

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
TULANE UNIVERSITY, NEW ORLEANS, LOUISIANA 70118**Mono- and Di(tertiary phosphine and arsine) Complexes of Ruthenium(II) and Ruthenium (III)¹⁻³**

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A variety of di(tertiary phosphines and arsines) (L_2) react with " $RuCl_3 \cdot 3H_2O$ " in ethanol to produce the Ru(II) complexes $trans-[Ru(L_2)_2Cl_2]$. When L_2 is bis(diphenylarsino)methane, $[Ru(L_2)_3Cl_2]$ is obtained in which both mono- and bidentate diarsine ligands are present. This complex reacts with carbon monoxide to produce $[Ru(L_2)_2(CO)_2Cl_2]$ which contains only monodentate ligands. The same species results when this ligand is reacted with the mixture of ruthenium carbonyl complexes produced by reductive carbonylation of " $RuCl_3 \cdot 3H_2O$ " in ethanol. The same procedure using the ligands bis(diphenylphosphino)methane and *cis*-1,2-bis(diphenylarsino)ethylene produces $Ru(L_2)(CO)_2Cl_2$. Reaction of $trans-[Ru(DPM)_2Cl_2]$ (DPM = bis(diphenylphosphino)methane) with carbon monoxide gives a cationic complex, $trans-[Ru(DPM)_2(CO)Cl]Cl$. $[Ru(DPM)_2Cl_2]$ also reacts with $NOBF_4$ to produce initially the Ru(III) complex $[Ru(DPM)_2Cl_2]BF_4$. This complex reacts further with NO or alkyl nitrites to produce $[Ru(NO)Cl(DPM)_2](BF_4)_2$. With the mixture of ruthenium carbonyl complexes, *trans*- β -styryldiphenylphosphine or -arsine (L) initially give *mer*- $[RuL_3(CO)Cl_2]$ which react further with carbon monoxide to give *cis*- $[Ru(CO)_2L_2Cl_2]$. Similar reactions using *cis*- β -styryldiphenylphosphine or -arsine give only *cis*- $[RuL_2(CO)_2Cl_2]$. A number of other nitrosyl complexes $[Ru(NO)(L_2)Cl_3]$ could be prepared starting from $Ru(NO)Cl_3$. The nmr and infrared spectra of the complexes are discussed. Attempts to reduce the Ru(II) complexes to Ru(0) species were generally unsuccessful.

Introduction

As a part of our study of oxidative additions to platinum metal complexes, we wished to study the reactions of some four-coordinate Ru(0) compounds. While a variety of five-coordinate Ru(0) complexes have been prepared and found to undergo oxidative elimination reactions,⁴⁻⁸ little work has apparently been done with coordinatively unsaturated species. At the time this work was begun, the only example of this latter class of compounds was $[Ru(DMPE)_2]$ (DMPE = 1,2-bis(dimethylphosphino)ethane)⁹ although the nitrosyl complex $[Ru(NO)Cl(P(C_6H_5)_3)_2]$ has subsequently been prepared and found to undergo oxidative addition with a variety of small molecules.¹⁰ Since $[Ru(DMPE)_2]$ was produced by reduction of $trans-[Ru(DMPE)_2Cl_2]$ we decided to investigate the utility of this route to other Ru(0) complexes utilizing the variety of di(tertiary phosphines and arsines) at our disposal. We report here on the results of this and related studies.

Experimental Section

All reactions were carried out in an atmosphere of prepurified nitrogen or Matheson CP grade carbon monoxide and the solvents were appropriately dried and distilled before use. Bis(diphenylphosphino)methane, bis(diphenylarsino)methane, and 1,2-bis(diphenylarsino)ethane were purchased from Strem Chemicals, Inc. and hydrated ruthenium(III) chloride was obtained from Alfa Inorganics. The sample of $Ru(NO)Cl_3$ was obtained from D. F. Goldsmith Chemical and Metal Corp. The published

procedures were used to prepare *cis*-¹¹ and *trans*-1,2-bis(diphenylphosphino)ethylene,¹² *cis*-1,2-bis(diphenylarsino)ethylene,¹³ bis(diphenylphosphinomethyl) ether,¹⁴ *cis*- and *trans*- β -styryldiphenylphosphine,¹⁵ *cis*- and *trans*- β -styryldiphenylarsine,¹⁶ and phenylethynylidiphenylphosphine.¹⁷

Microanalyses were by Galbraith Microanalytical Laboratory, Knoxville, Tenn. and Meade Microanalytical Laboratory, Amherst, Mass. Proton nmr spectra were obtained on a Varian A-60 spectrometer using deuteriochloroform solutions and tetramethylsilane as an internal standard unless otherwise specified. Infrared spectra were measured on Beckman IR-5A and IR-11 instruments using Nujol mulls. Molecular weights were determined using a Mechrolab osmometer at 37° and chloroform solutions unless otherwise specified. Conductance data were obtained using a Thomas-Serfass Model RCM 15B1 conductance bridge and a cell which had been calibrated with 0.1 *M* aqueous potassium chloride. The high-pressure carbonylation reactions were carried out in a stainless steel Parr bomb of approximately 10-ml capacity.

Five general procedures were used to prepare the majority of the complexes reported in this paper. A typical example of each is detailed below together with specific details for unique preparations.

Method A.—Hydrated ruthenium(III) chloride (0.17 g, 0.65 mmol) in 25 ml of 95% ethanol was added to a hot benzene-ethanol solution (1:4, v/v; 100 ml) of the appropriate diphosphine or diarsine ligand (2.6 mmol) and the resulting mixture was refluxed under nitrogen for 6 hr. The precipitated product was filtered from the hot solution and recrystallized from hot chloroform by the addition of ethanol.

