	444 vs, 392 w
24	306 s, 262 vs, 231 s. br	446 vs, 384 w, 362 w, 280 w
25		455 vs, 385 w, 373 w, 282 w, 256 w, 230 w, 216 w
26	306 s, 265 vs, 231 s	440 s, 422 sh, 389 w, 282 w
27	310 s, 304 s, 267 s br, 239 m	435 vs, 396 sh, 222 m
28	302 vs, 262 vs, 230 s	444 vs, 422 sh, 386 w, 282 w
29	303 vs, 269 vs, 237 vs	450 s, 437 s, 387 w, 285 sh, 216 w
30		455 vs, 389 w, 279 m
31	306 vs, 260 vs br, 237 vs	435 vs, 389 w, 282 w
32		450 vs, 389 w, 305 w, 276 m, 249 m br, 225 m
33	304 vs, 265 vs, 231 s	445 vs, 430 m, 407 m, 379 m, 320 m, 285 w

<sup>a</sup> v, very; w, weak; m, medium; s, strong; sh, shoulder; br, broad. <sup>b</sup> May be due either to bridging  $\nu$ (M-Cl) or to  $\nu$ (M-Cl) *trans* to CH<sub>2</sub>. <sup>c</sup> Assignment tentative owing to nearby strong ligand absorption. <sup>d</sup> Strong band in this region in 23, 24, 26, 27, 28, 29, 31, and 33 tentatively assigned to  $\nu$ (M-Cl) *trans* to CH<sub>2</sub>.

Most of the previously reported compounds of divalent rhodium are diamagnetic.<sup>15</sup> In many cases, this is probably due to strong Rh-Rh interaction, as evidenced by the structure of Rh<sub>2</sub>(CH<sub>3</sub>COO)<sub>4</sub>·2H<sub>2</sub>O, in which the

(15) W. P. Griffith, "The Chemistry of the Rarer Platinum Metals (Os, Ru, Ir and Rh)," Interscience Publishers, New York, N. Y., 1967, Chapter 6, pp 328, 345, 364.

**Table III.** Variation of Molar Susceptibility,  $\chi_m'$ , and Effective Magnetic Moment,  $\mu_{\text{eff}}$ , of *trans*-RhCl<sub>2</sub>{(*o*-tol)<sub>3</sub>P}<sub>2</sub> (Blue-Green Modification) with Temperature

<i>T</i> , °K	10 <sup>6</sup> $\chi_m'$ <sup>a</sup>	1/ $\chi_m'$	$\mu_{\text{eff}}$ , BM	1/ $\chi_m''$ <sup>b</sup>	$\mu_{\text{eff}}$ , BM <sup>c</sup>
304.8	2110	473.9	2.28	584.8	2.05
291.7	2198	454.9	2.27	555.0	2.06
273.8	2322	430.6	2.26	520.2	2.06
257.5	2451	408.0	2.26	487.6	2.06
241.5	2582	387.3	2.24	458.3	2.06
221.9	2775	360.3	2.23	421.0	2.06
200.2	3007	332.6	2.20	383.6	2.05
185.1	3208	311.7	2.19	356.1	2.05
166.6	3542	282.3	2.18	318.3	2.05
147.6	3934	254.2	2.16	283.0	2.05
129.5	4457	224.3	2.16	246.5	2.06
114.5	5027	198.9	2.15	216.2	2.07
95.5	5993	166.8	2.15	178.8	2.08
80.8	7122	140.4	2.15	148.8	2.09

<sup>a</sup> Including a diamagnetic correction of  $464 \times 10^{-6}$  cgsu; this is composed of an estimated value of  $20 \times 10^{-6}$  cgsu for Rh(II),  $20.1 \times 10^{-6}$  cgsu for Cl (ref 58, p 403), and  $202 \times 10^{-6}$  cgsu for (*o*-tolyl)<sub>3</sub>P, estimated from the experimental value of  $167 \times 10^{-6}$  cgsu for (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P ("Handbook of Chemistry and Physics," R. C. Weast, Ed., 48th ed, The Chemical Rubber Co., Cleveland, Ohio, 1967-1968, p E117) and Pascal's constants for the substituents. <sup>b</sup>  $\chi_m'' = \chi_m' - 400 \times 10^{-6}$  cgsu (t.i.p. contribution, see text). <sup>c</sup> Magnetic moment corrected for t.i.p.

Rh-Rh distance is 2.45 Å.<sup>16</sup> Recently, the binuclear ion [Rh<sub>2</sub>(H<sub>2</sub>O)<sub>10</sub>]<sup>4+</sup> has been characterized;<sup>17</sup> preliminary magnetic measurements suggest that this is 6-10% dissociated into the paramagnetic monomeric form. The supposedly divalent rhodium complexes formed by methylphenylarsine, RhX<sub>2</sub>{CH<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>As}<sub>3</sub> (X = Cl, Br, and I),<sup>18</sup> are in fact hydridorhodium(III) complexes, RhHX<sub>2</sub>{CH<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>As}<sub>3</sub>,<sup>19</sup> but the structure of the paramagnetic bipyridyl complexes of rhodium(II), [RhCl(bipy)<sub>2</sub>]NO<sub>3</sub>·2H<sub>2</sub>O and [RhCl(bipy)<sub>2</sub>]ClO<sub>4</sub>·2H<sub>2</sub>O<sup>20</sup> is presently unknown. The only other genuine paramagnetic rhodium(II) complexes reported hitherto are the maleonitriledithiolate complex [(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>2</sub>[Rh(MNT)<sub>2</sub>], for which  $\mu_{\text{eff}} = 1.91$  BM and  $g_{\text{av}}(\text{rms}) = 2.11$ ,<sup>21</sup> the hexamethylbenzene complex [Rh{C<sub>6</sub>(CH<sub>3</sub>)<sub>6</sub>}]<sup>2+</sup> ( $\mu_{\text{eff}} = 1.32 \pm 0.08$  BM),<sup>22</sup> and the unstable bis- $\pi$ -cyclopentadienyl complex Rh(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> ( $g_{\parallel} = 2.033$  and  $g_{\perp} = 2.002$ ), which rapidly dimerizes to diamagnetic Rh<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)<sub>4</sub>.<sup>23</sup> Octahedrally coordinated rhodium(II) ions can also be stabilized in a zinc tungstate lattice ( $g(\text{rms}) = 2.21$ ).<sup>24</sup>

The different behavior of triphenylphosphine and tri-*o*-tolylphosphine with rhodium(III) chloride prompted us to investigate the behavior with the two intermediate phosphines, phenyldi-*o*-tolylphosphine, Ph(*o*-tol)<sub>2</sub>P, and diphenyl-*o*-tolylphosphine, Ph<sub>2</sub>(*o*-tol)P. Ethanolic rhodium(III) chloride reacts with a 5 molar excess of

Ph(*o*-tol)<sub>2</sub>P at room temperature to give a red microcrystalline precipitate of formula RhCl<sub>2</sub>{Ph(*o*-tol)<sub>2</sub>P}<sub>2</sub> (5). This is not isomorphous with the corresponding palladium(II) compound (6), and its magnetic moment at room temperature (0.8-1.1 BM on different samples) is well below the value expected for one unpaired spin; no temperature-range studies have been carried out. The far-infrared spectrum of 5 in the 350-cm<sup>-1</sup> region is more complex than that of 6 (Table II), which may indicate that it has a more complicated structure. Thus, complex 5 may contain square-planar Rh(II) with strong intermolecular metal-metal interaction, or it could be a halogen-bridged dimer containing square-planar rhodium(I) and octahedral rhodium(III), analogous to the complex Rh<sub>2</sub>Cl<sub>1</sub>{(C<sub>2</sub>H<sub>5</sub>)(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P}<sub>4</sub>.<sup>25</sup> We favor the first alternative on the basis of the far-infrared spectrum and the reaction with CO discussed below. The ligand Ph<sub>2</sub>(*o*-tol)P reacts with ethanolic rhodium(III) chloride to give an amorphous red solid, for which the analytical data fit approximately the formula RhCl{Ph<sub>2</sub>(*o*-tol)P}<sub>2</sub>. The infrared spectrum shows no band due to  $\nu(\text{Rh-H})$  or  $\nu(\text{CO})$ , and we have been unable to obtain a satisfactory far-infrared spectrum. The compound may be analogous to the chlorine-bridged dimer [RhCl(Ph<sub>3</sub>P)<sub>2</sub>]<sub>2</sub>.

The results indicate that tertiary phosphines can reduce rhodium(III) either by a two-electron process to rhodium(I) via an intermediate hydride RhHCl<sub>2</sub>L<sub>3</sub> which eliminates HCl,<sup>25</sup> or by a one-electron reduction to rhodium(II). The latter process is important with tri-*o*-tolylphosphine, but can evidently occur to a small extent even with triphenylphosphine, since samples of RhCl(Ph<sub>3</sub>P)<sub>3</sub> prepared from rhodium(III) chloride and triphenylphosphine show esr signals attributed to ~100 ppm of rhodium(II) impurity.<sup>5</sup>

Inspection of a molecular model suggests that tri-*o*-tolylphosphine stabilizes paramagnetic, square-planar divalent rhodium because one *o*-methyl group of each phosphine lies above and below the metal atom, respectively, so as to give a "pseudooctahedral" complex. The methyl groups can block intermolecular Rh-Rh contacts and hinder the approach of reagents. Similar explanations have been advanced to account for the apparent S<sub>N</sub>1 substitution mechanism for [PtCl(Et<sub>1</sub>-dien)]<sup>+</sup><sup>26</sup> (Et<sub>1</sub>-dien = (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>), for the stability of planar *ortho*-substituted aryls of Ni(II), Co(II), and Fe(II)<sup>27</sup> and for the stability of five-coordinate organorhodium(III) complexes such as RhBr(1-naphthyl)(R<sub>3</sub>P)<sub>2</sub>.<sup>28</sup> It is also likely that the low solubility in organic solvents of all the planar complexes of (*o*-tol)<sub>3</sub>P prepared in this work compared with the corresponding complexes of Ph<sub>3</sub>P, (*m*-tol)<sub>3</sub>P, and (*p*-tol)<sub>3</sub>P assists in stabilizing the rhodium(II) complex in the solid state.

The pseudooctahedral model suggests the possibility of an intramolecular interaction of the methyl hydrogen atoms with the nonbonding d electrons of the metal. An interaction of this type involving ammine hydrogen atoms has been postulated in complexes such as *trans*-PtX<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub> (X = Cl, Br, and I) to explain unexpected multiplicities of bands arising from N-H stretching and

(16) M. A. Porai-Koshits and A. S. Antsyshkina, *Proc. Acad. Sci. USSR, Chem. Sect.*, **146**, 902 (1962).

(17) F. Maspero and H. Taube, *J. Am. Chem. Soc.*, **90**, 7361 (1968).

(18) F. P. Dwyer and R. S. Nyholm, *J. Proc. Roy. Soc. N. S. Wales*, **75**, 127 (1942).

(19) J. Lewis, R. S. Nyholm, and G. K. N. Reddy, *Chem. Ind. (London)*, 1386 (1960).

(20) B. Martin, W. R. McWhinnie, and G. M. Waind, *J. Inorg. Nucl. Chem.*, **23**, 207 (1961).

(21) E. Billig, S. I. Shupack, J. H. Waters, R. Williams, and H. B. Gray, *J. Am. Chem. Soc.*, **86**, 926 (1964).

(22) E. O. Fischer and H. H. Lindner, *J. Organometal. Chem.*, **1**, 307 (1964).

(23) E. O. Fischer and H. Wawersik, *ibid.*, **5**, 559 (1966).

(24) M. G. Townsend and J. W. Orton, *J. Chem. Phys.*, **45**, 4135 (1966).

(25) A. Sacco, R. Ugo, and A. Moles, *J. Chem. Soc., A*, 1670 (1966).

(26) W. H. Baddley and F. Basolo, *J. Am. Chem. Soc.*, **86**, 2075 (1964).

(27) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1718 (1960); 285 (1961); P. G. Owston and J. M. Rowe, *ibid.*, 3411 (1963).

(28) J. Chatt and A. E. Underhill, *ibid.*, 2088 (1963).

