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Rhodium(I) Complexes Containing Mono- and Ditertiary Phosphines and Arsines[1]

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Rhodium dicarbonyl chloride dimer, $[Rh(CO)_2Cl]_2$, reacts with *cis*- and *trans*-β-styryldiphenylarsine, *cis*-β-styryldiphenylphosphine, bis(1-propynyl)phenylphosphine, and tris(ferrocenyl)phosphine to give complexes of the type $[Rh(CO)ClL_2]$ (L = phosphine or arsine). Using an excess of *cis*-1,2-bis(diphenylphosphino)ethylene or bis(diphenylphosphinomethyl) ether, ionic complexes of the type $[Rh(L\text{-}L)_2]X$ (L-L = diphosphine, X = anion) are obtained. Polymeric complexes of formula $[Rh(CO)Cl(L\text{-}L)]_n$ (L-L = diphosphine) result from the reaction with *trans*-1,2-bis(diphenylphosphino)ethylene and bis(diphenylphosphino)acetylene. By contrast, complexes of the same empirical formula prepared from bis(diphenylphosphino)methane and its arsenic analog are dimers. When used in a 2:1 molar ratio, *cis*-1,2-bis(diphenylphosphino)ethylene and $[Rh(CO)_2Cl]_2$ give $[Rh(L\text{-}L)_2][Rh(CO)_2Cl_2]$ (L-L = diphosphine). An analogous reaction with the arsenic analog gives $[Rh(CO)(L\text{-}L)_2][Rh(CO)_2Cl_2]$ (L-L = diarsine). A number of bromo analogs were also prepared. Conductance and infrared spectral data are presented and the structures of the complexes are discussed.

Introduction

To date, only a few scattered reports of Rh(I) complexes of polydentate, tertiary arsines and phosphines have appeared.[2-4] Our current interest in oxidative addition reactions of square-planar, d^8, transition metal compounds has required a number of phosphine and arsine complexes of Rh(I). Thus, it appeared that a more thorough study of the reactions of various Rh(I) species with a variety of ditertiary phosphines and arsines would serve both to expand the knowledge of this area and to provide some interesting compounds for further study. We report here the results of this effort together with those of a study on the complexing tendencies of some monotertiary phosphines and arsines containing unsaturated groups.

Experimental Section

All reactions were carried out in an atmosphere of prepurified nitrogen and the solvents were appropriately dried and distilled before use. Rhodium dicarbonyl chloride dimer, bis(diphenylphosphino)methane, and bis(diphenylarsino)methane were purchased from Strem Chemicals, Inc., and hydrated rhodium(III) chloride was obtained from Alfa Inorganics. 1,2-Bis(diphenylarsino)ethane was purchased from the Aldrich Chemical Co. and the published procedures were used to prepare *cis*- and *trans*-1,2-bis(diphenylphosphino)ethylene,[5] bis(diphenylphosphinomethyl) ether,[6] bis(diphenylphosphino)acetylene,[7] *cis*-1,2-bis(diphenylarsino)ethylene,[8] *cis*-β-styryldiphenylphosphine,[9] *cis*- and *trans*-β-styryldiphenylarsine,[10] tris(ferrocenyl)phosphine,[11] and bis(1-propynyl)phenylphosphine.[12]

Microanalyses were by Galbraith Microanalytical Laboratory, Knoxville, Tenn. Molecular weights were determined osmometrically at 37°. Infrared spectra were obtained on Beckman IR-5A, IR-8, and IR-11 instruments using Nujol mulls unless otherwise specified. All complexes showed bands due to the phosphine or arsine ligand and only significant additional ones are reported. Nmr spectra were obtained on a Varian A-60 spectrometer in deuteriochloroform solution using tetramethylsilane as an internal standard.

The conductance data were obtained using a Thomas-Serfass Model RCM15B1 conductance bridge and a cell which had been calibrated with 0.1 *M* potassium chloride. Measurements were made on acetonitrile (spectrograde) solution in the concentration range 10^{-4}–10^{-2} *M*.

The X-ray powder data were obtained with a Debye-Scherrer powder camera of 57.296-mm radius using Ni-filtered Cu Kα radiation (λ 1.5418 Å).

Four general procedures were used for the preparation of the complexes reported in this work. A typical example of each is detailed below.

Method A.—To a warm benzene solution (5 ml) of rhodium dicarbonyl chloride dimer (0.1 g, 0.26 mmol) was added 1.04 mmol of the appropriate phosphine or arsine dissolved in 5 ml of benzene. Carbon monoxide was evolved and if precipitation did not readily occur, diethyl ether was added to the cloud point and the solution was cooled at −5° overnight to obtain the solid product. This was washed with diethyl ether and dried *in vacuo*.

Method B.—To a solution of rhodium dicarbonyl chloride dimer (0.1 g, 0.26 mmol) in absolute ethanol (10 ml) was added 0.52 mmol of the appropriate diphosphine or diarsine in benzene (5 ml). Carbon monoxide was evolved and diethyl ether was then added while the solution was agitated with a nitrogen stream to produce crystals of the product. This was collected, washed with diethyl ether, and dried *in vacuo*.

Method C.—An aqueous ethanolic solution (20 ml) of hydrated rhodium(III) chloride (0.1 g, 0.38 mmol) was refluxed for 5 hr under an atmosphere of carbon monoxide. To the resulting pale yellow solution[13a] (which apparently contains predominantly $Rh(CO)_2Cl_2^-$)[13b] was added 0.38 mmol of the appropriate diphosphine or diarsine in 5 ml of benzene whereupon carbon monoxide evolution occurred. If necessary, precipitation was induced by the addition of diethyl ether. The collected product was then washed with diethyl ether and dried *in vacuo*. In the cases where method A was also used, identical products were obtained by both routes.

