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A Reinvestigation of the Reaction between Nitrosylruthenium Trichloride and Several Tertiary Phosphines and Arsines[1]

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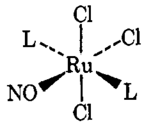
RuCl$_3$(NO) reacts with various monodentate tertiary phosphines and arsines in ethanol or 2-ethoxyethanol to yield two different structural isomers of the complex RuCl$_3$(NO)L$_2$ (L = phosphine or arsine). Ionic species of the type RuCl$_2$(NO)L$_3{}^+$ (L = P(CH$_3$)$_2$C$_6$H$_5$ or As(CH$_3$)$_2$C$_6$H$_5$) are also present in these reaction mixtures and have been characterized as the corresponding chloride and tetraphenylborate salts. The ^{1}H nmr and far-infrared data are used to determine the stereochemistries of the above complexes together with those of the corresponding tribromo and triiodo derivatives, RuX$_3$(NO)L$_2$ (X = Br or I), obtained from the above complexes by simple metathetical replacement reactions.

Introduction

The reaction of nitrosylruthenium trichloride with several tertiary phosphines and arsines in ethanol or higher boiling alcohols has previously been reported[2,3] to yield complexes of the type RuCl$_3$(NO)L$_2$ (L = phosphine or arsine) but no structural data on the products were reported. In the course of our research for potential routes to species of the type RuCl(NO)L$_2$ we have examined the reaction of nitrosylruthenium trichloride with P(CH$_3$)$_2$C$_6$H$_5$, As(CH$_3$)$_2$C$_6$H$_5$, P(CH$_3$)(C$_6$H$_5$)$_2$, and As(CH$_3$)(C$_6$H$_5$)$_2$ and have found that in certain cases the reaction leads to two different structural isomers of RuCl$_3$(NO)L$_2$ and also to the formation of ionic species of the type [RuCl$_2$(NO)L$_3$]Cl when an excess of ligand is employed. The phenomenon of virtual coupling[4] has been employed in the interpretation of the ^{1}H nmr spectra of these complexes and used in conjunction with far-infrared data to make the necessary structural assignments. Of the three possible structural isomers I–III, we have only observed the formation of products with configurations I and III.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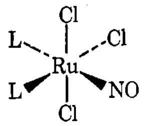
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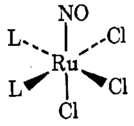
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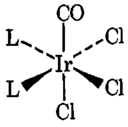
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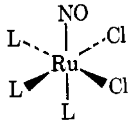
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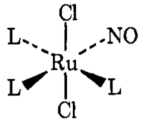
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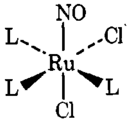
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Experimental Section

The infrared spectra were obtained on Perkin-Elmer Models 225 and 237 grating spectrophotometers using either cesium iodide or sodium chloride optics. Proton nmr spectra were taken on a Varian Associates Model A-56/60-D instrument with tetramethysilane as an internal standard. Conductivity measurements were made using a Beckman Model RC 16 B2 conductivity bridge and conventional dip-type bright platinum electrodes. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Materials.—Ruthenium trichloride was purchased from Engelhard Minerals and Chemicals Corp., and the ligands P(CH$_3$)$_2$C$_6$H$_5$, P(CH$_3$)(C$_6$H$_5$)$_2$, As(CH$_3$)$_2$C$_6$H$_5$, and As(CH$_3$)(C$_6$H$_5$)$_2$ were prepared as described previously.[5] Trichloronitrosylruthenium(II) was prepared by passing a slow stream of nitric oxide into a vigorously stirred solution of 3.3 g of ruthenium trichloride trihydrate in 90 ml of ethanol for 6–8 hr; assuming complete conversion to nitrosylruthenium trichloride, the resultant solution having an approximate concentration of 1 g/30 ml was used directly in the preparations described below. The complexes RuCl$_3$(NO)L$_2$ [L = P(C$_6$H$_5$)$_3$ or P(n-C$_4$H$_9$)$_3$] were prepared according to previously described methods.[2]