Method B.—Hydrated ruthenium(III) chloride (0.17 g, 0.65 mmol) was dissolved in 35 ml of absolute ethanol and refluxed for 6 hr while carbon monoxide was passed through the solution.¹⁸ To the resulting dark red solution was added a solution of 0.65 mmol of the appropriate diphosphine or diarsine in the minimum amount of benzene and the mixture was refluxed for an additional 2 hr with continued passage of carbon monoxide. Addition of diethyl ether to the cooled solution precipitated the product which was recrystallized from a chloroform-diethyl ether mixture.

Method C.—As in B but 1.95 mmol of the unsaturated phosphine or arsine was added in benzene solution and the resulting mixture was refluxed for 5 hr in a nitrogen atmosphere. Addition

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TABLE I
ANALYTICAL DATA FOR COMPLEXES

No.	Complex	Found				Calcd.				Mol wt	Method of prepn ^e	Color
		% C	% H	% Cl	% N	% C	% H	% Cl	% N			
1	<i>trans</i> -[RuCl ₂ (C ₆ H ₅) ₂ PCH ₂ P(C ₆ H ₅) ₂]	63.84	4.62	7.35	1015	63.84	4.71	7.54	941	C	Orange	
2	<i>trans</i> -[RuCl ₂ (C ₆ H ₅) ₂ PCH ₂ OCH ₂ P(C ₆ H ₅) ₂]	62.50	4.96	7.04	<i>b</i>	62.41	4.83	7.08	1001	A, C	Pale yellow	
3	<i>trans</i> -[RuCl ₂ (C ₆ H ₅) ₂ AsCH ₂ CH ₂ As(C ₆ H ₅) ₂]	54.61	4.39	6.35	1172	54.57	4.23	6.19	1145	A, C	Pale yellow	
4	<i>trans</i> -[RuCl ₂ (<i>cis</i> -(C ₆ H ₅) ₂ AsCH=CHAs(C ₆ H ₅) ₂)]	54.54	3.95	6.35	<i>b</i>	54.76	3.89	6.22	1141	A, C	Orange-yellow	
5	<i>trans</i> -[RuCl ₂ (C ₆ H ₅) ₂ AsCH ₂ As(C ₆ H ₅) ₂]	56.42	4.25	4.54	1518	56.70	4.19	4.46	1589	A	Pink	
6	<i>cis</i> -[Ru(CO) ₂ Cl ₂ (C ₆ H ₅) ₂ AsCH ₂ As(C ₆ H ₅) ₂]	53.38	3.77	6.58	1100	53.26	3.78	6.05	1172	B, C, D	White	
7	<i>cis</i> -[Ru(CO) ₂ Cl ₂ (<i>cis</i> -(C ₆ H ₅) ₂ AsCH=CHAs(C ₆ H ₅) ₂)]	47.67	3.16	9.67	766	47.21	3.11	9.95	712	B	Yellow	
8	<i>cis</i> -[Ru(CO) ₂ Cl ₂ (C ₆ H ₅) ₂ PCH ₂ P(C ₆ H ₅) ₂]	53.11	3.72	11.92	664	52.92	3.62	11.58	612	B	Yellow	
9	<i>trans</i> -[Ru(CO)Cl(C ₆ H ₅) ₂ PCH ₂ P(C ₆ H ₅) ₂ Cl]	63.41	4.62	7.35	949 (CH ₃ OH)	63.23	4.58	7.32	969		White	
10	<i>trans</i> -[Ru(CO)Cl(C ₆ H ₅) ₂ PCH ₂ P(C ₆ H ₅) ₂ BF ₄]	60.47	3.47	3.39	453 (CH ₃ CN)	60.05	4.35	3.48	1020		White	
11	<i>trans</i> -[Ru(CO)Cl(C ₆ H ₅) ₂ PCH ₂ P(C ₆ H ₅) ₂]PF ₆	56.58	4.09	3.27	503 (DMF)	56.81	4.11	3.29	1078		White	
12	<i>trans</i> -[Ru ₂ (CO) ₂ Cl ₂ (<i>trans</i> -(C ₆ H ₅) ₂ PCH=CHP(C ₆ H ₅) ₂)] ^a	60.13	4.37	8.71	913 (DMF)	60.46	4.19	8.92	(1589) ⁿ	C	Pale yellow	
13	<i>mer</i> -[Ru(CO) ₂ Cl ₂ (<i>trans</i> -(C ₆ H ₅) ₂ AsCH=CHC ₆ H ₅) ₂]	60.55	4.33	5.92	1186	61.22	4.30	6.16	1197	C	Pale yellow	
14	<i>mer</i> -[Ru(CO) ₂ Cl ₂ (<i>trans</i> -(C ₆ H ₅) ₂ PCH=CHC ₆ H ₅) ₂]	68.19	5.14	6.69	1103	68.80	4.83	6.66	1065	C	Pale yellow	
15	<i>cis</i> -[Ru(CO) ₂ Cl ₂ (<i>trans</i> -(C ₆ H ₅) ₂ AsCH=CHC ₆ H ₅) ₂]	56.56	3.64	8.21	869	56.62	3.84	7.94	893	D	White	
16	<i>cis</i> -[Ru(CO) ₂ Cl ₂ (<i>trans</i> -(C ₆ H ₅) ₂ PCH=CHC ₆ H ₅) ₂]	62.41	4.49	8.88	792	62.69	4.26	8.81	805	D	White	
17	<i>cis</i> -[Ru(CO) ₂ Cl ₂ (<i>cis</i> -(C ₆ H ₅) ₂ PCH=CHC ₆ H ₅) ₂]	62.09	3.91	8.71	787	62.69	4.26	8.81	805	B, C	White	
18	<i>cis</i> -[Ru(CO) ₂ Cl ₂ (<i>cis</i> -(C ₆ H ₅) ₂ AsCH=CHC ₆ H ₅) ₂]	56.44	3.82	7.88	860	56.62	3.84	7.94	893	B	White	
19	<i>mer</i> -[Ru(CO) ₂ Cl ₂ (C ₆ H ₅) ₂ PC≡CC ₆ H ₅)] ^e	68.40	4.29	7.48	1065	69.25	4.29	6.70	1058	B	Pale yellow	
20	<i>cis</i> -[Ru(CO) ₂ Cl ₂ (C ₆ H ₅) ₂ PC≡CC ₆ H ₅)] ^e	59.24	3.89	9.06	847	63.06	3.78	8.86	800	D	White	
21	<i>trans</i> -[Ru(CO) ₂ Cl ₂ (C ₆ H ₅) ₂ PCH ₂ P(C ₆ H ₅) ₂](BF ₄) ^g	54.47	4.12	3.76	<i>b</i>	58.44	4.32	6.90	1028		Brown	
22	[Ru(NO)Cl ₃ (C ₆ H ₅) ₂ PCH ₂ P(C ₆ H ₅) ₂]	47.91	3.83	16.58		54.15	4.01	3.20	1109		Yellow	
23	[Ru(NO)Cl ₃ (C ₆ H ₅) ₂ PCH ₂ P(C ₆ H ₅) ₂]	50.79	3.77	9.43		48.29	3.57	17.10	622	E	Orange	
24	[Ru(NO)Cl ₃ (C ₆ H ₅) ₂ AsCH ₂ As(C ₆ H ₅) ₂]	43.20	3.05	14.90		50.84	3.75	9.00	1182	E	Orange	
25	[Ru(NO)Cl ₃ (<i>cis</i> -(C ₆ H ₅) ₂ AsCH=CHAs(C ₆ H ₅) ₂)]	48.07	3.88	16.32		43.27	3.07	14.74	722	E	Orange	
26	[Ru(NO)Cl ₃ (C ₆ H ₅) ₂ PCH ₂ OCH ₂ P(C ₆ H ₅) ₂]	59.01	4.17	13.29		47.91	3.71	16.32	652	E	Orange	
27	[Ru(NO)Cl ₃ (<i>cis</i> -(C ₆ H ₅) ₂ PCH=CHC ₆ H ₅) ₂]	53.20	3.93	11.91		59.01	4.21	13.07	814	E	Orange	
28	[Ru(NO)Cl ₃ (<i>cis</i> -(C ₆ H ₅) ₂ AsCH=CHC ₆ H ₅) ₂]					53.26	3.80	11.80	902	E	Orange	