Method D.—A benzene solution (5 ml) of the appropriate diphosphine or diarsine (0.36 mmol) was added to 0.2 g (0.36 mmol) of $[(C_4H_9)_4N][Rh(CO)_2Br_2]$[14] in absolute ethanol. Carbon mon-

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(1) Taken in part from the M.S. thesis of J. P. Mitchener, Tulane University, 1968.

(2) A. Sacco and R. Ugo, *J. Chem. Soc.*, 3274 (1964).

(3) R. J. Mawby and L. M. Venanzi, *Experientia, Suppl.*, **9**, 240 (1964).

(4) W. Hieber and H. Lagally, *Chem. Ber.*, **100**, 148 (1967).

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(6) A. M. Aguiar, K. C. Hansen, and J. T. Mague, *J. Org. Chem.*, **32**, 2383 (1967).

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(8) A. M. Aguiar, J. T. Mague, H. J. Aguiar, T. G. Archibald, and G. Prejean, *J. Org. Chem.*, **33**, 1681 (1968).

(9) A. M. Aguiar and D. J. Daigle, *ibid.*, **30**, 3527 (1965).

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(13) (a) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, *A*, 1437 (1966); (b) B. R. James and G. L. Rempel, *Chem. Commun.*, 158 (1967).

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oxide was evolved and the product precipitated upon addition of diethyl ether. This was collected, washed with diethyl ether, and dried *in vacuo*.

Except for the complexes designated in Table I as having insufficient solubility for molecular weight determination, the complexes reported here are generally soluble in polar organic solvents, especially chlorinated ones.

Results and Discussion

Analytical, infrared spectral, and X-ray powder data for the complexes are presented in Tables I–III, respectively. The results of the conductance measurements are given in Figures 1 and 2. The complexes will be discussed according to the type of molecular formula which they were found to possess. In the general formulas to be used in the subsequent discussion, L will represent a monotertiary phosphine or arsine, L-L a ditertiary phosphine or arsine, and X a halogen.

$[Rh(CO)ClL_2]$ Complexes.—It has been established that phosphines containing unsaturated groups such as vinyl[15] and *o*-allylphenyl[16] will react to form transition metal complexes in which both the phosphorus and the double bond are coordinated to the metal atom. Since rhodium forms a considerable number of olefin and acetylene complexes, it was of interest to determine if similar behavior would be shown by this element. Accordingly, the reactions of rhodium dicarbonyl chloride dimer, $[Rh(CO)_2Cl]_2$, with *cis*- and *trans*-β-styryldiphenylphosphine, *trans*-β-styryldiphenylarsine, and bis(1-propynyl)phenylphosphine were investigated. The crystalline products obtained (**1**–**4**) all exhibited a single sharp band in the infrared region characteristic of a terminal carbonyl group bound to rhodium(I) (Table II).[13a] They analyze as $Rh(CO)ClL_2$ and are monomeric and undissociated in benzene solution. A further inspection of their infrared spectra shows that the bands attributable to the carbon–carbon multiple bond stretching frequencies are in the same positions as in the free ligands thus indicating that coordination of these multiple bonds did not occur. The far-infrared spectra of **1**–**4** were measured over the range 170–350 cm^{-1}. As can be seen from Table II, a strong band attributable to a terminal Rh–Cl stretching frequency[17,18] was found for each. The shoulder observed in **3** is probably due to chlorine isotopic splitting.[17] The complexes thus appear to be strictly analogous to *trans*-$Rh(CO)Cl((C_6H_5)_3P)_2$[19] and have been formulated accordingly. One notable feature of **2** is the high energy of the carbonyl stretching frequency. This would appear to indicate a particularly strong π-acid character for bis(1-propynyl)phenylphosphine.