Trichloronitrosylbis(dimethylphenylphosphine)ruthenium(II), Configuration I, RuCl$_3$(NO)[P(CH$_3$)$_2$C$_6$H$_5$]$_2$.—A solution of 1.0 g of trichloronitrosylruthenium in 30 ml of ethanol was slowly added to a heated solution of 1.0 ml of dimethylphenylphosphine (~2 mol equiv) in 40 ml of benzene. After refluxing gently for 2 hr the volume of the deep orange solution was reduced to bring about precipitation of the product (1.5 g, 69% yield) which was recrystallized by dissolving the solid in 25 ml of dichloromethane, adding 15 ml of ethanol, and evaporating the resultant solution under reduced pressure until crystallization commenced. *Anal.* Calcd for C$_{16}$H$_{22}$NP$_2$Cl$_3$RuO: C, 37.41; H, 4.32; Cl, 20.71; P, 12.07. Found: C, 37.10; H, 4.34; Cl, 21.00; P, 11.85.

Trichloronitrosylbis(dimethylphenylphosphine)ruthenium (II), Configuration III, RuCl$_3$(NO)[P(CH$_3$)$_2$C$_6$H$_5$]$_2$.—A solution of 1.0 g of trichloronitrosylrutheniun in 30 ml of ethanol was slowly added to a heated solution of 1.0 ml of dimethylphenylphosphine (~2 mol equiv) in 30 ml of 2-ethoxyethanol. After refluxing gently for 20 min the clear orange solution was treated with an excess of n-hexane to precipitate the product (0.6 g, 28% yield) which was removed, washed with ethanol and n-pentane, and dried *in vacuo*. N.B. Often some product with configuration I was also present in the precipitated solid. Attempts to recrystallize the product led to formation of the compex with conformation I.

Trichloronitrosylbis(dimethylphenylarsine)ruthenium(II), Configuration III, RuCl$_3$(NO)[As(CH$_3$)$_2$C$_6$H$_5$]$_2$.—This compound was prepared by a process analogous to that used for the corresponding phosphine derivative. N.B. Prolonged refluxing in this reaction or refluxing the product with configuration III in dichloromethane or benzene leads to formation of the isomer with configuration Ia (see text). *Anal.* Calcd for C$_{16}$H$_{22}$NAs$_2$Cl$_3$RuO: C, 31.94; H, 3.69; Cl, 17.68. Found: C, 31.94; H, 3.73; Cl, 17.80.

Reaction between Trichloronitrosylruthenium(II) and Dimethylphenylarsine in Ethanol.—A solution of 1.0 g of trichloronitrosylruthenium in 30 ml of ethanol was slowly added to a solution of 1.6 ml of dimethylphenylarsine (~2.5 mol equiv) in 40 ml of ethanol. The mixture was refluxed gently for 2–3 hr and then cooled and stored overnight at 0°. A mixture of flaky orange crystals (Ia) (1.0 g, 39% yield) and dark red crystals (Ib) (0.4 g, 16% yield) was deposited and after 1 further day's storage the two products were quite efficiently separated by a wash and decantation technique using an ethanol–ether solution (1:1); the dark red crystals remained at the bottom of the solution while the other product was poured off in suspension. Both products had the same spectral properties in solution (see text) and are considered to be different crystalline forms of the product

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(1) Presented in part at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970; see Abstracts, No. INOR-130.

(2) J. Chatt and B. L. Shaw, *J. Chem. Soc. A*, 1811 (1966).

(3) M. B. Fairy and R. J. Irving, *ibid.*, *A*, 475 (1966).

(4) J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc., London*, 291 (1963).

(5) C. K. Ingold, F. R. Shaw, and I. S. Wilson, *J. Chem. Soc.*, 1280 (1928), and references therein.