**Table IV.** Absorption Frequencies ( $\text{cm}^{-1}$ ) Due to Stretching and Deformation Vibrations of Methyl Groups in Planar Complexes of *o*-, *m*-, and *p*-Tolylphosphine

Compound	$\nu(\text{asym})$	$\nu(\text{sym})$	$\delta(\text{asym})$	$\delta(\text{sym})$
$(p\text{-tol})_3\text{P}$	2980 w, 2950 w, 2930 s	2870 s	1500 s, 1460 sh, 1450 s	1395 s, 1350 w, 1310 s
<b>11</b>	2980-2935 sh br, 2925 s	2865 s	1495 s, 1445 s	1395 s, 1305 w
$(m\text{-tol})_3\text{P}$	2970 m, 2945 w, 2925 s	2865 s	1495 s, 1450 s	1390 s, 1345 w, 1305 s
<b>10</b>	2975 m, 2945 m, 2920 s	2865 s	1475 s, 1445 s	1395 s, 1300 m
$(o\text{-tol})_3\text{P}$	2970 m, 2940 m, 2920 m	2860 w	1470 s, 1455 s	1375 s
<b>1a</b>	2975 s, 2920 s	2860 sh	1470 s, 1445 s	1380 m
<b>2</b>	2975 s, 2950 sh, 2920 s	2860 sh	1465 s, 1440 s	1380 s
<b>4</b>	2980-2940 sh b, 2920 s	2860 m	1465 sh, 1440 s	1380 s
<b>7</b>	2975 s, 2950 sh, 2920 s	2865 w	1470 s, 1445 s	1380 m

**Table V.** Pmr Spectra of Rhodium Complexes Containing the Chelate Group  $(o\text{-C}_6\text{H}_4\text{CH}_2)(o\text{-CH}_3\text{C}_6\text{H}_4)_2\text{P}^a$ 

Compd no.	$\delta(\text{CH}_3)$ (obsd relative intensity)	Calcd relative intensity	$\delta(\text{CH}_2\text{-Rh})$ (obsd relative intensity)	Calcd relative intensity	$\delta(\text{aromatic})$ (obsd relative intensity)	Calcd relative intensity	$\delta(\text{other peaks})$ (obsd relative intensity)	Calcd relative intensity
<b>14a</b>	1.95, 2.01 (6)	6	3.6-4.5 (1.9)	2	6.5-9.8 (24)	22		
<b>14b</b>	2.00, 2.03 (6)	6	3.6-4.5 (1.8)	2	6.5-9.7 (25)	22		
<b>17</b>	1.38 (6)	6	3.8-4.2 (2.6)	2	6.2-7.8 (33)	32	2.2-2.7 (4.2) <sup>b</sup>	4
<b>18</b>	1.53 (6)	6	4.48 (2.0)	2	6.2-7.9 (38)	32	2.58 (4.5) <sup>c</sup>	4
<b>27</b>	2.13 (3), 2.30 (3)	6	2.7-3.9 (1.8)	2	6.5-8.2 (27)	24		
<b>26</b>	2.12 (3), 2.32, 2.38 (11.8) <sup>d</sup>	15	2.9-3.9 (2.5)	2	6.6-8.1 (24)	24		
<b>11</b>	2.43 (6)	6			6.9-7.4 (8)	8		
<b>24</b>	2.05 (2.6), 2.30, 2.37 (12) <sup>e</sup>	15	2.7-3.9 (2.3)	2	7.6-7.1 (27)	24		
<b>10</b>	2.37 (6)	6			6.9-7.3 (8)	8		

<sup>a</sup> Peak positions ( $\delta$ ) are measured in hertz downfield of TMS as internal reference. Measurements were carried out in  $\text{CDCl}_3$  containing a small amount of  $\text{CHCl}_3$ , for which no allowance has been made in calculating the intensity ratios. <sup>b</sup>  $\text{CH}_2$  protons of  $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ . <sup>c</sup>  $\text{CH}_2$  protons of  $(\text{C}_6\text{H}_5)_2\text{AsCH}_2\text{CH}_2\text{As}(\text{C}_6\text{H}_5)_2$ . <sup>d</sup>  $\text{CH}_3$  protons of  $(p\text{-tol})_3\text{P}$  + protons of one  $\text{CH}_3$  group of  $(o\text{-C}_6\text{H}_4\text{CH}_2)(o\text{-CH}_3\text{C}_6\text{H}_4)_2\text{P}$  (cf. **11**). <sup>e</sup>  $\text{CH}_3$  protons of  $(m\text{-tol})_3\text{P}$  + protons of one  $\text{CH}_3$  group of  $(o\text{-C}_6\text{H}_4\text{CH}_2)(o\text{-CH}_3\text{C}_6\text{H}_4)_2\text{P}$  (cf. **10**).

deformation vibrations.<sup>29,30</sup> We observe no anomalous bands or splittings in the C-H stretching and deformation regions of the spectra of the planar Rh(I), Rh(II), Pd(II), and Pt(II) complexes of  $(o\text{-tol})_3\text{P}$  compared with the spectra of complexes of  $(m\text{-tol})_3\text{P}$  and  $(p\text{-tol})_3\text{P}$  (Table IV) and conclude that if there is any electronic interaction between the *o*-methyl groups and the metal, infrared spectroscopy is not a suitable method for its detection.

**Rhodium-Carbon  $\sigma$ -Bonded Complexes Derived from Tri-*o*-tolylphosphine.** Reaction between hydrated rhodium(III) chloride or bromide and a fourfold molar excess of tri-*o*-tolylphosphine in refluxing 2-methoxyethanol for  $\sim 1$  hr gives red solutions from which yellow, diamagnetic solids of apparent formula  $\text{RhX}_2\{(o\text{-tol})_3\text{P}\}$  ( $\text{X} = \text{Cl}, \text{Br}$ ; **12** and **13**) can be isolated. The chloro complex (**12**) can also be obtained by heating a suspension of the rhodium(II) complex **1**, with or without added tri-*o*-tolylphosphine, in 2-methoxyethanol; hydrogen chloride is evolved in both reactions. The complexes are soluble in benzene, chloroform, and acetone, and are trimeric in these solvents. Solutions in nitrobenzene are nonconducting, and the infrared spectra

show no evidence for Rh-H or CO groups. Under the same reaction conditions, triphenylphosphine,  $(m\text{-tol})_3\text{P}$ , and  $(p\text{-tol})_3\text{P}$  react with rhodium(III) chloride to give initially  $\text{RhCl}(\text{ligand})_3$  and finally  $\text{RhCl}(\text{CO})(\text{ligand})_2$  by decarbonylation of the alcohol.<sup>31</sup> The nature of the trimeric complexes has been elucidated by studying their reactions with various ligands; these are discussed in turn.

**A. Bidentate Ligands.** A solution of **12** in benzene reacts with 1,2-diphenylphosphinoethane (diphos), 1,2-diphenylarsinoethane (diars), and 2,2'-bipyridyl (bipy) to give yellow crystalline complexes of apparent formula  $\text{RhCl}_2(\text{bidentate})\{(o\text{-tol})_3\text{P}\}$  (**17-19**). The diphos and diars complexes are monomeric in chloroform, and all three are nonconducting in nitrobenzene. The pmr spectrum of the diars complex **18** shows four main areas of absorption (Table V), the observed ratio of intensities being 6:4.5:2:38. The peak at  $\delta$  2.58<sup>32</sup> (relative intensity 4.5) is assigned to the methylene protons of coordinated diars, and the peak at  $\delta$  1.53 (relative intensity 6) must be due to the methyl protons of tri-*o*-tolylphosphine, but it is clear from the intensity ratios that there can be only two such methyl groups in the mole-

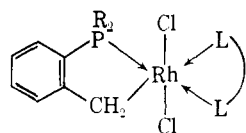
(29) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *J. Chem. Soc.*, 4461 (1955); 3203 (1958); L. A. Duncanson and L. M. Venanzi, *ibid.*, 3841 (1960).

(30) K. Nakamoto, P. J. McCarthy, J. Fujita, R. A. Condrate, and G. T. Behnke, *Inorg. Chem.*, **4**, 36 (1965).

(31) L. Vaska and J. W. Di Luzio, *J. Am. Chem. Soc.*, **83**, 2784 (1961); J. Chatt and B. L. Shaw, *Chem. Ind.* (London), 290 (1961).

(32) Peak positions ( $\delta$ ) are given in parts per million downfield of TMS as internal reference.

cule. The obvious structure compatible with the pmr spectrum is shown in I, in which a hydrogen atom has been lost from one of the methyl groups of tri-*o*-tolyl-



I, R = *o*-tolyl; L-L = diphos, diars, or bipy

phosphine, and a metal-carbon  $\sigma$  bond has been formed to the resulting methylene group to complete octahedral coordination about rhodium(III). The singlet at  $\delta$  4.48 (relative intensity 2) is assigned to the protons of the  $\text{CH}_2$ -Rh group.

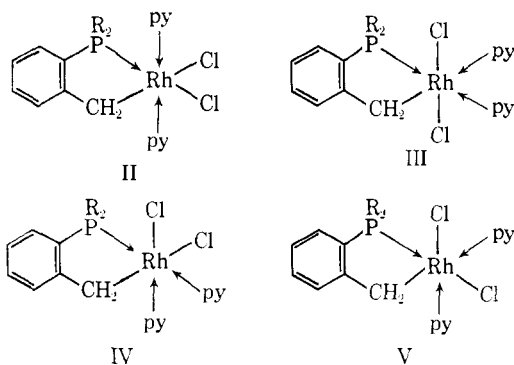
The pmr spectrum of the diphos complex (Table V) is similar to that of the diars complex, except that the  $\text{CH}_2$  protons of coordinated diphos appear as a doublet, presumably due to coupling with  $^{31}\text{P}$ , and the  $\text{CH}_2$  protons of the chelate group (*o*- $\text{C}_6\text{H}_4\text{CH}_2$ )-(*o*-tol) $_2\text{P}$  give a rather broad resonance at  $\delta$  4.0 ( $\sim 30$  Hz at half-peak height), presumably due to coupling with  $^{31}\text{P}$  and  $^{103}\text{Rh}$ . The bipyridyl complex is insufficiently soluble for pmr studies. The far-infrared spectrum of the diphos complex shows a strong band at  $339\text{ cm}^{-1}$  (Table I) which is characteristic of Cl *trans* to Cl in octahedral rhodium(III) complexes<sup>33,34</sup> and supports the configuration shown in I in preference to other geometric isomers. It may also be noted that only in this configuration are the protons of the pair of *o*-methyl groups equivalent, as is observed. The bipyridyl complex also shows strong absorption due to  $\nu(\text{Rh}-\text{Cl})$  at  $333\text{ cm}^{-1}$ , but in this case the stereochemical assignment is not certain because  $\nu(\text{Rh}-\text{Cl})$ 's for Cl *trans* to Cl and for Cl *trans* to pyridine are not greatly different.<sup>35</sup> The diars complex shows a very intense, broad band centered at  $313\text{ cm}^{-1}$  due to the ditertiary arsine, together with a shoulder at  $335\text{ cm}^{-1}$ , which may be due to  $\nu(\text{Rh}-\text{Cl})$ . The stereochemistry of the compound also is probably as shown in I.

**B. Pyridine.** The trimeric chloride reacts with excess pyridine to give a bis adduct<sup>36</sup>  $\text{RhCl}_2(\text{py})_2\{(\text{o-tol})_2\text{P}\}$  (14). Two different crystalline forms (14a and 14b) can be obtained by rapid or slow recrystallization, respectively, from chloroform-ethanol; these differ in their X-ray powder patterns and also in minor features of their infrared spectra. Their pmr spectra (Table V) show that the chelate group (*o*- $\text{C}_6\text{H}_4\text{CH}_2$ )-(*o*-tol) $_2\text{P}$  is present, and give evidence for the presence of geometric isomers in solution. The pmr spectrum of 14a shows two signals due to the *o*-methyl protons (total relative intensity 6), the higher field line being much stronger than the lower field line. There are also four signals in the range  $\delta$  3.6-4.5 (total relative intensity 1.9) assignable to the  $\text{CH}_2$ -Rh group, of which a signal at  $\delta$  4.46 is notably the most intense. Complex absorption in the range  $\delta$  6.5-9.8 (total relative intensity 24) is assigned to the pyridine and aromatic ring protons (expected value 22). Thus, in solution, 14a appears to consist predominantly of an isomer which shows one methyl resonance and one methylene resonance, *i.e.*, a molecule having a plane of symmetry (II or III).

(33) M. A. Bennett, R. J. H. Clark, and D. L. Milner, *Inorg. Chem.*, **6**, 1647 (1967).

(34) P. R. Brookes and B. L. Shaw, *J. Chem. Soc., A*, 1079 (1967).

(35) R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, **4**, 350 (1965).