The reactions of bis(1-propynyl)phenylphosphine

TABLE I: ANALYTICAL DATA FOR COMPLEXES

No.	Complex	Found % C	Found % H	Found % hal	Found Mol wt	Calcd % C	Calcd % H	Calcd % hal	Calcd Mol wt	Mp, °C	Method of prepn	% yield	Color and appearance
1	$Rh(\mathit{trans}\text{-}(C_6H_5)_2AsCH{=}CHC_6H_5)_2(CO)Cl$	58.70	4.18	. . .	822 (C_6H_6)	59.26	4.13	4.27	831	. . .	A	41	Yellow crystals
2	$Rh(C_6H_5P(C{\equiv}CCH_3)_2)_2(CO)Cl$	55.60	4.51	6.31	520 (C_6H_6)	55.72	4.12	6.58	539	166 dec	A	85	Yellow crystals
3	$Rh(\mathit{cis}\text{-}(C_6H_5)_2PCH{=}CHC_6H_5)_2(CO)Cl$	66.54	4.76	4.59	768 (C_6H_6)	66.27	4.62	4.78	743	184 dec	A	85	Yellow crystals
4	$Rh(\mathit{cis}\text{-}(C_6H_5)_2AsCH{=}CHC_6H_5)_2(CO)Cl$	58.87	4.30	. . .	843 (C_6H_6)	59.26	4.13	4.27	831	150–152	A	67	Yellow crystals
5	$Rh((C_{10}H_9Fe)_3P)_2(CO)Cl$	55.28	4.32	. . .	*a*	54.73	4.07	2.65	1338	227 dec	A	90	Orange crystals
6	$[Rh(\mathit{cis}\text{-}(C_6H_5)_2PCH{=}CHP(C_6H_5)_2)_2]Cl\cdot CH_2Cl_2$	63.56	4.92	9.20	915 ($CHCl_3$)	63.26	4.57	10.47	998	255 dec	A	85	Yellow crystals
7	$[Rh(\mathit{cis}\text{-}(C_6H_5)_2PCH{=}CHP(C_6H_5)_2)_2][B(C_6H_5)_4]$	74.76	5.20	0.00	*a*	75.12	5.30	0.00	1215	. . .	A	95	Yellow powder
8	$[Rh((C_6H_5)_2PCH_2OCH_2P(C_6H_5)_2)_2][BF_4]$	60.72	4.70	. . .	*a*	60.77	4.72	7.40	1028	225 dec	A	55	Yellow crystals
9	$[Rh(\mathit{trans}\text{-}(C_6H_5)_2PCH{=}CHP(C_6H_5)_2)(CO)Cl]_n$	57.90	4.10	6.29	*a*	57.61	3.94	6.30	$(563)_n$	246 dec	A, C	96	Yellow powder
10	$[Rh(\mathit{trans}\text{-}(C_6H_5)_2PCH{=}CHP(C_6H_5)_2)(CO)Br]_n$	54.52	3.76	12.78	*a*	53.39	3.66	13.16	$(607)_n$	215 dec	D	95	Yellow crystals
11	$[Rh((C_6H_5)_2AsCH_2CH_2As(C_6H_5)_2)(CO)Cl]_n{}^b$	49.71	3.90	5.64	*a*	49.68	3.71	5.43	$(653)_n$	250 dec	A, C	45	Yellow powder
12	$[Rh((C_6H_5)_2AsCH_2CH_2As(C_6H_5)_2)(CO)Br]_n{}^b$	47.64	3.02	10.94	*a*	46.51	3.48	11.46	$(697)_n$	259 dec	D	42	Yellow powder
13	$[Rh((C_6H_5)_2PC{\equiv}CP(C_6H_5)_2)(CO)Cl]_n$	57.24	3.13	6.27	*a*	57.82	3.60	6.32	$(561)_n$	261 dec	C	88	Yellow powder
14	$[Rh((C_6H_5)_2PCH_2P(C_6H_5)_2)(CO)Cl]_2$	56.70	4.28	6.60	*a*	56.70	4.02	6.44	1102	221 dec	A, C	74	Orange crystals
15	$[Rh((C_6H_5)_2AsCH_2As(C_6H_5)_2)(CO)Cl]_2$	48.12	3.45	5.41	1230 ($CHCl_3$)	48.89	3.48	5.45	1278	223 dec	A, C	80	Orange crystals
16	$[Rh((C_6H_5)_2AsCH_2As(C_6H_5)_2)(CO)Br]_2$	45.59	3.31	12.19	1280 ($CHCl_3$)	45.76	3.25	11.70	1336	310 dec	D	90	Red crystals
17	$[Rh(\mathit{cis}\text{-}(C_6H_5)_2PCH{=}CHP(C_6H_5)_2)_2][Rh(CO)_2Cl_2]$	57.56	4.07	6.65	1315 ($CHCl_3$)	57.62	3.95	6.30	1126	238 dec	B	84	Yellow crystals
18	$[Rh(\mathit{cis}\text{-}(C_6H_5)_2PCH{=}CHP(C_6H_5)_2)_2][Rh(CO)_2Br_2]$	53.70	3.71	13.40	1317 ($CHCl_3$)	53.40	3.66	13.16	1215	215 dec	D	78	Gold crystals
19	$[Rh(CO)(\mathit{cis}\text{-}(C_6H_5)_2AsCH{=}CHAs(C_6H_5)_2)_2][Rh(CO)_2Cl_2]$	50.08	3.29	5.16	1154 ($CHCl_3$)	49.69	3.34	5.33	1329	135 dec	B	70	Orange crystals
20	$[Rh(CO)(\mathit{cis}\text{-}(C_6H_5)_2AsCH{=}CHAs(C_6H_5)_2)_2][Rh(CO)_2Br_2]$	46.83	3.35	11.09	1241 ($CHCl_3$)	46.58	3.13	11.27	1418	114 dec	D	62	Orange crystals

[a] Insufficient solubility. [b] Probable formula uses $n = 2$.

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(19) L. M. Vallarino, *ibid.*, 2473 (1957).

TABLE II

INFRARED SPECTRAL DATA

Complex	$\nu_{C=O}$, cm^{-1}			ν_{Rh-X} (X = Cl, Br), cm^{-1}	Ratio
	Nujol mull	Solution	Solvent		
1	1953	1967	CH_2Cl_2	304	
2	1996	1996	CH_2Cl_2	298	
3	1953	1972	$CHCl_3$	302, 296 sh	
4	1951	1968	CH_2Cl_2	306	
5	1958	*a*		*b*	
9	1983	*a*		311	ν_{Rh-Br}/ν_{Rh-Cl} = 0.71
10	1980	*a*		221	
11	1964	*a*		311	ν_{Rh-Br}/ν_{Rh-Cl} = 0.71
12	1976	*a*		221	
13	1994	*a*		316	
14	1976, 1937 sh	*a*		298, 284 sh	
15	1965, 1929 sh	1968	CH_2Cl_2	302, 285 sh	ν_{Rh-Br}/ν_{Rh-Cl} = 0.68
16	1965, 1923 sh	1972	CH_2Cl_2	206	
17	2058, 1976	2066, 1988	CH_2Cl_2	322, 289	ν_{Rh-Br}/ν_{Rh-Cl} = 0.72, 0.72
18	2053, 1976	2066, 1988	CH_3NO_2	232, 207	
19	2060, 1984, 1961	2066, 1984, 1980 sh	$CHCl_3$	323,[c] 288	ν_{Rh-Br}/ν_{Rh-Cl} = 0.70, 0.70
20	2053, 1979 sh, 1964	2062, 1984	CH_2Cl_2	226, 201	

[a] Insufficient solubility. [b] Not observed. [c] Partially obscured by ligand absorption.