^a Compounds for which no preparative method is listed are described separately in the Experimental Section. ^b Insolubly soluble. ^c *Anal.* Calcd: F, 10.57. Found: F, 11.04. ^d *Anal.* Calcd: P, 11.69. Found: P, 11.87. ^e *Anal.* Calcd: P, 7.74. Found: P, 7.68. ^f *Anal.* Calcd: F, 7.40. Found: F, 6.84. ^g *Anal.* Calcd: F, 6.84. ^h *Anal.* Calcd: F, 13.71; P, 11.17. Found: F, 13.98; P, 11.78. ⁱ *Anal.* Calcd: N, 1.19. Found: N, 0.70.

TABLE II
CONDUCTIVITY DATA^{a,b}

Complex	Conc Range (equiv/l)	Λ_0 (ohm ⁻¹ cm ² equiv ⁻¹)	A
9	4.5×10^{-4} – 1.02×10^{-2}	130	150
10	2.35×10^{-4} – 1.01×10^{-3}	149	218
11	4.11×10^{-4} – 1.06×10^{-3}	141	215
21	4.22×10^{-4} – 9.59×10^{-3}	155	268
22	2.06×10^{-4} – 5.69×10^{-3}	320	784

^a Obtained on acetonitrile solutions. ^b Λ_0 (equivalent conductance at infinite dilution) and A, defined by the Onsager equation ($\Lambda_0 - \Lambda_e = A\sqrt{C}$), were estimated graphically from plots of the equivalent conductance, Λ_e , vs. the square root of the equivalent concentration, C.

of ether to the cooled solution precipitated the product which was recrystallized from a benzene-ether mixture.

Method D.—A solution of 0.3 g of the appropriate Ru(II) complex in 60 ml of benzene-ethanol (2:1, v/v) was refluxed for 5 hr while carbon monoxide was passed through it. The resulting solution was concentrated under reduced pressure and upon addition of diethyl ether the product precipitated. Recrystallization could be effected from an acetone-diethyl ether mixture.

Method E.—Ruthenium nitrosyl trichloride (0.17 g, 0.71 mmol) was dissolved in 15 ml of 2-methoxyethanol under nitrogen and the resulting red solution was filtered. The appropriate ligand (0.78 mmol) in 10 ml of dichloromethane was then added and the mixture was refluxed under nitrogen for 1/2 hr. Cooling at 0° overnight precipitated the product which was recrystallized from chloroform or dimethyl sulfoxide upon the addition of diethyl ether.

trans-[Ru((C₆H₅)₂PCH₂P(C₆H₅)₂)(CO)Cl]Cl.—Carbon monoxide was passed through a refluxing solution of 0.26 g of *trans*-[Ru((C₆H₅)₂PCH₂P(C₆H₅)₂Cl₂) in 100 ml of tetrahydrofuran-ethanol (3:2, v/v) for 5 hr. The solvent was stripped from the resulting clear solution at reduced pressure to give an oily solid which was dissolved in a minimum volume of acetone. Addition of diethyl ether precipitated the product which was recrystallized from acetone-ether. The corresponding tetrafluoroborate and hexafluorophosphate salts could be obtained by metathesis in methanol.

trans-[Ru((C₆H₅)₂PCH₂P(C₆H₅)₂Cl₂)BF₄].—A hot solution of *trans*-[Ru((C₆H₅)₂PCH₂P(C₆H₅)₂Cl₂) (0.21 g, 0.22 mmol) in benzene (45 ml) was treated with 0.26 g (2.24 mmol) of nitrosyl tetrafluoroborate in 5 ml of methanol. The resulting deep green solution was stirred under nitrogen for 30 min after which the addition of diethyl ether precipitated green crystals of a benzene solvate. Upon washing the green product with ether, the unsolvated product was obtained as brown crystals which were recrystallized from methanol.

trans-[Ru(NO)Cl((C₆H₅)₂PCH₂P(C₆H₅)₂)](BF₄)₂.—To 0.21 g (0.22 mmol) of *trans*-[Ru((C₆H₅)₂PCH₂P(C₆H₅)₂Cl₂) in 45 ml of hot benzene under nitrogen was added 0.08 g (0.78 mmol) of nitrosyl tetrafluoroborate in 8 ml of methanol. The resulting deep green solution was allowed to sit in a stoppered flask at room temperature for 5 days by which time the solution had become yellow and yellow crystals of the product had precipitated. These were recrystallized from methanol.