TABLE I

INFRARED (cm^{-1}) AND PHYSICAL DATA ON COMPLEXES

Complex	Confign	Color	ν(NO) region		340–250 cm^{-1} region	
			Nujol	$CHCl_3$	ν(Ru–Cl)	Other bands
$RuCl_3(NO)[P(C_6H_5)_3]_2$	I	Yellow-orange	1875 s	1870 s	333 s, 322 sh, 289 m	282 vw
$RuCl_3(NO)[P(n\text{-}C_4H_9)_3]_2$	I	Orange	1818 s	1843 s	336 s, 323 s, 287 m	
$RuCl_3(NO)[P(CH_3)_2C_6H_5]_2$	I	Orange	1855 s	1867 s	322 s, 290 m	
$RuCl_3(NO)[P(CH_3)_2C_6H_5]_2$	III	Yellow-orange	1874 s, 1865 sh 1858 s, 1853 sh	1856 s	324 s, 314 m, 290 s 278 s	
$RuBr_3(NO)[P(CH_3)_2C_6H_5]_2$	I	Orange	1855 s	1864 s	. . .	266[a]
$RuI_3(NO)[P(CH_3)_2C_6H_5]_2$	I	Maroon	1847 s	1856 s	. . .	. . .
$RuCl_3(NO)[As(CH_3)_2C_6H_5]_2$	Ia	Orange	1853 s, 1832 s	1863 s	336 s, 288 m	306 m, 279 w
$RuCl_3(NO)[As(CH_3)_2C_6H_5]_2$	Ib	Dark red	1854 s	1863 s	337 sh, 329 s, 284 m	313 m, 306 w
$RuCl_3(NO)[As(CH_3)_2C_6H_5]_2$	III	Yellow-orange	1868 s, 1859 s 1850 s, 1845 sh	1852 s	326 m, 311 s, 289 s 276 s	251 m
$RuBr_3(NO)[As(CH_3)_2C_6H_5]_2$	I	Orange-brown	1853 s	1858 s	. . .	305 s, 262 s[a]
$RuI_3(NO)[As(CH_3)_2C_6H_5]_2$	I	Brown	1842 s	1851 s	. . .	304 s
$RuCl_3(NO)[P(CH_3)(C_6H_5)_2]_2$	I	Orange	1878 s	1865 s	328 s, 324 sh, 284 w	
$RuBr_3(NO)[P(CH_3)(C_6H_5)_2]_2$	I	Orange-brown	1877 s	1865 s	. . .	262 s[a]
$RuI_3(NO)[P(CH_3)(C_6H_5)_2]_2$	I	Brown	1871 s	1860 s	. . .	310 m
$RuCl_3(NO)[As(CH_3)(C_6H_5)_2]_2$	I	Orange	1875 s	1868 s	333 m, 284 m	323 s
$RuBr_3(NO)[As(CH_3)(C_6H_5)_2]_2$	I	Orange-brown	1871 s	1858 s	. . .	322 s, 261 m[a]
$RuI_3(NO)[As(CH_3)(C_6H_5)_2]_2$	I	Maroon	1850 sh, 1844 s	1852 s	. . .	321 s
$\{RuCl_2(NO)[P(CH_3)_2C_6H_5]_3\}Cl$[b,c]	VII	Bright yellow	1879 s	1885 s	331 m, 280 s	351 w, 318 m
$\{RuCl_2(NO)[P(CH_3)_2C_6H_5]_3\}B(C_6H_5)_4$[b,d]	VII	Bright yellow	1846 s, 1825 w	1853 s	331 m, 284 s	355 w, 315 w
$\{RuCl_2(NO)[As(CH_3)_2C_6H_5]_3\}B(C_6H_5)_4$[b,e]	VII	Bright yellow	1840 s, 1822 w, sh	1852 s	328 m, 295 s	314 m, 308 m 282 m, 248 m

[a] ν(Ru–Br) absorption. [b] Conductances are recorded on *ca.* 10^{-3} *M* solutions in nitrobenzene. [c] $\Lambda_M = 25.3$ ohm^{-1} cm^2 mol^{-1}. [d] $\Lambda_M = 18.6$ ohm^{-1} cm^2 mol^{-1}. [e] $\Lambda_M = 19.8$ ohm^{-1} cm^2 mol^{-1}.

trichloronitrosylbis(dimethylphenylarsine)ruthenium(II)—configuration I. After removal of the above products the resultant orange-yellow filtrate was treated with an ethanol solution of sodium tetraphenylborate. The yellow salt, dichloronitrosyltris(dimethylphenylarsine)ruthenium(II) tetraphenylborate (0.5 g, 11% yield), precipitated and it was removed, washed with ethanol and ether, and dried *in vacuo*. N.B. With shorter reaction times some trichloronitrosylbis(dimethylphenylarsine)ruthenium(II)—configuration III was found to be present in the initial products isolated from this reaction.