TABLE III

POWDER DATA ON COMPLEXES[a] (*d*, Å)

17	**18**	**19**	**20**	**14**	**14a**[c]	**15**	**16**
11.26 s	11.14 s	12.05 m	12.05 s	11.43 s	11.53 s	11.63 vs	11.86 vs
9.90 vs	9.90 vs	*b* vs	9.31 vs	9.21 vs	9.27 vs	9.22 vs	9.48 vs
9.37 vs	9.34 m	7.83 s	7.95 s	8.45 s	8.45 m	8.51 m	8.71 vs
8.32 vs	8.42 vs	6.74 m	6.88 m	7.21 m	7.24 w		7.35 s
7.46 vw	7.39 m	5.98 s	6.01 s	6.02 w	6.11 m	6.04 s	6.12 s
6.90 vw	6.99 vw	5.24 m	5.49 w				5.73 w
6.43 s	6.53 s		5.06 w	5.52 s	5.52 s	5.51 m	5.57 s
5.90 m	6.04 m	4.33 w	4.48 w	4.98 s	4.98 s	5.02 m	5.16 s
5.60 m	5.67 w	4.06 m	4.02 m	4.54 w	4.56 vw	4.55 w	4.59 w
5.23 w	5.23 w	3.83 m	3.80 m	4.30 m	4.34 m	4.32 m	4.33 vs
4.95 w	4.94 vw	3.44 w	3.43 w	4.16 w	4.17 w		
	4.67 vw	3.26 m	3.27 w	4.02 m	4.03 m		4.13 w
4.24 s	4.27 s					3.75 w	3.75 w
	4.00 m			3.56 m	3.59 m	3.58 m	3.58 s
3.57 w				3.37 m	3.40 m	3.38 m	3.42 m
3.46 w	3.50 w					3.23 m	3.23 w
3.33 vw	3.15 w			3.09 s	3.09 s	3.11 m	3.14 s
3.19 m				2.93 w		2.99 m	2.99 w
3.03 m	3.05 w						
2.84 m	2.85 m						
2.72 w	2.69 m						
2.53 m	2.50 m						

[a] See Table I for molecular formulas. [b] Position uncertain owing to high background. [c] Prepared according to ref 4.

with $[(C_8H_{14})_2RhCl]_2$[20] and $((C_6H_5)_3P)_3RhCl$[21] were also investigated in an attempt to effect coordination of the triple bond, but only ill-defined solids were obtained. Infrared spectral studies of these materials showed that no coordination of the triple bond had occurred.

With *trans*-β-styryldiphenylarsine, a ligand-to-metal ratio of 1:1 was also employed in benzene and cyclohexane solutions, and, in both cases, an olive brown to brown powder was initially obtained. It could not be unequivocally determined, however, if the double bond had become coordinated in these cases owing to the poor quality of the infrared spectra. All attempts at purification of this initial substance, which did not analyze for a single simple product, led ultimately to the recovery of Rh(CO)Cl(*trans*-$(C_6H_5)_2AsCH{=}CHC_6H_5)_2$. Further reactions paralleling those attempted with $C_6H_5P(C{\equiv}CCH_3)_2$ were equally unsuccessful.

Also prepared in this study was what appears to be the first transition metal complex of the rather unusual ligand tris(ferrocenyl)phosphine. This ligand readily reacts with $[Rh(CO)_2Cl]_2$ to produce a complex which we formulate as $Rh(CO)Cl((C_{10}H_9Fe)_3P)_2$ on the basis of the data in Tables I and II (**5**). No band could be identified in the far-infrared spectrum as being due to the rhodium–chlorine stretching frequency, although an extremely broad absorption was faintly discernible near 300 cm^{-1}. We have no certain explanation for the absence of a band due to this vibration but it may be that the arrangement of the ferrocenyl groups is such as to suppress it. A similar suppression of an Os–H vibration by a solvent molecule in the solid has been noted previously.[22]

[Rh(L-L)$_2$]X Complexes.—The reaction of *cis*-1,2-bis(diphenylphosphino)ethylene with $[Rh(CO)_2Cl]_2$ in a 4:1 molar ratio produces complex **6** which contains two ligands per rhodium and no carbonyl groups (Tables I and II). The same reaction using bis(diphenylphosphinomethyl) ether gives initially an impure material of approximately the same composition from which **8** was prepared using $NaBF_4$ in boiling methanol. In acetonitrile solution **6** and **8** exhibit electrolytic

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

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

[22] J. Chatt and R. G. Hayter, *ibid.*, 2605 (1961).