Attempted Reduction of Ru(II) Complexes. Method 1.—A 100-ml, 3-neck flask fitted with a nitrogen inlet, outlet, and rubber septum was charged with 0.16 mmol of the appropriate Ru(II) complex and 30 ml of tetrahydrofuran which had been freshly distilled from sodium-benzophenone complex. To this was added dropwise a tetrahydrofuran solution of sodium naphthalenide until a permanent green color remained. The resulting solution was stirred magnetically for up to 30 min after which the solvent was removed under reduced pressure. The resulting oily residue was triturated with degassed diethyl ether to produce the crude product which was then treated further as described below.

Method 2.—In a glass-lined, stainless steel Parr bomb of 10-ml capacity was combined 0.3 mmol of the appropriate Ru(II) complex, 9 mmol of zinc dust, and 6 ml of *N,N*-dimethylformamide (dried over molecular sieves). The bomb was flushed with carbon monoxide, pressured to 60 psi, and heated at 100° for 24 hr. After cooling and venting, the bomb was opened and the resulting solution filtered from the excess zinc under nitrogen. Removal of the solvent under reduced pressure gave an oily residue which was triturated with diethyl ether to produce the crude solid product. These solids were successively extracted with benzene, ethanol, and chloroform from which the various products could be obtained by evaporation or by precipitation with diethyl ether.

Results and Discussion

Analytical, conductance, and infrared spectral data are presented in Tables I-III. In the following discussion the abbreviations L₂ and L will be used to designate a ditertiary and a monotertiary group Va ligand, respectively.

A number of workers have previously reported on the utility of the red solution which results from the action of carbon monoxide on hydrated ruthenium(III) chlo-

TABLE III

Complex	INFRARED SPECTRAL DATA (CM ⁻¹)		ν(Ru—Cl)
	ν(C≡O)	ν(N≡O)	
1			330
2			327
3			332
4			339
5			320 ^a
6	2045, 1980		313, ^a 286
7	2053, 2008		339
8	2058, 1992		338
9	1961		310
10	1965		310
11	1980		310
12	1965		300, 275, 265
13	1949		301, 276
14	1961		291, 264
15	2045, 1984		307, 288
16	2045, 1980		311, 288
17	2049, 1996		312, 288
18	2049, 1980		310, 284
19 ^b	1965		305, 270
20 ^c	2045, 1992		319, 284
21			342
22		1852	<i>d</i>
23		1866	328, 281
24		1848, 1832	338 sh, 290
25		1869	326, ^a 278
26		1880	330, 293
27		1855	331, 292
28		1852	340, 288

^a Assignment uncertain due to interference from ligand absorption. ^b ν(C≡C) at 2174 cm⁻¹. ^c νC≡C at 2169 cm⁻¹. ^d Not located.

ride in refluxing ethanol for the preparation of chloro-carbonyl-ruthenium(II) complexes of tertiary phosphines and arsines.^{18,19} While it is evident that anionic chlorocarbonylruthenium(II) species are present, attempts to determine their composition more precisely have so far not been successful.¹⁹ In a related study, Hui and James examined the uptake of carbon monoxide by solutions of ruthenium(II) chloride complexes (produced by hydrogen reduction of hydrated ruthenium(III) chloride) in *N,N*-dimethylacetamide solution.²⁰ The stepwise formation of mono- and dicarbonylruthenium(II) chloro species was proposed but the identity of the other ligands present was not determined. A similar sequence is indicated when the reduction is carried out using formic acid in aqueous HCl from which the species [Ru(CO)(H₂O)Cl₄]²⁻ and [Ru(CO)₂Cl₄]²⁻ can be precipitated by large cations.²¹ The mono- and dicarbonyl species in both systems are respectively green and yellow to pale orange which is in contrast to the blood red color observed for the final carbonylated solution in ethanol. While it is therefore unlikely that identical species are present in the latter system, our results and those reported previously^{18,19} together with the fact that stepwise coordination of up to two molecules of carbon monoxide occurs in the two different systems mentioned above suggest that the species present in the red solution contain either one or two carbonyl groups. We shall first discuss the complexes prepared from the red solution.

trans-[RuCl₂(L₂)₂] Complexes.—In the previous studies, complexes of the formula [RuCl₂(CO)₂L₂] and [RuCl₂(CO)L₃] were obtained from the red

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solution depending on the quantity of ligand used.^{18,19} We have obtained analogous dicarbonyl complexes with a variety of di(tertiary phosphines and arsines) (*vide infra*) but find in addition that when a threefold excess of the ligand (bis(diphenylphosphino)methane, bis(diphenylphosphinomethyl) ether, 1,2-bis(diphenylarsino)ethylene, and *cis*-1,2-bis(diphenylarsino)ethylene, respectively) is added, all the carbon monoxide is displaced and the complexes 1-4 are obtained. The trans stereochemistry is indicated by the appearance of a single band in the metal-chlorine stretching region of the infrared. Complex 1 is identical with the complex reported previously by Chatt and Hayter,²² who prepared it directly from hydrated ruthenium(III) chloride in refluxing ethanol and we have additionally confirmed the formulation of 2-4 by preparing identical compounds by this latter method.