R = *o*-tolyl; py = pyridine

The structure of 14b in the solid state has been shown by X-ray study<sup>36</sup> to be IV which provides excellent confirmation of the conclusions based on the pmr spectra of the entire series of complexes. The pmr spectrum (Table V) shows two methyl signals of almost equal intensity (total relative intensity 6), four signals of approximately equal intensity in the range  $\delta$  3.6-4.6 (total relative intensity 1.8) due to the Rh- $\text{CH}_2$  group, and complex absorption in the range  $\delta$  6.5-9.7 (total relative intensity 25, expected 22) due to the pyridine and aromatic ring protons. The methyl groups are not equivalent in structures IV and V, neither are the methylene protons, so that the pmr spectrum of 14b is consistent with the presence of a mixture of isomers IV and V in solution. The far-infrared spectrum of 14b in the solid state shows a doublet at  $320\text{ cm}^{-1}$  which is presumably due to  $\nu(\text{Rh}-\text{Cl})$  *trans* to pyridine; the value is too high for Cl *trans* to C or P as donors,<sup>37</sup> and rather low for Cl *trans* to Cl. Surprisingly, the far-infrared spectrum of 14a in the solid state shows a similar peak at  $318\text{ cm}^{-1}$ , which, if correctly assigned, means that neither structure II nor structure III can be present in the solid state, even though one or both are present in solution according to the pmr spectra. Structure V is the only other possibility for 14a in the solid state, but clearly more work is required to establish the species present in the solid state and in solution.

**C. Other Monodentate Ligands.** The trimeric chloride 12 reacts with triphenylphosphine to give a yellow monoadduct  $\text{RhCl}_2(\text{Ph}_3\text{P})\{(\text{o-tol})_2\text{P}\}$  (16) which is poorly soluble in most organic solvents. It is nonconducting in nitrobenzene and dimeric in chloroform. The far-infrared spectrum has bands at  $325\text{ cm}^{-1}$  (Cl *trans* to Cl) and  $276\text{ cm}^{-1}$  (Cl *trans* to  $\text{Ph}_3\text{P}$ ). Thus the complex is probably a chlorine-bridged dimer (VI or isomers thereof); the strong band at  $239\text{ cm}^{-1}$  in the infrared spectrum may be due to  $\nu(\text{Rh}-\text{Cl})$  *trans* to  $-\text{CH}_2$ .<sup>35</sup> A complex of similar stoichiometry is formed on addition of *p*-toluidine to the trimeric chloride, but this is too insoluble for molecular weight or pmr measurements.

The trimeric chloride 12 and bromide 13 react with carbon monoxide at  $25^\circ$  (1 atm) in benzene solution to give colorless complexes of formula  $\text{RhX}_2(\text{CO})\{(\text{o-tol})_2\text{P}\}$  (X = Cl, Br; 21 and 22), which are insoluble in all organic solvents. Their infrared spectra show strong bands at  $\sim 2090$ - $2070\text{ cm}^{-1}$  in the range

(36) A. D. C. Towl, Ph.D. Thesis, University of Sheffield, 1968.

(37) D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *J. Chem. Soc.*, 734 (1964).

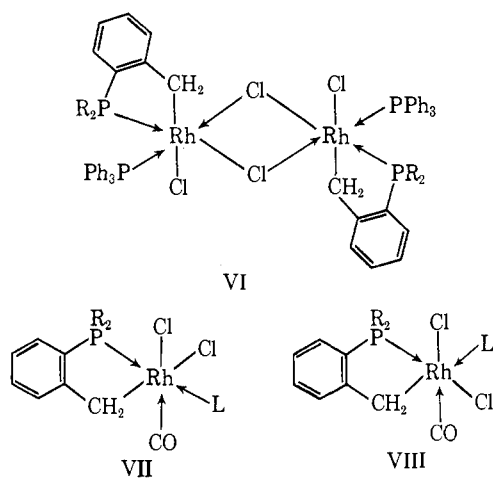
(38) B. L. Shaw and A. C. Smithies, *J. Chem. Soc., A*, 1047 (1967).

**Table VI.** Comparison of the Infrared Spectra of Tri-*o*-tolylphosphine and Its Metal Complexes with Those of *trans*-2,2'-*o*-(Di-*o*-tolylphosphino)stilbene and Its Complexes in the Range 1300–800 cm<sup>-1</sup>

( <i>o</i> -tol) <sub>3</sub> P	S <sup>a</sup>	7	1a and 2	34b	35	36 <sup>b</sup>
	1316 m <sup>c</sup>			1312 w <sup>c</sup>	1312 w <sup>c</sup>	1310 w <sup>c</sup>
	1249 w			1227 m	1229 m	1220 s
1201 s	1203 m	1201 s	1202 s	1202 m	1201 m	1201 s
	964 vs <sup>d</sup>			916 vs <sup>d</sup>	915 vs <sup>d</sup>	914 s <sup>d</sup>
	827 w			829 w	829 w	829 s <sup>e</sup>
801 s	810 m	802 s	805 s	804 m	804 m	804 s

<sup>a</sup> S = *o*-{(*o*-tol)<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>P(*o*-tol)<sub>2</sub>}. <sup>b</sup> Acetone solvate. <sup>c</sup> Olefinic in-plane (i.p.) deformation frequency. <sup>d</sup> Olefinic out-of-plane (o.o.p.) deformation frequency. <sup>e</sup> C–S stretching frequency.

typical of rhodium(III) carbonyl complexes. The carbonyl complexes react with a variety of monodentate ligands (triarylphosphines, pyridine) to give a series of colorless, monomeric complexes of general formula RhX<sub>2</sub>(CO)L{(*o*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)-(*o*-tol)<sub>2</sub>P} (23–33) (Table I), which show in their pmr spectra several broad resonances due to the CH<sub>2</sub>–Rh group in the range δ 2.7–3.9 and two singlets of equal intensity due to the *o*-methyl groups (Table V). The far-infrared spectra of all the chloro complexes (Table VI) show three strong bands



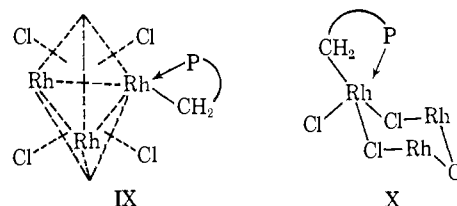
R = *o*-tolyl; L = pyridine, triarylphosphines

due to  $\nu(\text{Rh}-\text{Cl})$  at 301–306 cm<sup>-1</sup> (Cl *trans* to CO), at 265–270 cm<sup>-1</sup> (Cl *trans* to P), and a strong band at 230–240 cm<sup>-1</sup> which may be due to  $\nu(\text{Rh}-\text{Cl})$  *trans* to CH<sub>2</sub>. Thus, a mixture of isomers VII and VIII is probably present in the solid state and in solution.

Complex 12 is also soluble without decomposition in solutions containing Cl<sup>-</sup> and CN<sup>-</sup>, but the nature of the species in solution has not yet been investigated.

From these results, it is clear that the trimeric complexes 12 and 13 must be formulated as [RhX<sub>2</sub>{(*o*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)-(*o*-tol)<sub>2</sub>P}]<sub>3</sub> (X = Cl, Br), although we have been unable to obtain satisfactory pmr spectra to obtain direct proof of this. The far-infrared spectrum of the chloride shows a very strong band at 331 cm<sup>-1</sup>, indicating mutually *trans* chlorines, and a medium band at 247 cm<sup>-1</sup> which may be due either to bridging chlorines or to Cl *trans* to CH<sub>2</sub>. The simplest structure which can be considered consists of a trigonal bipyramid having octahedrally coordinated rhodium atoms at the equatorial vertices and bridging chlorines projecting from the center of each triangular face (IX). Alternatively, there could be three terminal chlorines and three chlorines bridging each edge of the Rh<sub>3</sub> triangle, so that each rhodium atom is effectively five-coordinate (X)

(only four of the six chlorines and one of the chelate  $\sigma$ -bonded groups are shown). The second structure is in better agreement with the far-infrared data, and the coordinative unsaturation of the metal atoms perhaps explains the reactivity of the complex toward other ligands. The simplest structure for the carbonyl complexes 21 and 22 is dimeric with halogen bridges,



analogous to VI, but it is not obvious on this basis why the compounds should be so insoluble. Possibly they also are trimeric, as in X with CO filling the sixth coordination position on each rhodium atom.

It is of interest that the chlorine bridges of complex 12 are not split by sterically hindered ligands. Thus, although monomeric derivatives are obtained with diphenyl-*o*-tolylphosphine (28) and pyridine (29 and 30), there is no reaction with 2,2'-bipyridyl, 2,6-lutidine, phenyldi-*o*-tolylphosphine, or tri-*o*-tolylphosphine. Complex 12 reacts with 1,2-diphenylphosphinoethane to give yellow, crystalline RhCl<sub>2</sub>(CO)(diphos){(*o*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)-(*o*-tol)<sub>2</sub>P} [ $\nu(\text{CO}) = 2070 \text{ cm}^{-1}$ ] (33) in which it is likely that only one ligand atom of the di-*tert*-ary phosphine is attached to the metal.

Preliminary experiments indicate that similar octahedral organorhodium(III) complexes can be obtained starting from phenyldi-*o*-tolylphosphine and diphenyl-*o*-tolylphosphine, and the use of ligands of this type may well extend the range of  $\sigma$ -bonded organo-transition metal complexes.

The chelate organorhodium(III) complexes described herein are thermally very stable; many of them melt in the range 200–250° without decomposition. It seems surprising, therefore, that relatively few monodentate organorhodium(III) complexes are known. Attempts to prepare them by the standard methods, *e.g.*, RhCl<sub>3</sub>L<sub>3</sub> + Grignard or organolithium reagents, have usually been unsuccessful, except with sterically hindered aryls such as 2-naphthyl, which give the five-coordinate complexes mentioned above.<sup>28</sup> Also, the dimethyl sulfide complex RhCl<sub>3</sub>{(CH<sub>3</sub>)<sub>2</sub>S}<sub>3</sub> reacts with CH<sub>3</sub>MgI to give a binuclear methyl complex Rh<sub>2</sub>I<sub>2</sub>(CH<sub>3</sub>)<sub>4</sub>{(CH<sub>3</sub>)<sub>2</sub>S}<sub>3</sub>, from which a mononuclear cyclopentadienyl derivative Rh(C<sub>5</sub>H<sub>5</sub>)(CH<sub>3</sub>)<sub>2</sub>{(CH<sub>3</sub>)<sub>2</sub>S}<sub>3</sub> can be made.<sup>39</sup> Recently, a number of octahedral rhodium(III) alkyls and aryls

(39) H. P. Fritz and K. E. Schwarzshans, *J. Organometal. Chem.*, **5**, 283 (1966).



Table VII. Pmr Spectra of Rhodium Complexes of Stilbene Ligands Derived by Oxidative Coupling of Tolyolphosphines

Compound	$\delta(\text{CH}_3)$ (obsd relative intensity)	Calcd relative intensity	$\delta(\text{CH}=\text{CH})$ (obsd relative intensity)	Calcd relative intensity	$\delta(\text{aromatic})$ (obsd relative intensity)	Calcd relative intensity	$\delta(\text{other peaks})$
( <i>o</i> -tol) <sub>3</sub> P	2.34 (3)	3			6.6-7.3 (3)	4	
Ph( <i>o</i> -tol) <sub>2</sub> P	2.34 (6)	6			6.5-7.4 (14)	14	
Ph <sub>2</sub> ( <i>o</i> -tol)P	2.34 (3)	3			6.6-7.4 (15)	14	
{( <i>o</i> -tol) <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> CH: } <sub>2</sub>	2.37 (12)	12	7.64 (1.8)	2	6.9-7.5 (27)	24	
<b>36</b> <sup>a</sup>	2.42 (6), 2.85 (6)	12	3.50 (2) <sup>b</sup>	2	6.9-7.5 (30)	24	2.11 (6), <sup>c</sup> 2.21 (w), <sup>f</sup> 3.02 (w)
<b>37</b>	2.75 (6) <sup>d</sup>	6	3.50 (2) <sup>b</sup>	2	6.7-8.3 (29)	26	2.30 (w), 2.35 (w), 2.40 (w), 2.64 (w)
<b>37</b>	2.31, 2.64 (6)	6	3.50 (2.1) <sup>b</sup>	2	6.7-8.3 (28)	26	2.12 (w), 2.75 (w)
<b>38</b>			3.60 (2) <sup>b</sup>	2	7.0-8.2 (32)	30	2.08 (6) <sup>e</sup>

<sup>a</sup> Sample recrystallized from acetone and dried at 25° (10<sup>-3</sup> mm). <sup>b</sup> Appears as a 1:1:2:2:1:1 sextet due to coupling with <sup>103</sup>Rh (*J* = 1.0 Hz) and with <sup>31</sup>P (*J* = 1.8 Hz). <sup>c</sup> Peak due to 1 mole of acetone per mole of complex, which is absent if complex is first dried at 80° (10<sup>-3</sup> mm). <sup>d</sup> Relative intensity calculated including weaker methyl resonances in column 8; these are responsible for ~15-20% of the total. <sup>e</sup> Peak due to 1 mole of acetone per mole of complex, which disappears when sample is recrystallized from chloroform. <sup>f</sup> Abbreviation: w, weak.

have been made by adding alkyl or acyl halides to planar rhodium(I) complexes such as RhCl(CO)(R<sub>3</sub>P)<sub>2</sub><sup>40</sup> and RhCl(Ph<sub>3</sub>P)<sub>3</sub>.<sup>6,41</sup> Ethylrhodium(III) complexes have been made by treating rhodium(I)-ethylene complexes with HCl.<sup>42,43</sup> Six-coordinate alkyls of the type RhCl<sub>2</sub>R(CO)(Ph<sub>3</sub>P)<sub>2</sub> may be in equilibrium with five-coordinate acyls RhCl<sub>2</sub>(COR)(Ph<sub>3</sub>P)<sub>2</sub>, and readily lose alkyl halide to give RhCl(CO)(Ph<sub>3</sub>P)<sub>2</sub>.<sup>6</sup> In our complexes, however, the stability of the chelate  $\sigma$ -bonded structure prevents both reductive elimination and CO insertion.