Dichloronitrosyltris(dimethylphenylphosphine)ruthenium(II) Chloride, $\{RuCl_2(NO)[P(CH_3)_2C_6H_5]_3\}Cl$.—One gram of trichloronitrosylruthenium was refluxed together with 2.4 ml of dimethylphenylphosphine (~5 mol equiv) in 60 ml of ethanol for 3 hr. The volume of the resultant clear orange-yellow solution was reduced to ~20 ml and carefully treated with an excess of ether to precipitate the bright yellow product (2.5 g, 90% yield) which was removed, washed with ether, and dried *in vacuo*. *Anal.* Calcd for $C_{24}H_{33}NP_3Cl_3RuO$: C, 44.20; H, 5.10; Cl, 16.32; P, 14.28. Found: C, 43.97; H, 5.30; Cl, 16.61; P, 14.13.

Dichloronitrosyltris(dimethylphenylphosphine)ruthenium(II) Tetraphenylborate, $\{RuCl_2(NO)[P(CH_3)_2C_6H_5]_3\}B(C_6H_5)_4$.—This compound was prepared by dropwise addition of an ethanol solution of sodium tetraphenylborate to a stirred, filtered solution of the corresponding chloride salt prepared as above. The yellow product which precipitated almost quantitatively was filtered, washed with aqueous ethanol and ether, and dried *in vacuo*. *Anal.* Calcd for $C_{48}H_{53}NP_3Cl_2RuBO$: C, 61.60; H, 5.71; Cl, 7.58; P, 9.93. Found: C, 61.68; H, 5.82; Cl, 7.75; P, 10.02.

Dichloronitrosyltris(dimethylphenylarsine)ruthenium(II) Tetraphenylborate, $\{RuCl_2(NO)[As(CH_3)_2C_6H_5]_3\}B(C_6H_5)_4$.—This compound was prepared by a procedure similar to that used for the corresponding phosphine derivative above. *Anal.* Calcd for $C_{48}H_{53}NAs_3Cl_2RuBO$: C, 54.01; H, 5.01; As, 20.98. Found: C, 53.62; H, 4.84; As, 20.82.

Trichloronitrosylbis(methyldiphenylphosphine)ruthenium(II), Configuration I, $RuCl_3(NO)[P(CH_3)(C_6H_5)_2]_2$.—One gram of trichloronitrosylruthenium was refluxed together with 1.8 ml of methyldiphenylphosphine (2.5 mol equiv) in 60 ml of ethanol for 1 hr. The product (2.0 g 74% yield) precipitated from the hot solution and was removed from the cooled solution and washed with ethanol. Recrystallization was achieved by dissolving the solid in ~20 ml of dichloromethane, adding 10 ml of ethanol, and reducing the solution volume under reduced pressure to bring about crystallization of the product. *Anal.* Calcd for $C_{26}H_{26}NP_2Cl_3RuO$: C, 49.01; H, 4.09; Cl, 16.68. Found: C, 48.77; H, 4.05; Cl, 16.84.

Trichloronitrosylbis(methyldiphenylarsine)ruthenium (II), Configuration I, $RuCl_3(NO)[As(CH_3)(C_6H_5)_2]_2$.—This compound was prepared by a similar method to that described above for the corresponding methyldiphenylphosphine derivative (yield 65%). *Anal.* Calcd for $C_{26}H_{26}NAs_2Cl_3RuO$: C, 43.03; H, 3.61; Cl, 14.68; As, 20.65. Found: C, 42.74; H, 3.73; Cl, 14.50; As, 20.29.

Complexes of the type $RuX_3(NO)L_2$ [where X = Br or I and L = $P(CH_3)_2C_6H_5$, $P(CH_3)(C_6H_5)_2$, $As(CH_3)_2C_6H_5$, or $As(CH_3)(C_6H_5)_2$] were prepared from either the corresponding trichloro derivatives (X = Cl) or from the ionic species $[RuCl_2(NO)L_3]B(C_6H_5)_4$ [L = $P(CH_3)_2C_6H_5$ or $As(CH_3)_2C_6H_5$] by simple metathetical reactions and the following are the typical preparations of each method.