The interaction of bis(diphenylarsino)methane with the red solution produces only carbonyl complexes. However, when an excess of this ligand is reacted with hydrated ruthenium(III) chloride in ethanol, the novel complex 5 is produced. The data in Table I confirm that it is a monomer in solution and in addition it behaves as a nonelectrolyte in *N,N*-dimethylformamide. The ¹H nmr spectrum of 5 shows, in addition to the phenyl proton resonance, two singlets at τ 7.28 and τ 5.17 having relative intensities of 2:1. These can be assigned to the methylene protons and indicate the presence of two monodentate and one bidentate diarsine molecules. That the higher field peak is not due to free ligand (τ 7.37) is shown by the complete insensitivity of either peak to the addition of various amounts of the free ligand. The ambidentate behavior of bis(diphenylarsino)methane has been reported previously and similar differences in the chemical shifts of the methylene protons for the two modes of coordination have been noted.²³ The only significant absorption in the metal-chlorine stretching region is a broad band at 324 cm⁻¹ with a slight shoulder at 320 cm⁻¹. While this could be taken as indicating trans chlorines, the ligand absorbs strongly in this region as well, making assignment uncertain. That 5 very probably is the trans isomer despite our inability to definitely identify $\nu(\text{Ru}-\text{Cl})$ is indicated by the fact that no significant absorption is observed at 250-290 cm⁻¹ where the lower of the two bands associated with the vibrations of a *cis* Cl-Ru-Cl moiety would be expected. The trans isomer is also the more reasonable on steric grounds.

Carbonyl Complexes.—The treatment of the red solution of ruthenium carbonyl species with a stoichiometric amount of bis(diphenylarsino)methane, *cis*-1,2-bis(diphenylarsino)ethylene, or bis(diphenylphosphino)methane produces the complexes 6-8, respectively. The complexes are monomeric in chloroform and nonelectrolytes in *N,N*-dimethylformamide solution. In discussing the stereochemistries of these and the other carbonyl complexes prepared in this work, reference will be made to the various configurations depicted in Figure 1. The data in Table II clearly show that in 7 and 8 the chlorines are mutually trans and the carbonyl groups *cis* thus establishing the stereochemistry

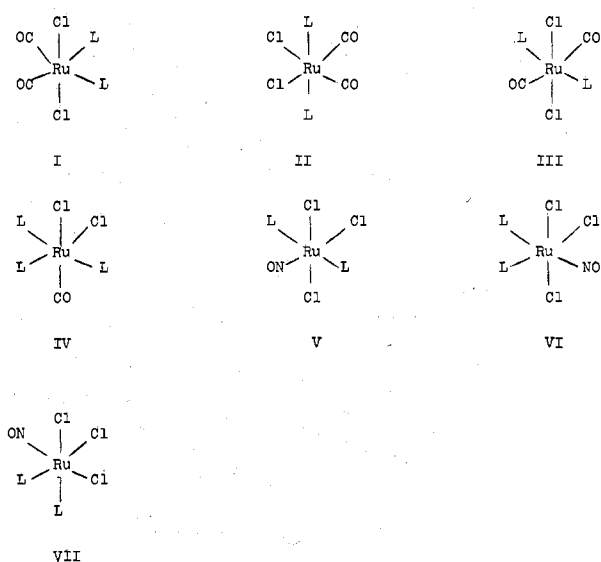


Figure 1.—Possible configurations for ruthenium(II) carbonyl and nitrosyl complexes. L represents a monodentate ligand or half of a chelating ligand.

as I. The ¹H nmr spectrum of 6 shows in addition to phenyl proton resonances only *one* singlet at τ 6.41 which can be assigned to the methylene protons of the diarsine ligand. The above data are most consistent with the presence of *monodentate* ligands. As with 5, the presence of ligand absorption in the metal-chlorine stretching region makes it difficult to determine the stereochemistry of the chlorines. In addition to a broad band at 324 cm⁻¹ there are sharp bands at 332 and 286 cm⁻¹ and a shoulder at 313 cm⁻¹. The band at 324 cm⁻¹ is undoubtedly a ligand absorption while the one at 286 cm⁻¹ is in the range where the lower energy band associated with the vibrations of the *cis* Cl-Ru-Cl moiety has been found in similar complexes having configuration II (*cf.* 15-18 and reference 24). From these data, and assuming *cis* chlorines, the other Ru-Cl band would be expected around 310 cm⁻¹. It is possible that the shoulder at 313 cm⁻¹ is this band, the band at 332 cm⁻¹ being rather high to be assigned to this vibration. While it is possible that the 332-cm⁻¹ band is due to the admixture of an isomer with trans chlorines (I or II), this possibility is not supported by the infrared spectrum in the carbonyl stretching region. Thus only two strong absorptions are observed and these are in the ranges found for complexes of configuration II.²⁵ The energies associated with the carbonyl stretching vibrations for complexes of configuration I are generally 10-15 cm⁻¹ higher (*cf.* 15-18 and reference 25). Therefore, if such a mixture of isomers were present, four carbonyl bands would be expected (or three if the second isomer were III). We conclude that 6 has configuration II and that the 332-cm⁻¹ band is due to a ligand vibration. Complex 6 can also be prepared from 5 by treatment with carbon monoxide in boiling ethanol. The relative ease of this transformation (which involves at least the opening of the chelate ring if not the complete displacement of the chelating ligand) and the failure of all attempts to prepare 5 from the red solution testify to the reluctance of

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(23) M. W. Anker, R. Colton, and I. B. Tompkins, *Aust. J. Chem.*, **21**, 1143 (1968).

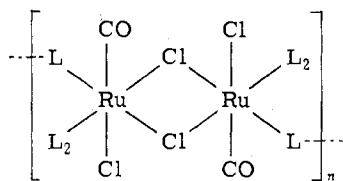
(24) M. S. Lupin and B. L. Shaw, *J. Chem. Soc., A*, 741 (1968).