A noteworthy feature of the structure of RhCl<sub>2</sub>(py)<sub>2</sub>-(*o*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)-(*o*-tol)<sub>3</sub>P (**14b**) determined by Towl<sup>36</sup> is that the Rh-Cl bond *trans* to CH<sub>2</sub> is considerably longer (2.53 Å) than that *trans* to pyridine (2.34 Å). The latter is normal, but the former is the longest Rh<sup>III</sup>-Cl bond length so far observed; *cf.* the Rh-Cl bridge bond lengths of 2.47 and 2.51 Å in Rh<sub>2</sub>Cl<sub>2</sub>( $\pi$ -allyl)<sub>4</sub>.<sup>44</sup> Similar lengthenings of bonds *trans* to metal-carbon  $\sigma$  bonds have been observed in monomeric octahedral complexes of platinum(IV),<sup>36</sup> iridium(III),<sup>45</sup> and chromium(III),<sup>46</sup> and in monomeric planar complexes of platinum(II)<sup>47</sup> and gold(III),<sup>36</sup> and they indicate the high *trans* effect of  $\sigma$ -bonded carbon as a ligand atom.

**Coupling-Dehydrogenation Reaction of Rhodium Halides with *o*-Tolyolphosphines.** Prolonged reaction of rhodium trichloride with a sixfold molar excess of tri-*o*-tolylphosphine in 2-(2-methoxyethoxy)ethanol or 2-methoxyethanol gives a yellow solution from which a yellow, diamagnetic complex of apparent formula RhCl{(*o*-tol)<sub>3</sub>P}<sub>2</sub> (**34**) can be isolated in ~30% yield. In these solvents, the carbonyl complex **7** does not seem to be formed, although under the same conditions triphenylphosphine, (*m*-tol)<sub>3</sub>P, and (*p*-tol)<sub>3</sub>P give excellent yields of RhCl(CO)(ligand)<sub>2</sub>, (**10** and **11**). Analytical data on samples of **34** crystallized from different solvents suggest that up to 1 mole of solvent per mole of complex may be present; this cannot be removed even after prolonged pumping at elevated temperatures. The complex is slightly soluble in aromatic hydrocarbons

and in chloroform, but is insoluble in most other solvents. In dilute chloroform solutions, **34** is monomeric and it is nonconducting in nitrobenzene. The infrared spectrum shows no bands due to  $\nu(\text{CO})$  or  $\nu(\text{Rh-H})$  vibrations in the 2000-cm<sup>-1</sup> region, but there are a number of bands in the region 1500-800 cm<sup>-1</sup> (Table VI) which are not present in the spectra of (*o*-tol)<sub>3</sub>P and its metal complexes; the most conspicuous is an intense band at 916 cm<sup>-1</sup>. This absorption initially led us to consider the possibility of the presence of Rh=O or Rh-OR groups in the molecule, particularly as the reaction of rhenium compounds with tertiary phosphines in alcoholic media gives oxoalkoxyrhenium compounds,<sup>48</sup> which absorb in the 900-1100-cm<sup>-1</sup> region. However, the same complex is obtained if the reaction is carried out in other alcohols or in acetophenone, which suggests that alkoxy groups are absent. It can be noted here that in boiling *n*-heptanol the yield of **34** is only ~5%, the main product being the carbonyl complex **7** (83%). In ethylene glycol, both complexes are formed after 5 hr of refluxing, but the carbonyl is extensively decomposed to rhodium metal. In benzyl alcohol (bp 206°), the yield of **34** is 22% and no carbonyl is formed, whereas in *p*-chlorobenzyl alcohol (bp 235°) only the carbonyl can be isolated in 53% yield. The bromo compound "RhBr{(*o*-tol)<sub>3</sub>P}<sub>2</sub>" (**35**) can be made from the reaction of rhodium tribromide with the ligand in 2-methoxyethanol or 2-(2-methoxy)ethoxyethanol in ~5% yield, the main product being RhBr(CO){(*o*-tol)<sub>3</sub>P}<sub>2</sub>.

On treatment with sodium thiocyanate in refluxing acetone, **34** is converted to the corresponding thiocyanate (**37**), which is soluble in benzene, chloroform, and acetone, and is monomeric in benzene. The pmr spectrum of the acetone solvate of **37** in CDCl<sub>3</sub> (Table VII) shows four main areas of absorption: a complex set of peaks at  $\delta$  6.9-7.5 (A) (relative intensity 28), a sextet centered at  $\delta$  3.50 (B) (relative intensity 2), a singlet at  $\delta$  2.11 (C) (relative intensity 6), and two singlets of equal intensity at  $\delta$  2.42 and 2.85 (D) (total relative intensity 12). There are also two weak singlets at  $\delta$  2.21 and 3.02 (E). Peak C is due to 1 mole of acetone per mole of complex; this is retained when the complex is kept at 25° (10<sup>-3</sup> mm) but is removed at 80° (10<sup>-3</sup> mm) (as shown by the disappearance of peak

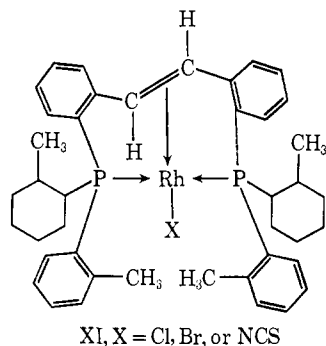
(40) R. F. Heck, *J. Am. Chem. Soc.*, **86**, 2796 (1964).  
 (41) K. Ohno and J. Tsuji, *ibid.*, **90**, 99 (1968).  
 (42) R. Cramer, *ibid.*, **87**, 4717 (1965).  
 (43) J. Powell and B. L. Shaw, *J. Chem. Soc., A*, 211 (1968).  
 (44) M. McPartin and R. Mason, *Chem. Commun.*, 16 (1967).  
 (45) M. McPartin and R. Mason, *ibid.*, 545 (1967).  
 (46) J. J. Daly and R. P. A. Sneeden, *J. Chem. Soc., A*, 736 (1967).  
 (47) B. N. Figgis, J. Lewis, R. F. Long, R. Mason, R. S. Nyholm, P. J. Pauling, and G. B. Robertson, *Nature*, **195**, 1278 (1962).

(48) J. Chatt and G. A. Rowe, *J. Chem. Soc.*, 4019 (1962); N. P. Johnson, C. J. L. Lock, and G. Wilkinson, *ibid.*, 1054 (1964).

C in the nmr spectrum and the disappearance of a band at  $1720\text{ cm}^{-1}$  in the infrared spectrum). Peaks D are clearly assignable to the methyl protons of an *o*-tolylphosphino group, but the intensity ratio of aromatic to methyl resonances is approximately 2:1, instead of the expected 4:3, suggesting that methyl protons have been lost in the formation of the complex.

From the reaction of **34** with excess aqueous ethanolic sodium cyanide a white crystalline solid, mp  $263^\circ$ , can be isolated almost quantitatively.<sup>49</sup> This is not tri-*o*-tolylphosphine, mp  $125^\circ$ , and its infrared spectrum has a number of bands in the region  $1300\text{--}800\text{ cm}^{-1}$  (Table VI) which do not appear in the spectrum of  $(o\text{-tol})_3\text{P}$ ; of these, the most intense is a band at  $964\text{ cm}^{-1}$ . Analysis and molecular weight measurements suggest a dimeric formulation  $[(o\text{-tol})_3\text{P}]_2$ , but the pmr spectrum shows a singlet due to methyl protons at  $\delta$  2.37 (relative intensity 12), complex aromatic absorption at  $\delta$  6.9–7.5 (relative intensity 27), and a singlet at  $\delta$  7.64 (relative intensity 2). Again, the intensity ratio of aromatic to methyl absorptions is approximately 2:1. The evidence suggests that the new phosphine is *trans*-2,2'-*o*-(di-*o*-tolylphosphino)stilbene,  $o\text{-}\{(o\text{-tol})_2\text{PC}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{P}(o\text{-tol})_2\}$ , formed by the coupling of two molecules of tri-*o*-tolylphosphine with the loss of four hydrogen atoms. The singlet at  $\delta$  7.64 can be assigned to the equivalent olefinic protons and the strong band at  $964\text{ cm}^{-1}$  in the infrared spectrum is typical of a C–H o.o.p. deformation vibrational frequency of a *trans*-disubstituted olefin;<sup>50a</sup> the weak band at  $1316\text{ cm}^{-1}$  may be due to the corresponding i.p. vibration.<sup>50b</sup>

Molecular models indicate that in the rhodium complex the stilbene can behave as a tridentate ligand, with two mutually *trans*-phosphorus atoms and the double bond attached to the metal (XI); the phenyl rings must, of course, be twisted out of the plane of the double bond. Peak B in the nmr spectrum of the rhodium complex can



be assigned to the olefinic protons which have been shifted upfield on coordination and split into a doublet by coupling with  $^{103}\text{Rh}$  ( $J = 1.0\text{ Hz}$ ) and further split into a pair of 1:2:1 triplets by coupling with the two *trans*-phosphorus atoms ( $J = 1.8\text{ Hz}$ ). Coordination of the double bond is also evidenced by the shift in the C–H o.o.p. deformation frequency from  $964\text{ cm}^{-1}$  in the ligand to  $916\text{ cm}^{-1}$  in the complex. No bands assignable to  $\nu(\text{C}=\text{C})$  can be identified either in the ligand or in the complex. Because the ligand is centrosymmetric, this vibration should be infrared inactive, and in the complex the band is probably too weak to be

(49) Parallel experiments showed that sodium cyanide quantitatively displaces tri-*o*-tolylphosphine unchanged from **1** and **7**.

(50) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, Methuen and Co., London, 1958: (a) p 45; (b) p 52.

located. Inspection of the molecular model further suggests that the plane of the coordinated double bond may be approximately at right angles to the plane containing the metal and the other ligand atoms, as occurs in Zeise's salt and other platinum(II)–olefin complexes.<sup>51</sup> Thus, the complex can be regarded as a square-planar olefin complex of rhodium(I), analogous to  $\text{RhCl}(\text{C}_2\text{H}_4)(\text{Ph}_3\text{P})_2$ ,<sup>5</sup> but much more stable to dissociation than this complex owing to the rigidity of the tridentate chelate group. Alternatively, the remarkably high upfield shift (4.1 ppm) of the olefinic protons on coordination may suggest that, in this case, the bonding is better described in terms of a pair of  $\sigma$  bonds to the metal leading to a five-coordinate complex of rhodium(III).

The only symmetry element in XI is a  $\text{C}_2$  axis passing through the center of the double bond and the metal, so that the methyl groups of each di-*o*-tolylphosphino group are not equivalent and should give a doublet in the pmr spectrum, as is observed. It is more difficult to account for the two weak methyl peaks (E). An obvious explanation would be the presence of an impurity such as the rhodium complex of the corresponding *cis*-stilbene ligand. However, a recrystallized sample of the *trans*-ligand, which shows no impurity peaks in its pmr spectrum, reacts with the rhodium(I)–cyclooctene complex  $\text{RhCl}(\text{C}_8\text{H}_{14})_2$ <sup>52</sup> to give a complex identical with **34**. This reacts with sodium thiocyanate to give a product identical in all respects, including the weak peaks at  $\delta$  2.21 and 3.02, with that obtained from the reaction of  $\text{RhCl}_3$  with  $(o\text{-tol})_3\text{P}$ . We think it likely that the weak peaks are due to a conformer of XI arising from restricted rotation about the phosphorus–aryl bond. The peaks broaden when the temperature of the solution is raised to  $55^\circ$ , but a more detailed study will be required to test the hypothesis.