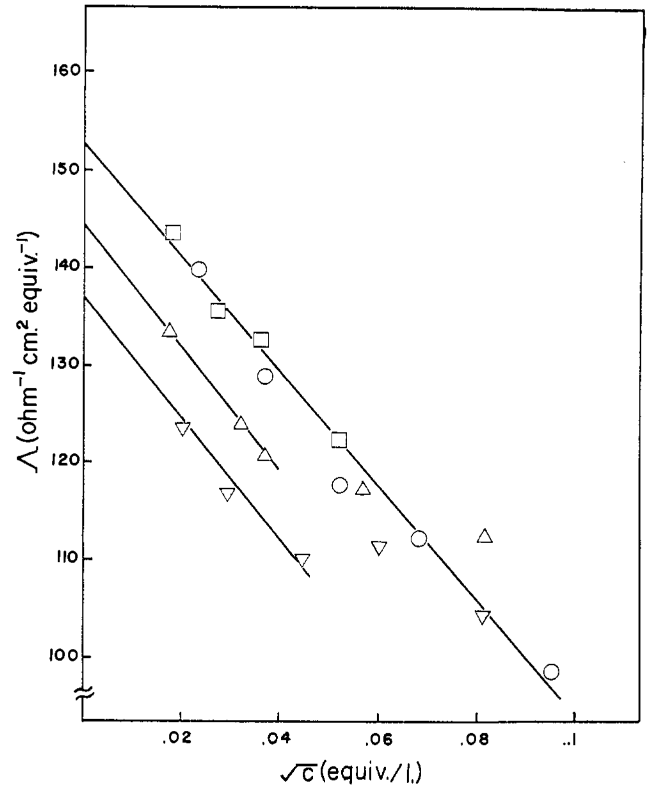

Figure 1.—Conductance of $[Rh(L\text{-}L)_2]X$ complexes in acetonitrile: ▽, 6; △, 8; ○, $[(C_6H_5)_2(C_6H_5CH_2)_2P]Br$; □, $[Rh(\textit{cis}\text{-}(C_6H_5)_2AsCH{=}CHAs(C_6H_5)_2)_2]BF_4 \cdot CH_3OH$.

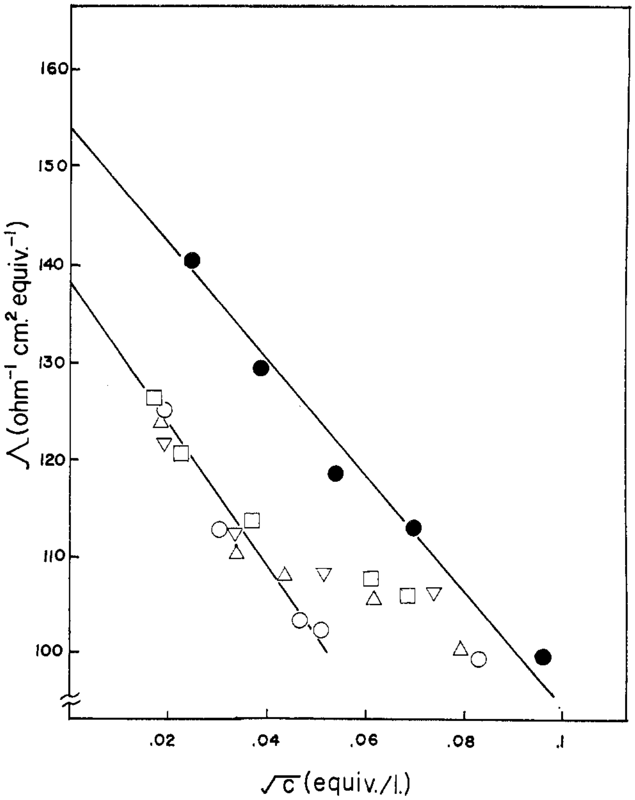

Figure 2.—Conductance of complexes containing the $Rh(CO)_2X_2^-$ ion in acetonitrile: ○, **17**; □, **18**; △, **19**; ▽, **20**; ●, $[(C_6H_5)_2(C_6H_5CH_2)_2P]Br$.

behavior, but, as can be seen from Figure 1, noticeable association is observed at higher concentrations. Because of the resulting curvature in the plots of equivalent conductance, Λ_e, *vs.* the square root of the equivalent concentration, the validity of an extrapolation to obtain the conductance at infinite dilution (Λ_0) is questionable. However, at lower concentrations, the plots are nearly linear, and, if it is assumed that association is not very significant here, approximate values of Λ_0 can be obtained which are in the range found previously for 1:1 electrolytes in this solvent.[23] Also included in Figure 1 are the corresponding data for the 1:1 electrolytes $[Rh(\textit{cis}\text{-}(C_6H_5)_2AsCH{=}CHAs(C_6H_5)_2)_2]BF_4 \cdot CH_3OH$[8] and diphenyldibenzylphosphonium bromide for which association appears to be less. The similarity in behavior of **6** and **8** to that for these known compounds indicates that they should be considered as essentially 1:1 electrolytes as well. They thus appear to be analogous to the complex $[Rh((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)_2]Cl$[2] in both their mode of preparation and their physical behavior. We have therefore formulated them as monomeric, square-planar complexes of rhodium(I) containing chelating diphosphines. Further evidence for the ionic nature of these complexes is the facile replacement of group X. For example **6** is immediately converted to **7** in methanol solution upon adding sodium tetraphenylboron.

Complex **6** reacts readily with sodium borohydride in absolute ethanol to produce a red-brown crystalline product which shows a sharp band of medium intensity in the infrared region at 1898 cm⁻¹ which can be assigned to an Rh–H stretching frequency. No reliable analytical data could be obtained on this complex owing to its marked sensitivity to air and moisture but it was evident that all of the chloride had been replaced. The behavior observed here closely parallels that reported[2] for the analogous complex, $[Rh((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)_2]Cl$, which gives $[RhH((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)_2]$ (ν_{Rh-H} 1902 cm⁻¹) under these conditions. The data thus strongly suggest that the complex be formulated as $RhH(\textit{cis}\text{-}(C_6H_5)_2PCH{=}CHP(C_6H_5)_2)_2$. Attempts were also made to prepare a hydride from **8** but these were unsuccessful.

Like its arsine analog,[8] **6** was obtained as a solvate, here with dichloromethane. The solvent molecule is tenaciously held—even at 100° *in vacuo* very little is lost—and its presence has been confirmed by nmr. These measurements also indicate the presence of slightly less than one molecule of CH_2Cl_2 per rhodium which accounts for the somewhat low value found for chlorine.

$[Rh(L\text{-}L)(CO)X]_n$ Complexes.—Three complexes of this type were prepared in which L-L is either *trans*-1,2-bis(diphenylphosphino)ethylene (**9**, **10**) or bis(diphenylphosphino)acetylene (**13**) and X is chlorine or bromine (Table I). They all appear to contain a single terminal carbonyl group bound to rhodium(I) (Table II) and this, together with the analytical data in Table I, suggests the common empirical formula Rh(CO)X-

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[23] A. Davidson, D. V. Howe, and E. T. Shawl, *Inorg. Chem.*, **6**, 458 (1967).