(25) P. John, *Chem. Ber.*, **103**, 2178 (1970).

bis(diphenylarsino)methane to behave as a chelating ligand in these systems.

In an attempt to ascertain if a similar complex containing *monodentate* bis(diphenylphosphino)methane could be prepared, **1** was treated with carbon monoxide at reflux in a mixture of tetrahydrofuran and ethanol. Instead of rupture of a chelate ring, one chlorine is replaced to give the cationic monocarbonyl complex **9**. The formulation is supported by the conductivity data in Table III which show it to be a 1:1 electrolyte and by the formation of **10** and **11** by metathesis in methanol. By contrast with all of the other complexes reported here, **9**–**11** exhibit only very weak absorptions in the Ru–Cl stretching region. The band at 310 cm^{-1} is the most prominent feature and it is assigned as $\nu(\text{Ru}-\text{Cl})$ which indicates that the chlorine is trans to the carbonyl group. We have no ready explanation for the weakness of the absorption however. In the ^1H nmr spectrum of a freshly prepared solution of **9** in CD_3OD the methylene protons of the diphosphine ligand appear as a broad multiplet centered at τ 4.60. Within 15 min this signal has decreased noticeably in intensity and a new singlet has appeared at τ 5.20 which is attributable to CD_3OH . After 24 hr the methylene proton resonance has essentially disappeared while the hydroxyl signal has become quite pronounced. One plausible process which could account for this exchange involves the interaction of the metal directly with the methylene protons of the coordinated diarsine thereby weakening the C–H bonds and making them susceptible to attack by the solvent. This explanation invokes the so-called " β effect" in which a hydrogen on a carbon β to the metal is labilized by interaction with metal orbitals.²⁶

The interaction of a threefold excess of the non-chelating ligand *trans*-1,2-bis(diphenylphosphino)ethylene with the red solution produces the immediate precipitation of **12** for which the analytical data indicate the simplest formula to be $\text{Ru}_2(\text{L}_2)_3(\text{CO})_2\text{Cl}_4$. The infrared spectral data in Table II are best explained by a structure like



in which two diphosphine molecules are monodentate and the third serves to bridge adjacent dimeric units. Thus the band at 300 cm^{-1} can be assigned to the vibration of the terminal chlorine trans to the carbonyl group²⁴ while the other two can be associated with vibrations of the bridging chlorines. In the chloro-bridged species $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$ the bridging chlorines absorb at 317 and 290 cm^{-1} .²⁷ The lower values which we find can be attributable to the fact that here the chlorines are trans to phosphine ligands.²⁴ We have not been able to satisfactorily determine the degree of oligomerization for **12** because of the low solubility of the complex, a property which suggests that the simplest formula is not the true molecular formula. The

compound is moderately soluble in *N,N*-dimethylformamide but the low molecular weight observed clearly indicates disruption of the complex. Alternative formulations involving only diphosphine bridges, in addition to being improbable on steric grounds are also not fully consistent with the observed infrared spectrum unless one invokes solid state or isotopic splitting.

A number of examples of complexes of unsaturated tertiary phosphines and arsines have been reported in which the double bond is coordinated in addition to the group V atom.^{28–31} We have investigated the reaction of the unsaturated species *cis*- and *trans*- β -styryldiphenylphosphine, their arsine analogs, and phenylethyndiphenylphosphine with the red solution of ruthenium carbonyl species. However, in no instance did we obtain evidence for coordination of the multiple bond. Instead, the reaction of an excess of the ligands *trans*- β -styryldiphenylarsine, its phosphorus analog, or phenylethyndiphenylphosphine with the red solution in a nitrogen atmosphere produces the monocarbonyl complexes **13**, **14**, and **19**, respectively. Comparison of their infrared spectra with previously published data²⁴ indicates that they have the *meridional* configuration IV. Treatment of these monocarbonyl complexes with carbon monoxide in refluxing benzene converts them to the dicarbonyl complexes **15**, **16**, and **20** which can be assigned configuration II on the basis of their infrared spectra^{24,25} (Table II). Although the same dicarbonyl complexes can be obtained directly from the red solution in the presence of carbon monoxide, the above route gives better yields. Attempts to regenerate the monocarbonyl complexes by treatment of the dicarbonyls with excess phosphine or arsine were unsuccessful; this reverse reaction only occurring if the dicarbonyl complex has configuration III.²⁴ Interaction of the red solution with *cis*- β -styryldiphenylphosphine and its arsenic analog produces only the dicarbonyl species **17** and **18** even if a large excess of the ligand and a nitrogen atmosphere are used. Models indicate that the steric requirements of these ligands make it very difficult to coordinate three of them to one metal. On the basis of the infrared spectra, **17** and **18** also have configuration II.

Nitrosyl Complexes.—Ruthenium forms a large number of nitrosyl complexes³² and the report¹⁰ that the Ru(0) nitrosyl complex $\text{Ru}(\text{NO})\text{Cl}(\text{P}(\text{C}_6\text{H}_5)_3)_2$, prepared by reduction of $\text{Ru}(\text{NO})\text{Cl}_3(\text{P}(\text{C}_6\text{H}_5)_3)_2$, would undergo oxidative addition reactions prompted us to explore the possibility of generating Ru(0) di(tertiary phosphine and arsine) complexes by similar routes. At the time this work was begun no such species had been reported although such a complex, $[\text{Ru}(\text{NO})((\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2)_2]\text{B}(\text{C}_6\text{H}_5)_4$, is now known but no preparative details have been published.³³

The reaction of **1** with an excess of nitrosyl tetrafluoroborate in benzene-methanol produces a deep green solution from which brown crystals of **21** can be

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(29) D. I. Hall and R. S. Nyholm, *J. Chem. Soc. A*, 1491 (1971).

(30) D. I. Hall and R. S. Nyholm, *Chem. Commun.*, 488 (1970).