Triiodonitrosylbis(dimethylphenylphosphine)ruthenium(II), Configuration I, $RuI_3(NO)[P(CH_3)_2C_6H_5]_2$.—Dichloronitrosyltris(dimethylphenylphosphine)ruthenium(II) tetraphenylborate (0.5 g, 0.5 mmol) was refluxed together with 1.5 g (11 mmol) of lithium iodide in 35 ml of 2-ethoxyethanol for 6 hr. The addition of water to the cooled dark orange solution caused the product to precipitate (0.3 g, 72% yield). The solid was removed, washed with ethanol and then *n*-pentane, and finally recrystallized from dichloromethane–ethanol by the procedure described above for the trichloro derivatives. *Anal.* Calcd for $C_{16}H_{22}NP_2I_3RuO$: C, 24.37; H, 2.81; I, 48.30; P, 7.86. Found: C, 24.59; H, 3.01; I, 48.52; P, 7.62.

Tribromonitrosylbis(dimethylphenylarsine)ruthenium(II), Configuration I, $RuBr_3(NO)[As(CH_3)_2C_6H_5]_2$.—Trichloronitrosylbis(dimethylphenylarsine)ruthenium(II), configuration I (0.4 g, 0.7 mmol), and 1.5 g (17 mmol) of lithium bromide were refluxed together in 35 ml of 2-ethoxyethanol for 6 hr. The cooled dark red solution was treated with water to precipitate the product (0.4 g, 77% yield) which was removed, washed with ethanol–*n*-pentane, and dried *in vacuo*. Recrystallization was performed from dichloromethane–ethanol as described above. *Anal.* Calcd for $C_{16}H_{22}NAs_2Br_3RuO$: C, 26.15; H, 2.96; Br, 32.62; As, 20.39. Found: C, 26.18; H, 3.15; Br, 32.44; As, 20.47.

Results and Discussion

Reaction between $RuCl_3(NO)$ and Dimethylphenylphosphine.—Reaction of $RuCl_3(NO)$ and $P(CH_3)_2C_6H_5$ in benzene–ethanol (1:1) yields a deep orange solution from which the product $RuCl_3(NO)[P(CH_3)_2C_6H_5]_2$, configuration I, crystallizes out on reducing the solution volume and cooling to 0°. The mull infrared spectrum of this product exhibits a strong band due to N–O stretching at 1855 cm^{-1} (1867 cm^{-1} in chloroform) (Table I), and in dichloromethane solution the methyl resonance in the ^1H nmr spectrum is a 1:2:1 triplet at 2.02 ppm consistent with a structure in which the phosphine ligands are mutually trans (Table II). By employing shorter reaction times in 2-ethoxyethanol as the solvent, it is possible to isolate a product with configuration III by addition of *n*-hexane to the reaction mixture. This product is less soluble in common organic solvents than the isomer with configuration I and its mull infrared spectrum shows a more complex absorption due to N–O stretching, *i.e.*, 1874 (s), 1865 (sh), 1858 (s), and 1853 cm^{-1} (sh), but in chloroform solution only a single band at 1856 cm^{-1} is observed. The ^1H nmr spectrum in dichloromethane solution shows two doublets centered at 2.10 and 1.68 ppm due to a cis phosphine arrangement and the far-infrared spectrum has bands due to Ru–Cl stretching at 324, 314, 290, and 278 cm^{-1}. Correlation of these data with those reported for the analogous iridium carbonyl complex, $IrCl_3(CO)[P(CH_3)_2C_6H_5]_2$, configuration IV,[6] suggests the above product has configuration III rather than configuration II. If the reaction between $RuCl_3(NO)$ and $P(CH_3)_2C_6H_5$ is performed in ethanol with the phosphine present in an excess, treatment of the resultant clear orange-yellow solution with diethyl ether brings about precipitation of the bright yellow ionic species $\{RuCl_2(NO)[P(CH_3)_2C_6H_5]_3\}Cl$, configuration VII. Once again three possible configurations exist for compounds of this formulation, V–VII. This product is a 1:1 electrolyte in nitrobenzene solution and its ^1H nmr spectrum in the same solvent shows two 1:2:1 triplet resonances at 2.32 and 2.07 ppm, indicating that two of the phosphines are mutually trans, and a doublet at 1.84 ppm due to the remaining ligand cis to the other two phosphines. The presence of two distinct triplet resonances is only consistent with structure VII where there is no plane of symmetry along the P–Ru–P axis, thus accounting for the nonequivalence of the two methyl groups on the trans phosphines.[7] Treatment of an ethanol solution of $\{RuCl_2(NO)[P(CH_3)_2C_6H_5]_3\}Cl$ with sodium tetraphenylborate in ethanol brings about immediate precipitation of the corresponding tetraphenyborate salt, $\{RuCl_2(NO)[P(CH_3)_2C_6H_5]_3\}B(C_6H_5)_4$.