(L-L). In addition, no band could be identified for **13** as being due to either a free or a coordinated $-C\equiv C-$ group[24] indicating that the triple bond is not coordinated and that there is probably no appreciable departure from linearity in the $PC\equiv CP$ unit. The far-infrared spectra of **9** and **13** each show a band attributable to a terminal rhodium–chlorine stretching frequency while in **10** this has been replaced by a new band at lower energy which can be most reasonably assigned to a terminal rhodium–bromine stretch (Table II). This assignment is in accord with previous work[18] and gives good agreement with the theoretical value for the ratio of the metal–halogen stretching frequencies.

The most reasonable formulation which is in accord with both the analytical and spectroscopic data for these complexes is a polymer involving bridging diphosphine molecules (Figure 3a). It is evident that neither bridging carbonyls nor bridging halogens are present and the diphosphine ligands are clearly incapable of chelating. However, they are bifunctional and it is very likely that both ends would coordinate but to different metal atoms. The extreme insolubility of these complexes further supports the polymeric formulation. Although this is not unequivocal proof, complexes of similar ligands which have identical empirical formulas but are known to be dimers (*vide infra*) are measurably soluble.[25] Furthermore, identical products in essentially the same yield are obtained whether the ratio of ligand to rhodium used in the preparation is 1:1 or 2:1 thus suggesting that there is no great tendency for a stable complex such as $Rh(CO)Cl(L\text{-}L)_2$ to form. We therefore feel that the molecular complexity should be greater than 2, and in view of the stereochemistry of the phosphine ligands, it is probably quite high.

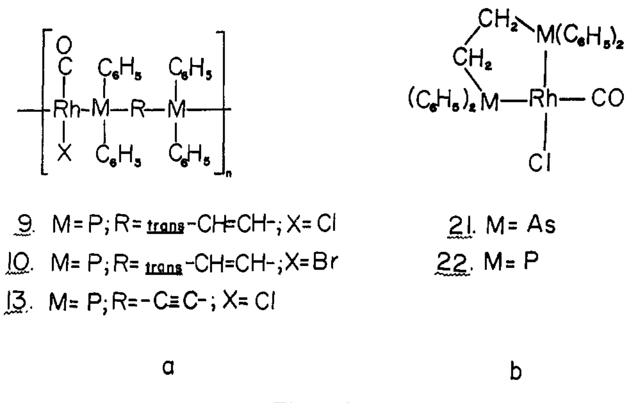

Figure 3.

The similarity of the infrared spectra of these complexes in the carbonyl and metal–halogen regions to those discussed for the complexes having the general formula $Rh(CO)XL_2$ strongly suggests the *trans* arrangement about the metal shown in Figure 3a. An analogous polymeric *trans* formulation has been proposed previously for the complexes of empirical formula $Rh((C_6H_5)_2M\text{-}M(C_6H_5)_2)(CO)Cl$ (M = P, As).[4]

Again the high energy of the carbonyl stretching frequency in **13** is notable indicating that the π-acid character of a tertiary phosphine is enhanced when it contains a 1-alkynyl group.

Complexes Containing 1,2-Bis(diphenylarsino)ethane.—Although the formation of complexes of empirical formula $Rh(CO)Cl(L\text{-}L)$ with the two diphosphines discussed in the previous section is not surprising, the formation of this type of complex from 1,2-bis(diphenylarsino)ethane and $[Rh(CO)_2Cl]_2$ (**11**) or $Rh(CO)_2Br_2^-$ (**12**) when an excess of the ligand was used was unexpected. The great similarity between 1,2-bis(diphenylphosphino)ethane and *cis*-1,2-bis(diphenylphosphino)ethylene in their coordination tendencies with rhodium(I) leads one to expect that the saturated diarsine should behave much as does its unsaturated analog *cis*-1,2-bis(diphenylarsino)ethylene. Thus, under mild conditions with $[Rh(CO)_2Cl]_2$, for instance, the latter gives $Rh(cis\text{-}(C_6H_5)_2AsCH{=}CHAs(C_6H_5)_2)_2(CO)^+$ (isolated as the tetraphenylboron salt[26]) while, under more strenuous conditions in the presence of the tetrafluoroborate ion, $[Rh(cis\text{-}(C_6H_5)_2AsCH{=}CHAs(C_6H_5)_2)_2]BF_4\cdot CH_3OH$ is formed.[8] In the present case, however, no analogous complexes with the saturated diarsine could be isolated. Under mild conditions the only well-defined products were **11** and **12** while more strenuous conditions led only to decomposition. Although a formulation such as **21** (Figure 3b) might be envisaged for **11** and **12**, this is unlikely since the carbonyl absorptions (Table II) are in the range which is normally found for a carbonyl group *trans* to a halogen in Rh(I) complexes.[13] By contrast, Hieber has reported that in the diphosphine complex (**22**), the carbonyl group absorbs at 2010 cm^{-1}.[4,27] Since one would not expect a very significant difference in π acidity between phosphorus and arsenic here, it thus appears quite likely that the carbonyl group is *trans* to the halogen.

In contrast to the reactions of $[Rh(CO)_2Cl]_2$ with *trans*-1,2-bis(diphenylphosphino)ethylene and bis(diphenylphosphino)acetylene, that with 1,2-bis(diphenylarsino)ethane does not rapidly produce a precipitate as one might expect if a polymer analogous to **9** or **13** were being formed. The infrared spectrum of the initial reaction mixture (excess of ligand used) in chloroform showed a single carbonyl band at 1972 cm^{-1}. This is not consistent with the presence of **21** in solution but rather suggests a species analogous to *trans*-$Rh(CO)Cl((C_6H_5)_3As)_2$[19] containing two monodentate diarsines, a five-coordinate cation such as that found in **19**, or a dimer similar to that shown in Figure 4 (M = As; X = Cl, Br). However, with this datum it is not possible to distinguish between them. What-

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[24] J. T. Mague and G. Wilkinson, *Inorg. Chem.*, **7**, 542 (1968).