(31) L. V. Interrante and G. V. Nelson, *Inorg. Chem.*, **7**, 2059 (1968), and references therein.

(32) W. P. Griffith, "The Chemistry of the Rarer Platinum Metals," Interscience, London, 1967.

(33) C. G. Pierpont, A. Pucci, and R. Eisenberg, *J. Amer. Chem. Soc.*, **93**, 3050 (1971).

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(27) M. J. Cleare and W. P. Griffith, *J. Chem. Soc., A*, 372 (1969).

obtained after filtration and washing with ether. The product can alternatively be obtained as a green benzene solvate if the ether washing is omitted. The complex behaves as a 1:1 electrolyte in acetonitrile and its formulation as a Ru(III) species is confirmed by its exhibiting a magnetic moment of 2.02 BM³⁴ at 298°K. The trans stereochemistry is demonstrated by the appearance of a single Ru-Cl stretch in the infrared spectrum (Table II). The ability of NOX (X = Cl, Br), NOBF₄, and NOPF₆ to act as oxidizing agents has been noted previously.³⁵⁻³⁸ If on the other hand, the green solution prepared as above is left to stand in a stoppered flask under nitrogen at room temperature for several days, the color slowly lightens to yellow and crystals of the Ru(II) nitrosyl complex **22** precipitate. Although we cannot locate the Ru-Cl absorption in the far-infrared, we consider it to be the nitrosyl analog of **10**, for the following reasons: (1) analysis shows the presence of one chlorine, (2) the complex behaves as a 2:1 electrolyte, (3) chlorine is a better ligand than tetrafluoroborate so the chlorine is very likely coordinated since Ru(II) complexes are predominantly six-coordinate. We have no explanation for the absence of $\nu(\text{Ru-Cl})$ but note that in **10** this band was quite weak. There are two plausible routes by which the conversion of **21** into **22** could occur under the conditions detailed above. The simplest process would involve the replacement of chloride in **21** by NO, the most likely source of which would be the NOBF₄ reduced in the formation of **21**. Here the NO acts in its usual manner as a three-electron donor thus effectively reducing the ruthenium back to the divalent state. In support of this, we find that the action of NO on solutions of **21** in benzene-methanol or dichloromethane in the presence of NaBF₄ readily produces **22**. Alternatively, the conversion might involve reaction of **21** with methyl nitrite which would be produced by the interaction of the excess NOBF₄ with the methanol in the solvent mixture.³⁹ To test this hypothesis, solid NOBF₄ was treated with methanol and the methyl nitrite produced (identified from its infrared spectrum) was bubbled through a solution of **21** and NaBF₄ in methanol-benzene which was contained in a serum-capped flask. Over a period of three days the solution slowly became yellow and crystals of **22** precipitated. Unfortunately, these results are not as conclusive as would be desired since upon opening the flask used to generate the methyl nitrite, brown vapors were noted which were probably NO₂ thus suggesting some NO was generated as well. It is possible, however, to generate **22** from **21** by treatment of a benzene-methanol solution of the latter with amyl nitrite so that despite the uncertainty in the previous experiment, it is possible to produce **22** using an alkyl nitrite rather than NO directly. It is also possible that both processes occurred in the original reaction but we have not been able to obtain evidence which allow us to be more definite on this point. A number of neutral nitrosyl

complexes were also prepared from ruthenium nitrosyl trichloride and the appropriate ligand in 2-methoxyethanol. Using stoichiometric quantities of bis(diphenylphosphino)methane, *cis*-1,2-bis(diphenylarsino)ethylene, or bis(diphenylphosphinomethyl) ether, complexes of the formula [Ru(NO)Cl₃(L₂)] (**23**, **25**, and **26**, respectively) were obtained. The far-infrared spectra of **23** and **26** each exhibit two strong bands assignable to Ru-Cl vibrations indicating a *meridional* configuration for the three chlorines. Because the diphosphine ligand must occupy two adjacent coordination sites, these two complexes must have configuration VI. This appears to be the first reported example of this configuration for complexes of this sort. Comparison of our data with those recently reported by Townsend and Coskran⁴⁰ shows that no unequivocal distinction can be made between configurations V and VI on the basis of far-infrared data alone. We are unable to definitely assign a configuration to **25**. The far-infrared spectrum in the region of interest consists of strong bands at 326, 293, and 278 cm⁻¹. Of these only the 278-cm⁻¹ band can be confidently assigned to $\nu(\text{Ru-Cl})$ as the ligand also absorbs strongly around 325 and 290 cm⁻¹. We are inclined to favor configuration VI for **25** since it was prepared in an analogous manner to the previous two complexes. On the other hand the Ru-Cl band assigned here corresponds very closely to the lowest band observed for [Ru(NO)Cl₃(P(CH₃)(C₆H₅)₂)₂] which was shown by ¹H nmr to have configuration VII.⁴⁰

In one experiment, Ru(NO)Cl₃ was reacted with a twofold excess of bis(diphenylphosphino)methane. Besides **23**, a small quantity of the more soluble **1** was also obtained, a result which is somewhat surprising in view of the general inertness of the NO ligand to substitution in Ru(II) complexes.³²

The unsaturated ligands *cis*- β -styryldiphenylphosphine and its arsenic analog react with ruthenium nitrosyl trichloride in 2-methoxyethanol to give complexes **27** and **28** having the formula [Ru(NO)Cl₃(L)₂]. We assign these configuration V on the basis of their far-infrared spectra (two bands) and by comparison with the results of Townsend and Coskran⁴⁰ who found a distinct preference for this configuration in complexes of this type containing monodentate phosphines or arsines. As was the case in the carbonyl system, the product obtained with bis(diphenylarsino)methane, **24**, contains two monodentate diarsine ligands. Again ligand absorptions make it difficult to unequivocally identify the Ru-Cl absorptions but they are probably the bands at 338 and 290 cm⁻¹, the former appearing as a shoulder on the strong ligand absorption which appears at 329 cm⁻¹. We prefer configuration V rather than VI for **24** as the former is more plausible on steric grounds and, as mentioned above, is the one apparently preferred when monodentate ligands are present. In contrast to the previous report,⁴⁰ no examples of configuration VII were unequivocally identified. While all the other complexes exhibited a single strong band in the 1800-1900-cm⁻¹ range which is attributable to $\nu(\text{NO})$, for **24** there are two. However, in chloroform solution only a single absorption is observed at 1845 cm⁻¹ so we conclude that the appearance

(34) Reference 32, p 214.