The chief product from the reaction of rhodium(III) chloride with diphenyl-*o*-tolylphosphine in refluxing 2-methoxyethanol after 3 hr is, not surprisingly, the carbonyl complex  $\text{RhCl}(\text{CO})\{\text{Ph}_2(o\text{-tol})\text{P}\}_2$  (**9**). However, a yellow complex of apparent formula  $\text{RhCl}(\text{ligand})_2$  (**38**) can also be isolated in  $\sim 1\%$  yield. This is monomeric in benzene and nonconducting in nitrobenzene. The infrared spectrum shows no bands due to  $\nu(\text{Rh}–\text{H})$  or  $\nu(\text{CO})$ , but an intense band at  $917\text{ cm}^{-1}$  indicates that coupling and dehydrogenation have occurred to give the *o*-diphenylphosphinostilbene complex  $\text{RhCl}(\text{Ph}_2\text{PC}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{PPh}_2)_2$ . In agreement with this, the nmr spectrum (Table VII) shows aromatic absorption at  $\delta$  7.0–8.2 (relative intensity 28) and a sextet at  $\delta$  3.63 (relative intensity 1.8); the calculated intensity ratios are 28:2. The absence of methyl absorption in this case provides conclusive evidence that dehydrogenation of methyl groups occurs in these reactions.

The corresponding reaction with phenyldi-*o*-tolylphosphine is interesting because, in addition to the carbonyl complex  $\text{RhCl}(\text{CO})\{\text{Ph}(o\text{-tol})_2\text{P}\}_2$  (**8**), two isomeric stilbene complexes " $\text{RhCl}\{\text{Ph}(o\text{-tol})_2\text{P}\}_2$ " (**37a** and **37b**) are formed, which can be separated by their differing solubility in ether. Both are monomeric in benzene and show a strong  $\delta(\text{CH})$  band at  $912\text{ cm}^{-1}$  in

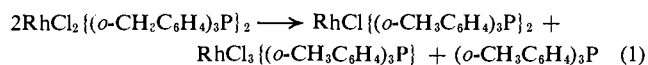
(51) J. A. Wunderlich and D. P. Mellor, *Acta Cryst.*, **7**, 130 (1954); P. R. Alderman, P. G. Owston, and J. M. Rowe, *ibid.*, **13**, 149 (1960).

(52) L. Porri, A. Lionetti, G. Allegra, and A. Immirzi, *Chem. Commun.*, 336 (1965).

their infrared spectra, but their X-ray powder patterns and pmr spectra differ. The characteristic sextet at  $\delta$  3.5 due to the coordinated olefinic protons is present in the spectra of both isomers, but the ether-soluble isomer **37a** shows one strong peak in the methyl region at  $\delta$  2.75, together with four other weaker peaks, whereas the ether-insoluble isomer **37b** shows two peaks of almost equal intensity at  $\delta$  2.31 and 2.64, together with two other weaker peaks. If structure XI is correct for the stilbene complexes, there is an obvious possibility of geometrical isomerism for the complex derived from  $\text{Ph}(o\text{-tol})_2\text{P}$  since the *o*-methyl groups can be either *trans* (and therefore equivalent) or *cis* (and therefore inequivalent). On this basis, **37a** is believed to be the *trans* isomer, **37b** the *cis* isomer. The weaker peaks again presumably are due to conformers arising from restricted rotation about the phosphorus-aryl bond. In the case of **37a** it is necessary to include these "weak" peaks in the proton count in order to obtain reasonable agreement with the expected ratios (Table VII), but in the cases of **36** and **37b** the intensity of the weak peaks is negligible.

**Mechanism of Reactions.** In the absence of kinetic data, little can be said about the mechanisms of the reactions discussed above, but it is clear that the rhodium(II) complex **1** is a key intermediate. It is frequently observed in the initial stages of the reactions carried out in 2-methoxyethanol or 2-(2-methoxyethoxy)ethanol that the products obtained by heating it with an excess of  $(o\text{-tol})_3\text{P}$  in a variety of solvents are essentially identical with those obtained starting from rhodium(III) chloride. Under identical conditions, however, neither the trimeric  $\sigma$ -bonded complex **12** nor the carbonyl complex **7** react with excess  $(o\text{-tol})_3\text{P}$  to give the stilbene complex **36**, and they cannot therefore be involved in its formation.

It seems likely that an important step in the reaction is the disproportionation of the rhodium(II) complex on heating to give a mixture of rhodium(I) and rhodium(III) complexes.



The rhodium(III) complex can eliminate HCl to give the trimeric  $\sigma$ -bonded species **12**.



We think that the coordinately unsaturated rhodium(I) complex  $\text{RhCl}\{(o\text{-tol})_3\text{P}\}_2$  is the likely precursor to the stilbene complex, and we suggest that dehydrogenation of the ligands proceeds by successive abstraction of hydrogen atoms from the *o*-methyl groups by the metal, followed by loss of hydrogen from the metal. Hydrogen transfers of this type occur in a number of complexes of  $d^8$  metals, such as  $\text{Ru}\{(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_3)_2\}$ ,<sup>53</sup>  $\text{Fe}\{(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2\}$ ,<sup>54</sup> and  $\text{IrCl}\{(\text{C}_6\text{H}_5)_3\text{M}\}_3$  ( $\text{M} = \text{P}, \text{As}, \text{and Sb}$ ).<sup>55</sup> The reversibility of hydrogen addition to the coordinately unsaturated species present in solutions of  $\text{RhCl}(\text{Ph}_3\text{P})_3$ <sup>5</sup> provides some support to the suggested mechanism.

(53) J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 843 (1965).

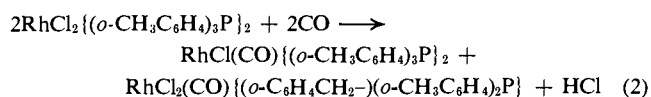
(54) G. Hata, H. Kondo, and A. Miyake, *J. Am. Chem. Soc.*, **90**, 2278 (1968).

(55) M. A. Bennett and D. L. Milner, *Chem. Commun.*, 581 (1967), and unpublished work.

The species  $\text{RhCl}\{(o\text{-tol})_3\text{P}\}_2$  could also dehydrogenate alcohols to give, finally, the carbonyl complex **7**; the extent to which this reaction competes with ligand dehydrogenation depends on the nature of the alcohol in a manner which is not immediately obvious. As expected, decarbonylation of the alcohol becomes more important as the number of *o*-tolyl groups decreases. Attempts to prepare the rhodium(I) complex  $\text{RhCl}\{(o\text{-tol})_3\text{P}\}_2$  by treating  $\text{RhCl}(\text{C}_8\text{H}_{14})_2$  with the ligand give an exceedingly air-sensitive material of approximate composition  $\text{RhCl}\{(o\text{-tol})_3\text{P}\}$  which has not yet been further investigated.

It is worth noting for comparison that *trans*-stilbenes can be prepared by the oxidative coupling of toluenes carrying strongly electron-withdrawing groups in the *ortho* or *para* positions.<sup>56</sup> The reactions are generally carried out under strongly alkaline conditions in the presence of air, often in the presence of a copper catalyst, and involve the bibenzyl  $(\text{ArCH}_2)_2$  as an intermediate. We have been unable to detect the formation of any complexes of the phosphine  $\{(o\text{-tol})_2\text{-PC}_6\text{H}_4\text{CH}_2\}_2$  in the reaction of  $\text{RhCl}_3$  with  $(o\text{-tol})_3\text{P}$ . By analogy with the organic reactions, however, the group  $\{(o\text{-tol})_2\text{P}\}_2\text{Rh}$  can be regarded as an electron-withdrawing substituent in an aromatic ring, a view which is consistent with the concept of strong  $\sigma$ -electron donation from the phosphorus atoms to the metal and double bond.

Evidence is available to support the proposed disproportionation of the rhodium(II) complex (eq 1). If **1** is added to benzene or 2-methoxyethanol and the solution is treated with CO at 25° (1 atm), a mixture of the rhodium(I) and rhodium(III) carbonyl complexes, **7** and **21**, is obtained in approximately equal amounts, as judged qualitatively by the intensity of the bands due to  $\nu(\text{CO})$ . A similar reaction occurs with the rhodium(II) complex **5**. The stoichiometry is presumably as follows.



However, if **1** is added to benzene which has been saturated with CO, the rhodium(II) is quantitatively reduced to the rhodium(I) carbonyl **7**. The corresponding  $\text{Ph}(o\text{-tol})_2\text{P}$  complex **5** behaves similarly. By contrast, the mixed valence  $\text{Rh(I)-Rh(III)}$  complex  $\text{Rh}_2\text{Cl}_4\{(\text{C}_2\text{H}_5)(\text{C}_6\text{H}_5)_2\text{P}\}_4$  reacts with CO to give a mixture of rhodium(I) and rhodium(III) carbonyl complexes,  $\text{RhCl}(\text{CO})\{(\text{C}_2\text{H}_5)(\text{C}_6\text{H}_5)_2\text{P}\}_2$  and  $\text{RhCl}_3(\text{CO})\{(\text{C}_2\text{H}_5)(\text{C}_6\text{H}_5)_2\text{P}\}_2$ .<sup>25</sup> These results support the formulation of  $\text{RhCl}_2\{\text{Ph}(o\text{-tol})_2\text{P}\}_2$  as a genuine complex of  $\text{Rh(II)}$ , rather than as a mixed valence complex of  $\text{Rh(I)-Rh(III)}$  with bridging chlorines.

There are several features of the reaction between rhodium(III) chloride and  $(o\text{-tol})_3\text{P}$  which cannot be accounted for solely on the basis of the proposed disproportionation. When the components are heated in 2-methoxyethanol for 75 min and the mixture is then treated with CO, the rhodium(III) carbonyl **21** is formed almost quantitatively, and there is no sign of the rhodium(I) carbonyl **7**. It is known that neither **21** nor its parent trimer **12** are precursors to the stilbene complex

(56) "Chemistry of Carbon Compounds," Vol. IIIB, E. H. Rodd, Ed., Elsevier Publishing Co., Amsterdam, 1956, p 1139, and references cited therein.

36, which is formed on longer heating, and at present we can offer no explanation for the observation. When the reaction is carried out in ethylene glycol, the formation of the rhodium(I) carbonyl complex 7 can be detected after about 75 min, but the stilbene complex 34 has not formed at this stage. After 2.5–5 hr, however, all the carbonyl complex has decomposed to rhodium metal, and 34 can be detected. This is difficult to reconcile with the idea that 7 and 34 are derived from a common intermediate  $\text{RhCl}\{(o\text{-tol})_3\text{P}\}_2$ , and all attempts to prepare 34 from 7 have been unsuccessful. Further work is clearly required to elucidate the mechanism of formation of the stilbene complexes.

## Experimental Section

**Measurements.** Magnetic susceptibilities were measured at room temperature on powdered samples using the Gouy method, following the procedure given by Figgis and Lewis.<sup>57</sup> The Gouy tube was calibrated with  $\text{Hg}[\text{Co}(\text{NCS})_4]$  ( $\chi_M = 16.44 \times 10^{-6}$  cgsu at 20°). Infrared spectra in the range 4000–400  $\text{cm}^{-1}$  were measured as Nujol and hexachlorobutadiene mulls on a Perkin-Elmer 337 double-beam grating spectrophotometer calibrated against polystyrene film, and in the range 455–200  $\text{cm}^{-1}$  as Nujol mulls between high-density polythene plates on a Grubb-Parsons double-beam grating spectrophotometer, Type DM 2, calibrated against water vapor. Frequencies are accurate to  $\sim \pm 2$   $\text{cm}^{-1}$ . Proton magnetic resonance spectra were measured on a Varian HA-100 instrument using  $\text{CDCl}_3$  solutions containing TMS as internal reference. X-Ray powder photographs of specimens ca. 1 mm thick were recorded on a Nonius-Guinier Mark II camera using nickel-filtered  $\text{Cu K}\alpha$  radiation. Conductivity measurements were made at 25°, on ca.  $10^{-3}$  M solutions in Analar nitrobenzene using a Wayne-Kerr universal bridge, Type B 221, and conventional dip-type bright platinum electrodes. The cell was calibrated with aqueous potassium chloride solution. Molecular weights were measured at 25° in Analar solvents using a vapor pressure osmometer (Model 301A, Mechrolab, Calif.) calibrated with benzil. Melting points (uncorrected) were recorded on samples sealed in evacuated capillaries on a Gallenkamp hot stage apparatus. Microanalyses were carried out by Dr. A. Bernhardt, Max-Planck Institut für Kohlenforschung, Mülheim (Ruhr) Germany, Messrs. Weiler and Strauss, Oxford, Department of Chemistry, University College, London, Department of Chemistry, Imperial College, B London, and the Analytical Department of ICI Heavy Organic Chemicals Division, Billingham, England. The latter also determined Rh:Cl:P ratios by X-ray fluorescence.

**Ligand Syntheses.** The isomeric tritolyphosphines were prepared by the literature method,<sup>58</sup> except that the Grignard reagent of the bromotoluene was kept at  $\sim -10^\circ$  by external Dry Ice cooling during the addition of phosphorus trichloride.