[25] Recently, the dichloromethane-soluble complex $[PdCl_2(L\text{-}L)]_2$ (L-L = bis(diphenylphosphino)acetylene) has been prepared in which the two diphosphines are bridging: H. A. Carty and A. Efrati, *Inorg. Nucl. Chem. Letters*, **4**, 427 (1968). Although a dimeric formulation of **13** (*cf.* Figure 4) is conceivable in light of this, we feel that the insolubility of our compound argues for a species of higher molecular complexity.

[26] J. T. Mague and J. P. Mitchener, *Chem. Commun.*, 911 (1968).

[27] We have also prepared this complex but find that in our hands the published directions (6 hr of refluxing in benzene) lead only to decomposition. However, at room temperature, the desired species can be readily obtained.

ever the species in solution, it is clear from the analytical data that the first two are not those isolated in solid form. Unfortunately, the complexes are not sufficiently soluble for a molecular weight determination. We prefer the dimeric formulation for **11** and **12** rather than a polymer (Figure 3a; M = As; R = $-CH_2CH_2-$; X = Cl, Br) since the former has been found for a complex of the similar ligand, bis(diphenylarsino)methane (*vide infra*).

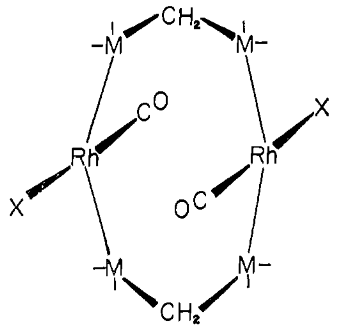
If less than a 4:1 molar ratio of ligand to $[Rh(CO)_2Cl]_2$ is used, a variety of yellow, orange, and red solutions result depending on the conditions. The infrared spectra of these solutions generally show several strong carbonyl absorptions in the 1950–2100-cm^{-1} region but no satisfactory interpretation has yet been possible. Although solids can be obtained from some of these solutions, their spectra seldom correspond to those of the solutions, and no simple formulations can be derived from the analytical data. It thus appears that several species are present in these solutions and studies are in progress to elucidate their behavior further.

$[Rh(CO)X(L\text{-}L)]_2$ Complexes.—The ligands bis(diphenylphosphino)methane and bis(diphenylarsino)methane are interesting in that they seem able to act either as chelating or as bridging groups. Their function as bidentate chelates has been well established in some Ru(II) complexes.[22,28,29] At the time this work was begun, the only report of their complexes with Rh(I)[4] showed them to act only as bridging groups.

We have prepared complexes **14–16** using these two ligands. From the data in Tables I and II and previous arguments it is evident that these complexes, which analyze as Rh(CO)X(L-L), contain both a terminal carbonyl group and a terminal halogen which are *trans* to each other. A single-crystal X-ray structure determination of **15** confirms this as well as the dimeric formulation.[30] The solubility of **14** was not sufficient for molecular weight determination. However, complexes **14** and **16** were found to be isomorphous with **15** from X-ray powder data (Table III) and are presumably isostructural.

The structures of these complexes, with the phenyl groups omitted for clarity, are shown in Figure 4. The most significant feature of **15** is the rather short Rh–Rh distance of *ca.* 3.1 Å which is noticeably shorter than that found in $[Rh(CO)_2Cl]_2$[31] (3.3 Å). This is probably primarily the result of the stereochemical requirements of the ligands, since the As–C–As angle in the ligand is 114° indicating considerable strain.

An unexpected result is the occurrence of the shoulders found on the low-energy sides of both the carbonyl and rhodium–chlorine bands in the solid-state spectra (Table II). Those in the far-infrared region appear to be too far from the main bands to be chlorine isotopic splittings. It may be, however, that some weak coupling occurs between corresponding modes in the halves of the molecule as a consequence of its compactness to give rise to the weak shoulders.



14. M = P; X = Cl
15. M = As; X = Cl
16. M = As; X = Br

Figure 4.

It has been reported[4] that $[Rh(CO)_2Cl]_2$ and bis(diphenylphosphino)methane react in cyclohexane to produce a slightly soluble yellow product of empirical formula $Rh(CO)Cl(C_6H_5)_2PCH_2P(C_6H_5)_2$. No molecular weight was reported owing to the insufficient solubility of the complex and the *trans* polymeric formulation shown in Figure 3a (M = P; R = $-CH_2-$) was assumed. We have reproduced this preparation but find that the yellow powder obtained (**14a**) has an X-ray powder pattern identical with those of **14–16** (Table III). Thus the earlier report appears to be in error and the complex should be formulated as a dimer. A recent report on the structure of $[(\pi\text{-}C_5H_5)Fe(CO)]_2[(C_6H_5)_2PCH_2P(C_6H_5)_2]$ provides another example of the type of bridging observed here.[32]

Complexes Containing $Rh(CO)_2X_2^-$.—If $[Rh(CO)_2Cl]_2$, $Rh(CO)_2Cl_2^-$, or $Rh(CO)_2Br_2^-$ in ethanol is allowed to react with *cis*-1,2-bis(diphenylphosphino)ethylene in a 1:2, 1:1, or 1:1 molar ratio, respectively, complexes **17** and **18** can be obtained. Although they also analyze as Rh(CO)X(L-L), their infrared spectra are decidedly different from those discussed in the previous section. In chloroform solution they behave as nonelectrolytes and appear essentially dimeric while in acetonitrile they form conducting solutions. In the latter solvent their behavior is comparable to that of **6** and **8** although the degree of association appears higher (Figure 2). Again one can estimate values of Λ_0 for these complexes which show them to be approximately 1:1 electrolytes in this solvent.