(35) J. R. Fowler and J. Kleinberg, *Inorg. Chem.*, **9**, 1005 (1970).

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(39) G. Olah, L. Noszko, S. Kuhn, and M. Szelke, *Chem. Ber.*, **89**, 2374 (1956).

(40) R. E. Townsend and K. J. Coskran, *Inorg. Chem.*, **10**, 1661 (1971).

of two bands in the mull spectrum is due to solid-state effects.

Attempted Preparations of Ru(0) Complexes.—Chatt and Davidson have reported the preparation of $\text{Ru}(\text{DMPE})_2$ (DMPE = 1,2-bis(dimethylphosphino)ethane) by the reduction of *trans*- $[\text{RuCl}_2(\text{DMPE})_2]$ with sodium naphthalenide in tetrahydrofuran followed by pyrolysis of the intermediate hydridonaphthyl complex.⁹ We have used this procedure in an attempt to reduce the analogous Ru(II) complexes **1**, **3**, and **4**. After treating a dry tetrahydrofuran solution of the appropriate complex with the reducing agent under nitrogen for periods of up to 30 min, the solvent was removed under vacuum to leave brown or green solids. Mull spectra of the crude solids were very ill-defined and did not show the presence of any hydrido species. Attempts at purification were frustrated by the very low solubility of these solids in most solvents that would not be likely to react with the anticipated products. This fact also made it impossible to attempt characterization by nmr. Pyrolysis experiments on the initial products were equally inconclusive as the residues obtained could also not be satisfactorily characterized. We suspect that decomposition of the complex occurred possibly *via* attack of the reducing agent on the ligand as has been noted previously for other systems involving aromatic di(tertiary phosphines).⁴¹ In order to determine whether this was a result of a high reactivity of the ligand itself or whether destruction of the ligand occurred because the bulky phenyl groups prevented the naphthalenide ion from getting to the metal, we investigated the reactions of the less-crowded complexes **6**, **13**, and **17** with sodium naphthalenide. Again the products obtained could not be satisfactorily characterized and although the infrared spectra were of poor quality it appeared that some starting material was still present. We conclude that this is not a feasible route to Ru(0) complexes of aromatic di(tertiary phosphines or arsines) although we can only speculate on the reasons for its failure. Attempts at reduction of **1**, **3**, and **4** with sodium borohydride or lithium aluminum hydride were also unsuccessful.

Another approach to zerovalent ruthenium complexes involves the reduction with zinc in *N,N*-dimethylformamide in the presence of carbon monoxide as reported by Collman and Roper for the preparation of $\text{Ru}(\text{CO})_3(\text{P}(\text{C}_6\text{H}_5)_3)_2$.⁴ While the anticipated products would be coordinatively saturated in contrast to the desired $[\text{Ru}(\text{L}_2)_2]$ complexes, the triphenylphosphine complex does undergo oxidative elimination reactions with small molecules so analogous complexes with our ligands could still be useful for the study of the interaction of small molecules with zerovalent Ru complexes of di(tertiary phosphines and arsines). Ac-

cordingly reduction of the complexes **1–3**, **5**, **6**, **12**, **15**, and **17** was attempted using this procedure. The only reaction in which a single, well-defined product was produced was with **1** but unfortunately this product was **9** even if high (~ 900 psi) pressures of carbon monoxide were used. In all other cases, the infrared spectra of the crude products showed a large number of carbonyl absorptions some of which could be attributed to starting material or known carbonylation products also containing Ru(II) (*e.g.*, **5** gave some **6**). In addition all the crude products still contained halogen indicating that complete reduction had not occurred. Attempts to separate the product mixtures by fractional crystallization or column chromatography were somewhat successful but yields were low and subsequent purification not particularly satisfactory. The spectrum of the product from **12** exhibited in addition to bands due to the starting material a new band at 1887 cm^{-1} which is comparable to that found for the triphenylphosphine complex prepared by Collman⁴ indicating that substantial reduction had occurred but no completely halogen-free product could be obtained. In only one instance were we able to obtain a product containing no halogen, namely one fraction of the material obtained from **5**. Analytical data indicate the probable formula to be $\text{Ru}(\text{CO})_3(\text{L}_2)_2$ while the ^1H nmr shows only one singlet at τ 7.43 which can be assigned to the methylene protons of the diarsine ligand. The latter data indicate that these ligands are monodentate and equivalent. The infrared spectrum in the terminal carbonyl region consists of four or five absorptions of varying intensity. The product evidently is a mixture of isomers but we have not enjoyed any success in further separating them. Subsequent experiments in which the reaction time and temperature, the carbon monoxide pressure, and the reducing agent were varied were no more successful and we conclude that this route to Ru(0) complexes of our ligands is also not profitable. After the conclusion of these studies, some reports have appeared describing relatively convenient preparations of $\text{Ru}_2(\text{CO})_{12}$ by reductive carbonylation of Ru(II) and Ru(III) species.^{42–44} However, the conditions used in these instances do not appear to be sufficiently different from ours to suggest that they might be better for producing *monomeric* Ru(0) complexes of di(tertiary phosphines or arsines).

Initial attempts at reducing the nitrosyl complexes following the published procedure¹⁰ met with little success. However, we have subsequently learned that the course of these reactions is very sensitive to reaction conditions⁴⁵ and further experiments indicate that Ru(0) species may be produced in these systems. Results of this work will be reported at a later date.

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