**Diphenyl-*o*-tolylphosphine,  $(\text{C}_6\text{H}_5)_2(o\text{-CH}_3\text{C}_6\text{H}_4)\text{P}$ ,  $(\text{Ph}_2(o\text{-tol}))\text{P}$ .** A Grignard reagent from *o*-bromotoluene (102 g, 0.60 mole) and magnesium (14.3 g, 0.59 g-atom), in 200 ml of anhydrous ether was cooled to  $\sim -10^\circ$  and treated dropwise with chlorodiphenylphosphine (114 g, 0.52 mole) in 250 ml of ether. The mixture was heated under reflux for 30 min then cooled to  $\sim 10^\circ$  and hydrolyzed cautiously with 5% hydrochloric acid. The ether layer was separated and the aqueous layer extracted once with 150 ml of ether. The combined ethereal solutions were dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated to ca. 150 ml. Addition of 400 ml of ethanol gave a white precipitate which was filtered off and recrystallized from ethanol to give 96 g (67%) of colorless crystals, mp 73°. *Anal.* Calcd for  $\text{C}_{19}\text{H}_{17}\text{P}$ : C, 82.6; H, 6.2. Found: C, 82.0; H, 6.4.

**Phenyldi-*o*-tolylphosphine,  $\text{C}_6\text{H}_5(o\text{-CH}_3\text{C}_6\text{H}_4)_2\text{P}$ ,  $\text{Ph}(o\text{-tol})_2\text{P}$ .** This was prepared similarly from *o*-bromotoluene (191 g, 1.11 moles), magnesium (27.2 g, 1.12 g-atoms), and dichlorophenylphosphine (70 g, 0.50 mole) as white crystals, mp 83° (35 g, 24%), from ethanol. *Anal.* Calcd for  $\text{C}_{20}\text{H}_{19}\text{P}$ : C, 82.7; H, 6.6. Found: C, 83.2; H, 7.0.

**Complexes.** Analytical data, colors, and melting points are in Table I. Unless otherwise stated, all complexes were dried at 25°

( $10^{-2}$  mm). All reactions were carried out in an atmosphere of oxygen-free nitrogen.

***trans*-Dichloro(tri-*o*-tolylphosphine)rhodium(II) (1a).** A mixture of hydrated rhodium(III) chloride (1.2 g, 0.0045 mole) and tri-*o*-tolylphosphine (6.0 g, 0.019 mole) in 400 ml of degassed ethanol was stirred at 25° for 24 hr. The blue-green precipitate was filtered and washed successively with 50 ml of ethanol, four 20-ml portions of acetone, and 50 ml of ether: yield 1.8 g (50%);  $\mu_{\text{eff}}$  at 23° =  $2.30 \pm 0.05$  BM.

**1b.** A mixture of hydrated rhodium(III) chloride (0.25 g, 0.0005 mole) and tri-*o*-tolylphosphine (1.4 g, 0.0053 mole) in 50 ml of degassed ethanol was stirred at 0° for 24 hr. The mauve precipitate was filtered and washed successively with 20 ml of ice-cold ethanol and 20 ml of ice-cold ether: yield 0.32 g (43%);  $\mu_{\text{eff}}$  at 22° =  $2.0 \pm 0.05$  BM.

The filtrate from the above experiments was treated with carbon monoxide at 25° (1 atm) for 5 hr. The pale yellow precipitate was filtered and washed successively with ethanol and ether. It was identified as *trans*- $\text{RhCl}(\text{CO})\{(o\text{-tol})_3\text{P}\}_2$  (7) by comparison of its infrared spectrum and X-ray powder pattern with those of an authentic sample (see below).

**Interconversion of 1a and 1b. A.** The blue-green modification (0.4 g) was dissolved in 40 ml of degassed dichloromethane in the absence of air, giving a purple solution. This was evaporated at ca.  $-10^\circ$  ( $10^{-2}$  mm) leaving 0.4 g of mauve solid, identified as 1b by its X-ray powder pattern and infrared spectrum.

**B.** A suspension of the mauve modification (0.7 g) in 20 ml of acetone was stirred at 25° for 20 min. The blue-green precipitate was filtered, washed with ether, and identified as 1a by its infrared spectrum and X-ray powder pattern.

***trans*-Dichlorobis(tri-*o*-tolylphosphine)palladium(II) (2).** To a solution of tri-*o*-tolylphosphine (0.51 g, 0.0017 mole) in 35 ml of ethanol was added dropwise a solution of  $\text{K}_2\text{PdCl}_4$  (0.27 g, 0.00082 mole) in 10 ml of water. A pale yellow suspension formed immediately. The solution was stirred for 2 hr at room temperature, after which the yellow precipitate was filtered, washed successively with aqueous ethanol, ethanol, and ether, and recrystallized from 1 l. of boiling toluene. The bright yellow crystals were washed with ether and dried at 80° ( $10^{-2}$  mm).

***trans*-Dibromobis(tri-*o*-tolylphosphine)palladium(II) (3).** This was prepared similarly starting from tri-*o*-tolylphosphine (0.54 g) and  $\text{K}_2\text{PdBr}_4$  (0.44 g). After recrystallization from toluene, 0.49 g of bright-orange solvated crystals were obtained (74% yield).

***trans*-Dichlorobis(tri-*o*-tolylphosphine)platinum(II) (4).** This was prepared similarly starting from tri-*o*-tolylphosphine (0.74 g) and  $\text{K}_2\text{PtCl}_4$  (0.5 g). The product was obtained as white crystals from chloroform-*n*-heptane, yield 0.67 g (67%).

***trans*-Dichlorobis(phenyldi-*o*-tolylphosphine)rhodium(II) (5).** A mixture of hydrated rhodium(III) chloride (0.22 g, 0.00084 mole) and phenyldi-*o*-tolylphosphine (1.2 g, 0.004 mole) in 50 ml of degassed ethanol was stirred for 12 hr at 25°. A red suspension began to form after 30 min. The red crystalline precipitate was filtered off, washed successively with ethanol and ether, and dried at 40° ( $10^{-2}$  mm). The pale orange-red filtrate was treated with carbon monoxide at 25° (1 atm) for 4 hr. The pale yellow precipitate ( $\sim 50$  mg) was identified as *trans*- $\text{RhCl}(\text{CO})\{\text{Ph}(o\text{-tol})_2\text{P}\}_2$  (8) by comparison of its infrared spectrum and X-ray powder pattern with those of an authentic sample (see below).

***trans*-Dichlorobis(phenyldi-*o*-tolylphosphine)palladium(II) (6).** This was prepared similarly to the corresponding tri-*o*-tolylphosphine complex, recrystallized from boiling toluene, washed with ether, and dried at 80° ( $10^{-2}$  mm) (64% yield).

**Attempted Reaction between Rhodium Trichloride and Diphenyl-*o*-tolylphosphine.** A mixture of hydrated rhodium(III) chloride (0.5 g) and the ligand (8 g) in degassed ethanol at 25° for 3 hr gave 1.6 g of an amorphous red solid, which was washed successively with ethanol and ether and dried at 40° ( $10^{-2}$  mm). Analytical data suggest that the compound is a mixture containing mainly  $\text{RhCl}\{\text{Ph}_2(o\text{-tol})\text{P}\}_2$  together with some  $\text{RhCl}\{\text{Ph}_2(o\text{-tol})\text{P}\}_3$  and/or  $\text{RhCl}_2\{\text{Ph}_2(o\text{-tol})\text{P}\}_2$ . *Anal.* Calcd for  $\text{C}_{38}\text{H}_{34}\text{Cl}_2\text{P}_2\text{HR}$ : C, 65.9; H, 5.0; Cl, 5.1; P, 9.0. Found: C, 64.1; H, 5.3; Cl, 5.7; P, 9.1. Calcd for  $\text{C}_{57}\text{H}_{51}\text{Cl}_3\text{P}_3\text{Rh}$ : C, 70.6; H, 5.3; Cl, 3.7; P, 9.6. Calcd for  $\text{C}_{38}\text{H}_{34}\text{Cl}_2\text{P}_2\text{Rh}$ : C, 62.6; H, 4.7; Cl, 9.7; P, 8.5.

**Hexachlorotriscis(*o*-di-*o*-tolylphosphino)benzyl}trirhodium(III) (12).** i. From  $\text{RhCl}_3$ . A mixture of hydrated rhodium(III) chloride (1-g, 0.0038 mole) and tri-*o*-tolylphosphine (4.7 g, 0.015 mole) in 250 ml of 2-methoxyethanol was heated under reflux for 75 min. The solvent was removed at  $10^{-2}$  mm and the yellow residue was washed with three 50-ml portions of hot *n*-hexane to remove excess ligand. The solid was dissolved in the minimum volume of sodium-dried

(57) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers Inc., New York, N. Y., 1960, Chapter 6, p 416.

(58) F. G. Mann and E. J. Chaplin, *J. Chem. Soc.*, 527 (1937).

benzene and chromatographed on a column of silica gel. The product was eluted with benzene containing 5% acetone and was recrystallized from 1:1 acetone-ether or 1:1 chloroform-ether, yield 0.62 g (34%).

ii. From *trans*-RhCl<sub>2</sub>{(*o*-tol)<sub>2</sub>P<sub>2</sub>}. A suspension of the rhodium(II) complex **1a** (0.35 g) in 75 ml of 2-methoxyethanol was heated under reflux for 75 min. Passage of nitrogen through the solution and then into acidified silver nitrate gave a precipitate of silver chloride, showing that HCl was produced. The orange solution was evaporated to dryness at 10<sup>-2</sup> mm and the yellow residue extracted with three 20-ml portions of *n*-pentane. Evaporation of the combined extracts to dryness gave tri-*o*-tolylphosphine, mp and mmp 125°. The pentane-insoluble residue was chromatographed as in *i* and the product obtained as yellow crystals from chloroform-ether. The same product was obtained by carrying out the reaction in the presence of a twofold molar excess of tri-*o*-tolylphosphine.

**Hexabromotris{*o*-(di-*o*-tolylphosphino)benzyl}trirhodium(III) (13).** This was prepared as under *i* above from rhodium(III) bromide (0.7 g) and tri-*o*-tolylphosphine (2.5 g) in 150 ml of 2-methoxyethanol. After chromatography and recrystallization from acetone-ether, 0.3 g (26%) of yellow crystals were obtained.

**Reactions of the Trimeric Complex 12 with Ligands.** i. **Pyridine.** Complex **14** (0.15 g) was dissolved in benzene (50 ml) and treated with pyridine (0.4 g) at 25°. After 15 min, 30 ml of *n*-heptane was added and the solution evaporated at 25° (15 mm) to ca. 20 ml to give 0.18 g (90%) of the orange-yellow bispyridine adduct **14a**. The X-ray powder pattern of the compound was unaltered after rapid recrystallization from chloroform-ethanol. If a solution in chloroform-ethanol was kept overnight, straw-colored needles of the chloroform adduct **14b** were obtained, which were not isomorphous with **14a**.

ii. ***p*-Toluidine.** The reaction was carried out as in *i*, using 0.5 g of *p*-toluidine. The mixture was refluxed for 4 hr and then evaporated to ca. 15 ml at 25° (15 mm). The microcrystalline precipitate of the monoadduct **15** was filtered and washed with ether, yield 0.19 g (87%).

iii. **Triphenylphosphine.** The reaction was carried out as in *i*, using 0.4 g of complex and 2 g of triphenylphosphine in 120 ml of benzene. Recrystallization from chloroform-ethanol gave 0.18 g (29%) of pale yellow microcrystals of the monoadduct **16**.

iv. **1,2-Bis(diphenylphosphino)ethane.** A solution of the complex **12** (0.15 g) in 50 ml of benzene was treated with a solution of the ditertiary phosphine (0.75 g) in 15 ml of benzene. The mixture was refluxed for 1 hr and cooled. *n*-Heptane (40 ml) was added and the solution evaporated at 15 mm. The crude product which precipitated was recrystallized from chloroform-ethanol to give yellow crystals of adduct **17** (0.16 g, 58%).

v. **1,2-Bis(diphenylarsino)ethane.** The reaction was carried out as in *iv* using 0.2 g of complex **12** and 1.1 g of ligand. The solution rapidly changed from red to yellow on addition of the ditertiary arsine. Pale yellow crystals (0.28 g, 69%) of adduct **18** were obtained from chloroform-ethanol.

vi. **2,2'-Bipyridyl.** The reaction was carried out as in *iv* using 0.15 g of complex **12** and 0.3 g of bipyridyl. The unrecrystallized product was a benzene solvate **19a**, and recrystallization from chloroform-ethanol gave a chloroform solvate **19b** (0.16 g, 58%). Both retained their solvent after heating at 80° (10<sup>-2</sup> mm) and were isomorphous.

**Reaction of Trimeric Bromo Complex 13 with *p*-Toluidine.** This was carried out as in *ii*, using 0.25 g of complex **13** and 0.6 g of *p*-toluidine. The yellow microcrystals of the monoadduct **20** (0.12 g, 40%) were washed with ether.