TABLE II

PROTON NMR DATA ON COMPLEXES

Complex	Confign	$\delta(^1H)^{a,b}$	$J_{PH}^{c,d}$
$RuCl_3(NO)[P(C_6H_5)_3]_2$	I	...	...
$RuCl_3(NO)[P(n\text{-}C_4H_9)_3]_2$	I	...	...
$RuCl_3(NO)[P(CH_3)_2C_6H_5]_2$	I	2.02 (t)	4.5
$RuCl_3(NO)[P(CH_3)_2C_6H_5]_2$	III	2.10 (d)	12.0[e]
		1.68 (d)	12.0[e]
$RuBr_3(NO)[P(CH_3)_2C_6H_5]_2$	I	2.22 (t)	4.5
$RuI_3(NO)[P(CH_3)_2C_6H_5]_2$	I	2.62 (t)	4.5
$RuCl_3(NO)[As(CH_3)_2C_6H_5]_2$	Ia	1.92 (s)	...
$RuCl_3(NO)[As(CH_3)_2C_6H_5]_2$	Ib	1.92 (s)	...
$RuCl_3(NO)[As(CH_3)_2C_6H_5]_2$	III	1.94 (s)	...
		1.63 (s)	...
$RuBr_3(NO)[As(CH_3)_2C_6H_5]_2$	I	2.09 (s)	...
$RuI_3(NO)[As(CH_3)_2C_6H_5]_2$	I	2.42 (s)	...
$RuCl_3(NO)[P(CH_3)(C_6H_5)_2]_2$	I	2.31 (t)	4.5
$RuBr_3(NO)[P(CH_3)(C_6H_5)_2]_2$	I	2.54 (t)	4.5
$RuI_3(NO)[P(CH_3)(C_6H_5)_2]_2$	I	2.72 (t)	4.5
$RuCl_3(NO)[As(CH_3)(C_6H_5)_2]_2$	I	2.18 (s)	...
$RuBr_3(NO)[As(CH_3)(C_6H_5)_2]_2$	I	2.38 (s)	...
$RuI_3(NO)[As(CH_3)(C_6H_5)_2]_2$	I	2.75 (s)	...
$\{RuCl_2(NO)[P(CH_3)_2C_6H_5]_3\}Cl^b$	VII	2.32 (t)	4.5
		2.07 (t)	4.5
		1.84 (d)	11.0[e]
$\{RuCl_2(NO)[P(CH_3)_2C_6H_5]_3\}B(C_6H_5)_4{}^b$	VII	2.20 (t)[f]	4.5
		2.02 (t)[f]	4.5
		1.67 (d)	11.0[e]
$\{RuCl_2(NO)[As(CH_3)_2C_6H_5]_3\}B(C_6H_5)_4{}^b$	VII	2.10 (s)	...
		1.94 (s)	...
		1.64 (s)	...

[a] Methyl resonances of the complexes in dichloromethane solution are reported. [b] Chemical shifts are in ppm (±0.02) and are referenced to tetramethylsilane. [c] Coupling constants are in Hz (±0.5). [d] Values are given for virtual J_{PH} coupling constants unless otherwise stated. [e] $^2J_{PH}$ coupling constant. [f] Triplets overlap slightly to give an apparent quintet.