The infrared spectrum of **17** in both the carbonyl and metal–chlorine regions is essentially identical with that reported for $[(C_4H_9)_4N][Rh(CO)_2Cl_2]$,[14] while that for **18** is consistent with the presence of the $Rh(CO)_2Br_2^-$ ion (Table II). All of the data are thus in accord with the complexes being formulated $[Rh(cis\text{-}(C_6H_5)_2PCH{=}CHP(C_6H_5)_2)_2][Rh(CO)_2X_2]$ (X = Cl,

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[28] J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 896 (1961).

[29] J. Chatt and R. G. Hayter, *ibid.*, 6017 (1963).

[30] J. T. Mague, in preparation.

[31] L. F. Dahl, C. Martell, and D. S. Wampler, *J. Am. Chem. Soc.*, **83**, 1761 (1961).

[32] R. J. Haines, A. L. Du Preeg, and G. T. W. Wittmann, *Chem. Commun.*, 611 (1968).

Br). Further support for this formulation comes from the successful separation of **17** into its two components. The addition of sodium tetraphenylboron to a cold methanolic solution of the complex precipitated a yellow powder identical with **7**. The filtrate was then treated with diphenyldibenzylphosphonium bromide to produce a yellow solid whose infrared spectrum in the carbonyl region was identical with that reported for salts of the $Rh(CO)_2Cl_2^-$ ion. As can be seen from the data in Table III, **17** and **18** are isomorphous and presumably isostructural.

The course of the analogous reactions using *cis*-1,2-bis(diphenylarsino)ethylene is quite similar. Here, orange, crystalline complexes **19** and **20** are formed which analyze as $Rh_2(CO)_3X_2(L\text{-}L)_2$. They are essentially nonelectrolytes in chloroform and molecular weight measurements in that solvent agree with the formulas derived from the analytical data. The infrared spectra in the carbonyl region are the same as for **17** and **18** with the exception that a third, strong but poorly resolved band appears between 1961 and 1984 cm^{-1}. In solution this band shifts to somewhat higher energies so that resolution becomes impossible for **20** with the instruments available. The far-infrared spectra, with the exception of differing ligand absorption, are essentially identical with those of **17** and **18** in the 170–350-cm^{-1} region (Table II).

The complexes form conducting solutions in acetonitrile and, as can be seen from Figure 2, behave as partially associated 1:1 electrolytes. All of the data are in accord with the formulation $[Rh(CO)(cis\text{-}(C_6H_5)_2AsCH{=}CHAs(C_6H_5)_2)_2][Rh(CO)_2X_2]$ (X = Cl, Br) containing the five-coordinate cation whose tetraphenylboron salt has been reported previously.[26] In solution, the carbonyl absorption for that complex was found to shift to higher energies by about 20 cm^{-1}. Thus, in the solution spectra of **19** and **20**, the band due to the carbonyl group in the cation is nearly coincident with the lower energy band for the anion explaining the apparent appearance of only two bands for **20**.

In summary, this study of the coordination tendencies of tertiary diphosphines and diarsines toward Rh(I) has utilized three types of ligands which can be distinguished by the group R (*cf.* Figure 3a) connecting the phosphorus or arsenic atoms. Where R = *cis*-CH=CH–, chelation would be expected and this was found to occur in all of the cases studied here. In no instance was isomerization of the ligand observed and no evidence was obtained to indicate that the ethylenic linkage was coordinated. Although molecular models show that it is possible for one of these ligands in a molecule to act as a bridge, this was not observed to occur.

The second type of ligand contains R = *trans*-CH=CH– or –C≡C– in which the stereochemistry of the ligand is such as to prevent it from acting as a chelate. Again, no isomerization[33] was observed for the *trans*-ethylenic linkage and no interaction with either the double or the triple bond appeared to occur. The two diphosphines studied here, as well as *trans*-1,2-bis(diphenylarsino)ethylene,[8] utilize both donor atoms in coordination to form what appear to be polymers. No evidence for stable monomers in which only one end of the ligand was coordinated could be obtained.

The third type of ligand contains a saturated linkage ($R = (-CH_2-)_n$ (n = 1, 2) or $-CH_2OCH_2-$) rendering the molecule flexible so that either chelation or bridging is possible. Although both modes of behavior have been reported for 1,2-bis(diphenylphosphino)ethane in Rh(I) complexes,[4] the only ligand of this type studied here for which the tendency to act as both a bridging group and as a chelate was apparent is bis(diphenylphosphinomethyl) ether. Thus, when preparations of **8** were attempted in the cold, a rather insoluble yellow powder showing a strong carbonyl band at about 1970 cm^{-1} was obtained. This could not be satisfactorily characterized, but it did appear to have the approximate composition Rh(CO)Cl(L-L) suggesting a formula analogous to either **9** or **14**. We prefer the latter since the solid is somewhat soluble in alcohols and can slowly be converted to **8** by refluxing in methanol in the presence of excess ligand and sodium tetrafluoroborate. We have not been able as yet to prepare a complex containing a chelating $R = -CH_2-$ ligand, but studies now in progress with bis(diphenylphosphino)methane show that several compounds besides that reported here can be isolated under the appropriate conditions.

Studies of the oxidative addition reactions which these complexes may undergo are now in progress and will be the subject of later papers.

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(33) W. R. Cullen, P. S. Dahliwal, and C. J. Stewart, *Inorg. Chem.*, **6**, 2256 (1967).