**Dichloro{*o*-(di-*o*-tolylphosphino)benzyl}carbonylrhodium(III) (21).** i. A solution of the trimeric complex **12** (0.5 g, 0.00035 mole) in 75 ml of benzene was treated with carbon monoxide at 25° (1 atm) for 5 hr. The white precipitate of **21** was filtered off and washed successively with ethanol and ether: yield 0.45 g (85%);  $\nu(\text{CO})$  (Nujol) 2090 s, 2074 cm<sup>-1</sup> sh.

ii. Hydrated rhodium(III) chloride (0.5 g, 0.0019 mole) and tri-*o*-tolylphosphine (2.5 g, 0.0082 mole) in 150 ml of degassed 2-methoxyethanol were heated under reflux for 75 min. The red solution was evaporated to dryness at 10<sup>-2</sup> mm and the residue dissolved in 100 ml of benzene. The solution was treated with carbon monoxide at 25° (1 atm) for 5 hr to give 0.77 g (80%) of the required product. Alternatively, the red solution in 2-methoxyethanol treated directly with CO gave an 87% yield of **21**.

iii. A suspension of **1** (0.5 g) in 2-methoxyethanol (75 ml) was heated under reflux for 75 min. The orange solution was then treated with carbon monoxide at 25° (1 atm) for 5 hr to give a white precipitate which was filtered off and washed with ether. The prod-

uct (0.17 g, 56%) was isomorphous with and had the same infrared spectrum as that obtained in *i* and *ii*.

**Dibromo{*o*-(di-*o*-tolylphosphino)benzyl}carbonylrhodium(III) (22).** This was prepared similarly to **21**, either by treating the trimeric bromo complex **13** with CO at 25° (1 atm) (87% yield), or by carbonylating the solution obtained by heating rhodium(III) bromide and tri-*o*-tolylphosphine in 2-methoxyethanol (98% yield):  $\nu(\text{CO})$  (Nujol) 2090 s, 2070 cm<sup>-1</sup> s.

**Reactions of the Carbonyl Complexes 21 and 22 with Ligands.**

i. **Triphenylphosphine and Related Ligands.** Complex **21** (0.6 g, 0.001 mole) and triphenylphosphine (3 g, 0.011 mole) in 60 ml of benzene were heated under reflux for 5 hr. The pale yellow solution was filtered and 40 ml of *n*-heptane added to the filtrate. The solution was evaporated to ca. 30 ml at 25° (15 mm) and the resulting solid was recrystallized from chloroform-ethanol, yield of **23** 0.75 g (82%).

The complexes **24**, **26**, **27**, and **28** containing triarylphosphines were prepared similarly.

ii. **Pyridine.** The reaction carried out as in *i* gave 0.22 g (95%) of the monoadduct **29**. The isomorphous bromo complex **30** was prepared similarly from **22** and pyridine in 93% yield. The analytical data in both cases indicate the presence of benzene of crystallization which was not removed at 80° (10<sup>-2</sup> mm).

iii. ***p*-Toluidine.** The carbonyl complexes **21** and **22** reacted with *p*-toluidine in refluxing benzene to give white and pale yellow crystals, respectively, of the monoadducts **31** and **32** in 80-90% yield.

iv. **1,2-Bis(diphenylphosphino)ethane.** Complex **21** (0.2 g) was heated with the ditertiary phosphine (0.8 g) in 80 ml of benzene for 3 hr. The orange solution was evaporated to dryness at 25° (15 mm) and the residue extracted with four 15-ml portions of *n*-pentane. The yellow solid was recrystallized from 1:3 chloroform-ethanol and washed successively with 10 ml of ethanol and 10 ml of *n*-pentane, yield of **33** 0.22 g (60%).

All these carbonyl complexes show one strong band at 2070 ± cm<sup>-1</sup> (Nujol) and at 2065 cm<sup>-1</sup> (CHCl<sub>3</sub>).

v. **Other Ligands.** Complex **21** was unchanged after attempted reaction with 2,2'-bipyridyl, 2,6-lutidine, phenyldi-*o*-tolylphosphine, and tri-*o*-tolylphosphine.

**Preparation of Diiodo{*o*-(di-*o*-tolylphosphino)benzyl}tri-*m*-tolylphosphinecarbonylrhodium(III) (25).** The chloro complex **24** (0.2 g, 0.00025 mole) was treated with a solution of sodium iodide (0.6 g, 0.004 mole) in 40 ml of acetone and boiled for 2 hr. After removal of solvent at 15 mm, the residual solid was extracted with three 10-ml portions of water and recrystallized twice from aqueous acetone. The product was washed with ethanol and finally recrystallized from 1:1 benzene-*n*-heptane, yield 0.13 g (53%).

**Disproportionation of *trans*-RhCl<sub>2</sub>{(*o*-tol)<sub>2</sub>P<sub>2</sub>}. Complex 1a** (0.2 g) was heated under reflux in 50 ml of benzene for 3 hr to give a yellow-brown solution. This was treated with carbon monoxide for 5 hr at 25° (1 atm) and evaporated to dryness at 15 mm. The residue was washed with 25 ml of ether and then extracted with six 10-ml portions of chloroform. The insoluble white residue was identified as **21** by comparison of its infrared spectrum and X-ray powder pattern with those of an authentic sample. The combined chloroform extracts were evaporated to dryness at 15 mm and the residue was recrystallized from chloroform-ethanol to give **7**, identified by its infrared spectrum and X-ray powder pattern.

**Disproportionation of *trans*-RhCl<sub>2</sub>{Ph(*o*-tol)<sub>2</sub>P<sub>2</sub>}. Complex 5** (0.8 g) was heated in 120 ml of benzene for 5 hr, and then treated with carbon monoxide as above. Complex **8** was obtained from the chloroform extracts, and a white insoluble residue of impure RhCl<sub>2</sub>(CO){(*o*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)(C<sub>6</sub>H<sub>5</sub>)(*o*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)P<sub>2</sub>} was also obtained. *Anal.* Calcd for C<sub>21</sub>H<sub>20</sub>Cl<sub>2</sub>OPRh: C, 51.1; H, 3.9; Cl, 14.4; P, 6.3. Found: C, 49.1; H, 4.0; Cl, 15.6; P, 6.4.

**Coupling-Dehydrogenation Reactions. Reaction of Rhodium(III) Chloride with Tri-*o*-tolylphosphine in Various Solvents.** Hydrated rhodium(III) chloride (0.24 g, 0.00091 mole) and tri-*o*-tolylphosphine (1.4 g, 0.0046 mole) in 50 ml of degassed 2-(2-methoxyethoxy)-ethanol were heated under reflux for 3 hr in a nitrogen atmosphere to give a clear orange solution. This was cooled and solvent was removed at 10<sup>-2</sup> mm. The yellow residue, which showed no band due to  $\nu(\text{CO})$  in its infrared spectrum, was washed with two 25-ml portions of *n*-pentane and dissolved in ~5 ml of sodium-dried benzene. The solution was chromatographed on silica gel. Elution with benzene containing 1% of acetone gave a yellow fraction, which when evaporated to dryness gave a yellow solid. This was recrystallized from 1:1 benzene-ethanol to give yellow microcrystals of the stilbene complex solvated with benzene, **34a** (0.24 g, 35%), which were dried at 80° (10<sup>-2</sup> mm) for 6 hr. Recrystallization from chloroform-ethanol gave a chloroform solvate, **34b**.

Similar results were obtained by carrying out the reaction in the following solvents (refluxing time and yield of stilbene complex in parentheses): 2-methoxyethanol (6 hr, 27%); acetophenone (7 hr, 21%); benzyl alcohol (5 hr, 22%). In no case was the formation of the carbonyl complex **7** detected. The analytical data on the chloroform solvate **34a** tended to vary slightly with different preparations and possibly with different drying times, apparently because of varying proportions of solvent molecules in the crystal lattice (0–0.15 mole per mole of complex). Thus, the product from the reaction carried out in benzyl alcohol gave the following figures. *Anal.* Calcd for  $C_{42}H_{38}ClP_2Rh \cdot 0.1CHCl_3$ : C, 66.8; H, 5.3; Cl, 6.1; P, 8.2; ratio Cl:P:Rh, 1.3:2:1. Found: C, 67.5; H, 5.3; Cl, 5.7; P, 7.8; ratio Cl:P:Rh, 1.3:1.8:1. The products from acetophenone and 2-methoxyethanol as reaction media were essentially solvent free. *Anal.* Calcd for  $C_{42}H_{38}ClP_2Rh$ : C, 67.9; H, 5.2; Cl, 4.7; P, 8.3. Found: C, 68.2; H, 5.2; Cl, 5.3; P, 8.1.

The reaction between rhodium(III) chloride (0.25 g) and tri-*o*-tolylphosphine (1.25 g) in refluxing 1-heptanol (70 ml) gave an orange-yellow solution after 6 hr, which deposited pale yellow crystals of the rhodium(I) carbonyl **7** (0.65 g, 83%), identified by its infrared spectrum and X-ray powder pattern. The orange filtrate was evaporated to dryness at  $10^{-2}$  mm, and the residual yellow solid washed with 25 ml of *n*-pentane. Chromatography in benzene on silica gel, elution with benzene containing 1% acetone, followed by evaporation of the yellow solution gave ~1% yield of **34**. In refluxing *p*-chlorobenzyl alcohol for 5 hr a 53% yield of **7** was isolated by chromatography, but no stilbene complex could be detected.

The reaction between 0.1 g of  $RhCl_3$  and 0.75 g of (*o*-tol)<sub>3</sub>P in refluxing ethylene glycol for various times (see below) gave a black solid which after removal of solvent at  $10^{-2}$  mm gave a black solid. This was extracted with four 25-ml portions of hot chloroform and the combined extracts were evaporated at 15 mm to give a yellow solid. The infrared spectrum of this solid showed a strong band at  $1975\text{ cm}^{-1}$  due to **7** and only a weak band at  $917\text{ cm}^{-1}$  due to **34** when the initial reaction had been carried out for ~75 min. In the case of 2.5- or 5-hr reaction times, however, the solid showed no band at  $1975\text{ cm}^{-1}$  and a strong band at  $917\text{ cm}^{-1}$ . The same products were obtained in the various solvents starting with  $RhCl_2 \cdot \{(o\text{-tol})_3P\}_2$  in place of  $RhCl_3$ .

**Reaction of Rhodium(III) Bromide with Tri-*o*-tolylphosphine.** Rhodium(III) bromide (0.5 g) and (*o*-tol)<sub>3</sub>P (2.3 g) in 50 ml of degassed 2-methoxyethanol were heated under reflux in a nitrogen atmosphere for 5 hr. The orange-brown solution was evaporated to dryness at  $10^{-2}$  mm to give a brown solid which had a strong band at  $1975\text{ cm}^{-1}$  in its infrared spectrum. Chromatography in benzene on silica gel and elution with benzene containing 1% of acetone gave yellow **35**, which was recrystallized from 1:1 benzene-ethanol, yield 70 mg (6%). A similar reaction in 2-(2-methoxy)ethoxyethanol gave a 4% yield of **35**.

**Thiocyanato-*trans*-2,2'-*o*-(di-*o*-tolylphosphino)stilbene}rhodium(I).** (**36**). To a suspension of **34** (0.76 g, 0.001 mole) in 90 ml of acetone was added sodium thiocyanate (1.2 g, 0.015 mole) and the mixture heated under reflux for 7 hr. The hot solution was filtered and water was added dropwise to the filtrate until a precipitate began to form. The volume of solution was then reduced to ca. 20 ml at 15 mm, 10 ml of water added to complete precipitation, and the yellow solid was filtered. It was washed with 50 ml of water and then recrystallized from acetone to give 0.52 g (66%) of orange crystals of the acetone solvate of **36** [ir maxima ( $\text{cm}^{-1}$ ) due to  $\nu(\text{CN})$  at  $2075\text{ vs.}$ ,  $\nu(\text{CS})$   $829\text{ vs.}$ , probably indicating N-bonded thiocyanate]. The solvent-free sample **36** was obtained after drying at  $110^\circ$  ( $10^{-2}$  mm) [ $\nu(\text{CN})$  ( $\text{cm}^{-1}$ )  $2125\text{ s, sharp;}$   $2075\text{ s, broad;}$   $2050\text{ s, sharp;}$   $\nu(\text{CS})$   $845\text{ w,}$   $710\text{ sh,}$  possibly indicating a mixture of N- and S-bonded thiocyanate, possibly also bridging thiocyanate].