Reaction between $RuCl_3(NO)$ and Dimethylphenylarsine.—Refluxing $RuCl_3(NO)$ and $As(CH_3)_2C_6H_5$ together for *ca.* 30 min in 2-ethoxyethanol and treating the resultant solution with *n*-hexane yields the complex $RuCl_3(NO)[As(CH_3)_2C_6H_5]_2$, configuration III, as an orange precipitate. The mull infrared spectrum (Table I) of this product shows a complex ν(NO) absorption at 1868 (s), 1857 (sh), 1850 (s), and 1845 cm^{-1} (sh), but in chloroform solution a single absorption at 1852 cm^{-1} is observed. Like the corresponding phosphine derivative this product has bands at 321 (m), 311 (s), 289 (s), and 276 cm^{-1} (s) which are again tentatively attributed to Ru–Cl stretching. In dichloromethane solution the ^1H nmr spectrum (Table II) of this isomer shows two singlet resonances at 1.94 and 1.63 ppm consistent with configuration III ($L = As(CH_3)_2C_6H_5$). A similar reaction in ethanol with a reaction time of *ca.* 2 hr again yields a clear orange solution but on cooling to 0° a mixture of flaky orange crystals (Ia) and dark red crystals (Ib) is deposited. The two products may be effectively separated by a repeated wash and decantation procedure using a 1:1 ethanol–ether mixture. The red crystals show one strong N–O stretching absorption at 1854 cm^{-1} in its mull infrared spectrum whereas the other product has two distinct strong absorptions at 1853 and 1832 cm^{-1}. However, in chloroform solution both products have identical spectra with one strong band at 1863 cm^{-1} and have similar molecular weights. Both products also give identical ^1H nmr spectra in dichloromethane and benzene solutions showing strong singlet resonances at 1.92 and 1.72 ppm, respectively. We consider the two products to be different crystalline forms of the complex $RuCl_3(NO)[As(CH_3)_2C_6H_5]_2$, configuration I, and interactions in the solid state are assumed responsible for the differences observed in the mull spectra of these compounds. In several reactions of this type the infrared spectrum of the initial products suggested that some $RuCl_3(NO)[As(CH_3)_2C_6H_5]_2$, configuration III, was also present in small amounts. This may be readily converted to product Ia above by prolonged refluxing in benzene, addition of ethanol, and evaporation of the resultant solution. In the above reactions the filtrate, after removal of the various products, still had a deep orange-yellow color. Addition of an ethanol solution of sodium tetraphenylborate to this filtrate caused immediate precipitation of the ionic product $\{RuCl_2(NO)[As(CH_3)_2C_6H_5]_3\}B(C_6H_5)_4$ whose ^1H nmr spectrum in nitrobenzene shows three singlet resonances of equal intensity at 2.10, 1.94, and 1.64 ppm consistent with configuration VII above with $L = As(CH_3)_2C_6H_5$.

Reaction between $RuCl_3(NO)$ and $P(CH_3)(C_6H_5)_2$ or $As(CH_3)(C_6H_5)_2$.—In reactions of this type in ethanol or 2-ethoxyethanol only one isomer was obtained, namely, that with configuration I. The product precipitates

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(6) B. L. Shaw and A. C. Smithies, *J. Chem. Soc. A*, 2784 (1968).

(7) J. M. Jenkins, M. S. Lupin, and B. L. Shaw, *ibid.*, *A*, 1787 (1966).

out from the hot solution and unlike the corresponding $P(CH_3)_2C_6H_5$ and $As(CH_3)_2C_6H_5$ reactions, ionic species of the type $RuCl_2(NO)L_3^+$ were not present in the filtrate after removal of the above product.

Triobromo and Triiodo Complexes.—Complexes of the type $RuX_3(NO)L_2$ ($X = Br$ or I; $L = P(CH_3)_2C_6H_5$, $P(CH_3)(C_6H_5)_2$, $As(CH_3)_2C_6H_5$, or $As(CH_3)(C_6H_5)_2$) may be readily obtained by metathetical replacement of chloride from the corresponding trichloro species or by replacement of chloride and 1 mol of L from the ionic derivatives $[RuCl_2(NO)L_3]B(C_6H_5)_4$ ($L = P(CH_3)_2C_6H_5$ or $As(CH_3)_2C_6H_5$). Such reactions are performed under reflux conditions in ethanol or 2-ethoxyethanol in the presence of a large molar excess of lithium bromide or iodide. The reaction time required for formation of the desired product is *ca.* 6–12 hr, but, with shorter reaction times in several preparations of this type, inseparable mixtures of complexes, presumably of the type $RuCl_xY_{3-x}(NO)L_2$ ($x = 1$ or 2; $Y =$ Br or I), were obtained. This was indicated by the presence of extra resonances at δ values intermediate to those of the trichloro complex and the derived tribromo or triiodo analogs in the ^1H nmr spectrum of dichloromethane solutions of the crude reaction products. In general, longer reaction times were required in the cases where $L = P(CH_3)(C_6H_5)_2$ or $As(CH_3)(C_6H_5)_2$ in order to achieve complete conversion to the required tribromo or triiodo derivatives.

Infrared and Nmr Data.—Unlike the corresponding iridium carbonyl systems,[5] the values of the ruthenium–chloride stretching frequencies in the far-infrared spectra of these complexes do not fall into completely separate groups depending on the ligand in the trans position. However, complexes with configuration I have two bands in the regions 337–322 and 290–284 cm^{-1} which are considered due to vibration of chlorine trans to chlorine and the nitrosyl group, respectively. Complexes with configuration III have four bands in their far-infrared spectra (Table I) in the ruthenium–chloride stretching region. As for the analogous $IrCl_3(CO)[P(CH_3)_2C_6H_5]_2$, configuration IV, the presence of the extra band is considered due to solid-state splitting, but in the absence of any tribromo or triiodo species of this configuration, unambiguous assignment of these bands is not possible. For the ionic derivatives $[RuCl_2(NO)L_3]Y$ ($L = P(CH_3)_2C_6H_5$, $Y =$ Cl or $B(C_6H_5)_4$; $L = As(CH_3)_2C_6H_5$, $Y = B(C_6H_5)_4$) the absorptions in the regions 331–328 and 295–280 cm^{-1} are tentatively assigned to ruthenium–chloride stretching, being by far the most intense absorptions in this region. Several ruthenium–bromine stretching frequencies have also been identified in the spectra of the complexes $RuBr_3(NO)L_2$ ($L = P(CH_3)_2C_6H_5$, $PCH_3(C_6H_5)_2$, $As(CH_3)_2C_6H_5$, or $AsCH_3(C_6H_5)_2$); see Table I.

For the proton nmr data on the complexes listed in Table II the δ values for a particular series of complexes containing the same ligand increase in the order $Cl < Br < I$ which has been interpreted previously[5,6] in terms of increased π bonding in the metal–halogen bond in the order $Cl < Br < I$.

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Substituted Chromium and Molybdenum Carbonyl Complexes of Some Cyanophosphine Ligands[1]

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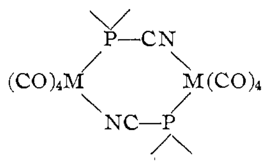
The reactions of the ligands $(C_6H_5)_2PCN$, $C_6H_5P(CN)_2$, $(CH_3)_2PCN$, $(C_2H_5O)_2PCN$, or $[(CH_3)_2N]_2PCN$ with $M(CO)_4C_7H_8$ ($M =$ Cr or Mo and C_7H_8 is norbornadiene) have been investigated. From these reactions, yellow crystalline complexes of the form $[M(CO)_4L]_2$, where L is a bridging cyanophosphine ligand, have been isolated. Their formulation is based on analytical data and their structure is proposed as



on the basis of the infrared and proton nmr spectral data. These bridged complexes react further with another molar equivalent of ligand L or a different ligand L′ to yield complexes of the type $M(CO)_4L_2$ and $M(CO)_4LL'$. The products from these reactions further support the proposed structure for the bridged species. The proton nmr, infrared, and some of the mass spectral data of these bridged complexes are presented and discussed.

Introduction

Cyanophosphine compounds $R_xP(CN)_{3-x}$ ($x = 0$, 1, or 2) have received very little attention as ligands in the area of metal coordination chemistry. In 1963 a disubstituted nickel carbonyl complex of $[(CH_3)_2N]_2PCN$[2] was reported in which coordination presumably occurred through the phosphorus atom. More recently, Kirk and Smith have reported that $P(CN)_3$

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(2) H. Noth and H. J. Vetter, *Chem. Ber.*, **96**, 1479 (1963).