**Reaction of Rhodium(III) Chloride with Phenyl-di-*o*-tolylphosphine in 2-Methoxyethanol.** A solution of hydrated rhodium(III) chloride (1 g, 0.0038 mole) and  $\text{Ph}(o\text{-tol})_2\text{P}$  (5.6 g, 0.019 mole) in 150 ml of degassed 2-methoxyethanol was heated under reflux in a nitrogen atmosphere for 24 hr to give a clear orange-yellow solution. This was cooled to room temperature and the pale yellow solid which precipitated after 24 hr was filtered. Recrystallization from 1:1 benzene-ethanol gave the rhodium(I) carbonyl **8** (0.65 g, 23%), identified by comparison of its infrared spectrum and X-ray powder pattern with those of an authentic sample. The filtrate was evaporated to dryness at  $10^{-2}$  mm and the yellow residue extracted with two 150-ml portions of *n*-pentane at room temperature, followed by 150 ml of ether. Evaporation of the ether extract to dryness at 15 mm gave a yellow solid which was dissolved in benzene and

chromatographed on alumina. The yellow fraction eluted with benzene containing 2% acetone when evaporated to dryness gave a yellow solid residue of **37a** (0.2 g, 7%), which was recrystallized from dichloromethane-*n*-hexane.

The ether-insoluble residue was washed with three 30-ml portions of ether and extracted with 100 ml of acetone at room temperature for 12 hr. The insoluble residue was filtered off and the filtrate kept at room temperature for a further 12 hr. A small amount of solid which precipitated was filtered off and the filtrate evaporated to dryness at 15 mm. The residual yellow solid was dissolved in benzene and chromatographed on alumina. The yellow fraction eluted with benzene containing 2% acetone gave a yellow solid **37b** (0.25 g, 9%) after removal of solvent; this was recrystallized from dichloromethane-*n*-hexane.

The infrared spectrum of the acetone-insoluble residue showed bands at  $1975$  and  $920\text{ cm}^{-1}$  suggesting that a mixture of **8** and **37** was present, but attempts to separate these were not successful. The same products were obtained by using  $RhCl_2\{\text{Ph}(o\text{-tol})_2P\}_2$  in place of  $RhCl_3$ .

**Reaction of Rhodium(III) Chloride with Diphenyl-*o*-tolylphosphine in 2-Methoxyethanol.** Hydrated rhodium(III) chloride (0.5 g, 0.0019 mole) and  $\text{Ph}_2(o\text{-tol})P$  (2.7 g, 0.0098 mole) in 75 ml of degassed 2-methoxyethanol were heated under reflux for 15 hr in a nitrogen atmosphere. A bright orange-red suspension which formed initially gradually dissolved to give a red solution, which turned orange-yellow on continued heating. The solution was cooled to room temperature and left for 12 hr. A pale yellow precipitate of **9** (1.1 g, 81%) was collected, washed with ether, and identified by its infrared spectrum and X-ray powder pattern. The filtrate was evaporated to dryness at  $10^{-2}$  mm and the yellow residue was dissolved in 15 ml of benzene. This was chromatographed on a column of silica gel and eluted with benzene containing 0.5% acetone. A faint yellow band, a small purple band, and an orange band were collected; solvent was removed at 15 mm and the yellow residue rechromatographed in benzene. A yellow solution eluted by benzene gave a yellow solid after removal of solvent; this was washed successively with 2 ml of ether and 5 ml of pentane and recrystallized from chloroform, yield of **38** ~1%.

**Attempted Reaction of *trans*- $RhCl(\text{CO})\{(o\text{-tol})_3P\}_2$  with Tri-*o*-tolylphosphine in Various Solvents.** A mixture of the carbonyl complex **7** (0.4 g) and (*o*-tol)<sub>3</sub>P (0.36 g) was heated under reflux in 50 ml of either acetophenone, 2-methoxyethanol, or ethylene glycol for 3–8 hr. In the first and last solvents, some rhodium metal was deposited, but in all cases the only complex isolated was unchanged **7** in yields of 70–90%.

**Attempted Reaction of the Trimeric Complex **14** with Tri-*o*-tolylphosphine in 2-Methoxyethanol.** Complex **12** (0.4 g) and (*o*-tol)<sub>3</sub>P (5.2 g) were heated under reflux in a nitrogen atmosphere in 150 ml of 2-methoxyethanol for 5 hr. The yellow solution was evaporated to dryness at  $10^{-2}$  mm and the residual yellow solid chromatographed in benzene on silica gel. No fractions were isolated by eluting with benzene containing 5% acetone or less. Elution with 4:1 benzene-acetone gave a yellow solution which, when evaporated to dryness at 15 mm, gave a yellow solid. The infrared spectrum and X-ray powder pattern were different from both **12** and **34a**, and there was no band due to  $\nu(\text{CO})$ . Analytical data fit approximately for  $RhCl\{(o\text{-tol})_3P\}_3$ , but the compound has not been further characterized as yet. *Anal.* Calcd for  $C_{21}H_{21}Cl_3P_3$ : C, 57.1; H, 4.3; Cl, 8.0; P, 7.0. Found: C, 57.4; H, 5.2; Cl, 10.1; P, 6.1.

**Displacement of *trans*-2,2'-*o*-(Di-*o*-tolylphosphino)stilbene from Complex **34**.** A suspension of complex **34** (0.25 g) in 50 ml of ethanol and 20 ml of water was treated with 1 g of sodium cyanide and the mixture boiled for 7 hr to give an almost colorless solution. This was evaporated to dryness at 15 mm and the residue extracted with water until the extract gave no test for  $\text{CN}^-$  ( $\text{AgNO}_3$ ). The water-insoluble residue was extracted with three 15-ml portions of hot benzene, and the combined extracts were evaporated to ca. 10 ml at 15 mm and set aside. The white crystalline precipitate was recrystallized from benzene to give 0.64 g (79%) of the stilbene ligand (mp  $263^\circ$ ) which was dried at  $25^\circ$  ( $10^{-2}$  mm). *Anal.* Calcd for  $C_{42}H_{38}P_2$ : C, 83.4; H, 6.3; P, 10.2; mol wt, 603. Found: C, 83.7; H, 6.2; P, 9.9; mol wt, 601 (0.0031  $M$   $C_6H_6$ ), 533 (0.0016  $M$   $C_6H_6$ ).

**Reactions of *trans*-2,2'-*o*-(Di-*o*-tolylphosphino)stilbene. 1.** With  $RhCl(\text{Ph}_3P)_3$ . To a solution of  $RhCl(\text{Ph}_3P)_3$  (0.24 g) in 15 ml of benzene was added a solution of the ligand (0.16 g) in 15 ml of benzene. After 14 hr at room temperature, almost no reaction had occurred. The mixture was then heated under reflux for 3 hr, cooled to room temperature, and chromatographed on silica gel.

A yellow solid obtained by eluting with benzene containing 0.5% acetone was identified as **34** (~10% yield) by its infrared spectrum and X-ray powder pattern.

2. With  $\text{RhCl}(\text{CO})(\text{Ph}_3\text{P})_2$ . Attempted reaction as in method 1 gave unchanged carbonyl complex.

3. With  $\text{RhCl}(\text{C}_5\text{H}_{14})_2$ . To a stirred solution of the stilbene ligand (0.25 g) in 30 ml of benzene was added 0.15 g of the cyclo-octene complex. An orange-yellow solution formed immediately, which was stirred at room temperature for 5 hr. Evaporation to dryness at 15 mm gave a yellow residue of **34a**, identified by its infrared spectrum and X-ray powder pattern. The solid was treated with sodium thiocyanate (0.52 g) in 30 ml of boiling acetone. The orange crystals (0.25 g, 75%) were identical (infrared, nmr, and X-ray) with **36**.

**Rhodium(I) Complexes of Tri-*p*-tolylphosphine and Tri-*m*-tolylphosphine.** 1.  $\text{RhCl}\{(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}\}_3$ . Treatment of  $\mu, \mu'$ -dichloro-bis(1,5-cyclooctadiene)dirhodium(I)<sup>59</sup> (0.1 g) with  $(p\text{-tol})_3\text{P}$  (0.7 g) in 30 ml of boiling *n*-hexane under nitrogen gave initially a yellow suspension which on refluxing gave a red precipitate. After 1 hr the solution was cooled to room temperature and evaporated to ca. 15 ml at 15 mm; the red microcrystalline precipitate was filtered and washed with *n*-pentane, yield 0.29 g (70%). *Anal.* Calcd for  $\text{C}_{63}\text{H}_{63}\text{Cl}_2\text{P}_3\text{Rh}$ : C, 71.9; H, 6.0; Cl, 3.4; P, 8.8. Found: C, 70.7; H, 6.3; Cl, 4.4; P, 9.1.

A similar reaction with  $(m\text{-tol})_3\text{P}$  gave an orange precipitate which was soluble in all organic solvents and could not be purified from excess ligand.

2.  $\text{RhCl}(\text{CO})\{(p\text{-tol})_3\text{P}\}_2$  (**11**). i. Treatment of  $\text{RhCl}\{(p\text{-tol})_3\text{P}\}_3$  (0.3 g) in 30 ml of benzene with CO at 25° (1 atm) gave a complex identical with that prepared by Vallarino<sup>10</sup> from  $[\text{RhCl}(\text{CO})_2]_2$  and the ligand.

ii. Hydrated rhodium(III) chloride (0.75 g) and  $(p\text{-tol})_3\text{P}$  (4.5 g)

in 150 ml of 2-methoxyethanol were heated under reflux in a nitrogen atmosphere for 6 hr. The solution was cooled to 0° and kept at this temperature overnight. Yellow crystals of **11** (1.5 g, 68%) were isolated. A similar reaction occurred in boiling 2-(2-methoxyethoxy)ethanol to give an 86% yield of crude product, 68% of recrystallized product.

3.  $\text{RhCl}(\text{CO})\{(m\text{-tol})_3\text{P}\}_2$  (**10**). i. An authentic sample was prepared by treating  $[\text{RhCl}(\text{CO})_2]_2$  (0.25 g) in 10 ml of benzene with  $(m\text{-tol})_3\text{P}$  (0.78 g). The crude product was recrystallized from 1:1 dichloromethane-ethanol and dried at 80° ( $10^{-2}$  mm),  $\nu(\text{CO})$  1975  $\text{cm}^{-1}$  (Nujol).

ii. The reaction was carried out as under 2ii; the product (88% yield of crude, 63% yield of recrystallized) was identical with that obtained above.

**Rhodium(I) Carbonyl Complexes of *o*-Tolylphosphines.** Authentic samples of **7**, **8**, and **9** were prepared from  $[\text{RhCl}(\text{CO})_2]_2$  in benzene and the ligand. Solvent was removed at 15 mm, the residue washed with ethanol to remove excess ligand, and the product recrystallized from benzene-ethanol [in the case of  $\text{Ph}_2(o\text{-tol})\text{P}$  and  $\text{Ph}(o\text{-tol})_2\text{P}$ ] or chloroform-ethanol [in the case of  $(o\text{-tol})_3\text{P}$ ].

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(59) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).

## Stereospecificity of the Dichlorobis(ethylenediamine)cobalt(III) Ion in an Optically Active Solvent

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**Abstract:** A stereospecific substitution reaction for the two chloride ligands in *cis*-dichlorobis(ethylenediamine)cobalt(III) chloride by an optically active solvent, 1,2-propanediol, has been observed. The study follows the reactions of the optical and geometrical isomers of the complex when they are dissolved in a particular optical isomer of the solvent. Absorption spectra and circular dichroism data have been interpreted as showing the solvent coordinated as a bidentate ligand with stereospecificity imposed upon the system by conformational interactions.

In the past, much work has been done on the production of optically active ions in solutions of optically inactive complexes. These effects have been named asymmetric syntheses, asymmetric inductions, and asymmetric transformations. Although these effects have generally been observed in common solvents, some interesting examples have been produced in optically active solvents. Asymmetric inductions in metal complexes have been demonstrated,<sup>1-3</sup> while asymmetric syntheses in an optically active solvent have been observed in a very limited number of systems.<sup>4</sup> One of

these involved the observation of circular dichroism activity in a solution of racemic *cis*-dichlorobis(ethylenediamine)cobalt(III) tetraphenylborate, *rac-cis*- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{B}(\text{C}_6\text{H}_5)_4$ , in the optically active solvent L-2,3-butanediol.<sup>4</sup> It was concluded from that study that an antiracemization reaction was occurring with the production of only one optical antipode of the complex ion in solution. A subsequent paper<sup>5</sup> indicated that the optically active species in solution was actually a solvolysis product with the solvent acting as a unidentate ligand. We wished to examine the reaction further in a similar optically active solvent, 1,2-propanediol, and to extend the study by using the optical and

(1) B. Bosnich, *J. Amer. Chem. Soc.*, **88**, 2606 (1966).

(2) R. A. Haines and A. A. Smith, *Can. J. Chem.*, **46**, 1444 (1968).

(3) A. A. Smith and R. A. Haines, *ibid.*, **47**, 2727 (1969).

(4) B. Bosnich, *J. Amer. Chem. Soc.*, **89**, 6143 (1967).

(5) B. Bosnich and D. W. Watts, *ibid.*, **90**, 6228 (1968).