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## Complexes of the Platinum Metals. 15.<sup>1</sup> Some Reactions of $[\text{Ru}(\text{NO}_3)_2(\text{CO})(\text{PPh}_3)_2]$ and $[\text{RuH}(\text{NO}_3)(\text{CO})(\text{PPh}_3)_2]$

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Received November 9, 1977

The reactions of  $[\text{Ru}(\text{NO}_3)_2(\text{CO})(\text{PPh}_3)_2]$  with primary alcohols, carbon monoxide, methyldiphenylphosphine, trifluoroacetic acid, sodium acetate, sulfur dioxide in methanol, acetylacetone, sodium *N,N*-dimethyldithiocarbamate, thioacetic acid, and phenylacetylene are shown to yield  $[\text{RuH}(\text{NO}_3)(\text{CO})(\text{PPh}_3)_2]$ ,  $[\text{Ru}(\text{NO}_3)_2(\text{CO})_2(\text{PPh}_3)_2]$ ,  $[\text{Ru}(\text{NO}_3)_2(\text{CO})(\text{PMePh}_2)_3]$ ,  $[\text{Ru}(\text{NO}_3)(\text{O}_2\text{CCF}_3)(\text{CO})(\text{PPh}_3)_2]$ ,  $[\text{Ru}(\text{O}_2\text{CMe})_2(\text{CO})(\text{PPh}_3)_2]$  or  $[\text{Ru}(\text{O}_2\text{CMe})\text{H}(\text{CO})(\text{PPh}_3)_2]$ ,  $[\text{Ru}(\text{S}(\text{O})_2\text{OMe})(\text{NO}_3)(\text{CO})(\text{PPh}_3)_2]$ ,  $[\text{Ru}(\text{acac})(\text{NO}_3)(\text{CO})(\text{PPh}_3)_2]$  or  $[\text{Ru}(\text{acac})\text{H}(\text{CO})(\text{PPh}_3)_2]$ ,  $[\text{Ru}(\text{S}_2\text{CNMe}_2)_2(\text{CO})(\text{PPh}_3)_n]$  ( $n = 1$  or  $2$ ),  $[\text{Ru}(\text{S}(\text{O})\text{CMe})_2(\text{CO})(\text{PPh}_3)_2]$  (two isomers), and  $[\text{Ru}(\text{C}\equiv\text{CPh})(\text{NO}_3)(\text{CO})(\text{PPh}_3)_2]$ , respectively. Likewise the alcoholysis product  $[\text{RuH}(\text{NO}_3)(\text{CO})(\text{PPh}_3)_2]$  reacts with carbon monoxide, acetylacetone, carbon disulfide, sodium *N,N*-dimethyldithiocarbamate, phenylacetylene, and diphenylacetylene to yield the products  $[\text{RuH}(\text{NO}_3)(\text{CO})_2(\text{PPh}_3)_2]$  or  $[\text{Ru}(\text{CO})_3(\text{PPh}_3)_2]$ ,  $[\text{Ru}(\text{acac})\text{H}(\text{CO})(\text{PPh}_3)_2]$ ,  $[\text{Ru}(\text{S}_2\text{CH})(\text{NO}_3)(\text{CO})(\text{PPh}_3)_2]$ ,  $[\text{Ru}(\text{S}_2\text{CNMe}_2)\text{H}(\text{CO})(\text{PPh}_3)_2]$ ,  $[\text{Ru}(\text{NO}_3)(\text{C}\equiv\text{CPh})(\text{CO})(\text{PPh}_3)_2]$ , and  $[\text{Ru}(\text{C}(\text{Ph})=\text{CHPh})(\text{NO}_3)(\text{CO})(\text{PPh}_3)_2]$ , respectively. The alcoholysis of  $[\text{Ru}(\text{NO}_3)(\text{O}_2\text{CCF}_3)(\text{CO})(\text{PPh}_3)_2]$  yields  $[\text{RuH}(\text{NO}_3)(\text{CO})(\text{PPh}_3)_2]$ . The ability of the complexes  $[\text{Ru}(\text{NO}_3)_2(\text{CO})(\text{PPh}_3)_2]$  and  $[\text{Ru}(\text{NO}_3)(\text{O}_2\text{CCF}_3)(\text{CO})(\text{PPh}_3)_2]$  to catalyze the dehydrogenation of primary alcohols has been demonstrated and their efficiency compared with that of  $[\text{Ru}(\text{O}_2\text{CCF}_3)_2(\text{CO})(\text{PPh}_3)_2]$ . Several lines of evidence indicate that the chelating power of nitrate anions is significantly greater than that of trifluoroacetate anions in the systems under investigation.

### Introduction

Low oxidation state platinum metal complexes are stabilized by phosphines, carbon monoxide, and related class "b" ligands, whereas catalytic activity in homogeneous solution is favored by the presence of vacant coordination sites and/or labile class "a" ligands. Therefore, a judicious combination of class "a" and class "b" ligands bound to the same metal ion should favor stability and catalytic activity in the resultant complex. To explore this idea we have synthesized a range of perfluorocarboxylato and nitrate complexes of the platinum metals containing phosphine and carbonyl or nitrosyl ligands and have examined their chemical reactivity. Our studies have revealed that monodentate perfluorocarboxylato or nitrate ligands trans to triphenylphosphine are especially reactive toward a variety of substrates. In particular, the complex  $[\text{Ru}(\text{O}_2\text{CCF}_3)_2(\text{CO})(\text{PPh}_3)_2]$  and its nitrate analogue  $[\text{Ru}(\text{NO}_3)_2(\text{CO})(\text{PPh}_3)_2]$  each display a range of reactions involving facile cleavage of a Ru–O bond trans to triphenylphosphine. In this paper we discuss the chemistry of  $[\text{Ru}(\text{NO}_3)_2(\text{CO})(\text{PPh}_3)_2]$  and its alcoholysis product  $[\text{RuH}(\text{NO}_3)(\text{CO})(\text{PPh}_3)_2]$ . The reactions of the corresponding trifluoroacetato derivatives were described in an earlier paper.<sup>2</sup>

### Experimental Section

General experimental techniques, conditions, and instrumentation employed were similar to those described in the preceding paper.<sup>1</sup> Analyses and melting point data are given in Table I. Spectroscopic data are collated in Table II. Synthesis of **carbonylbis(nitrato)bis(triphenylphosphine)ruthenium(II)** and **carbonylhydrido(nitrato)bis(triphenylphosphine)ruthenium(II)** were performed as described in the preceding paper.<sup>1</sup>

**Catalytic Dehydrogenation of Primary (and Secondary) Alcohols by Carbonylbis(nitrato)bis(triphenylphosphine)ruthenium(II) and Related Species.** The apparatus and technique employed have been described in a previous paper.<sup>3</sup> Each catalysis run was conducted using  $5.545 \times 10^{-5}$  mol of catalyst dissolved in 1-hexanol (12.6 g, 0.134 mol) or an equimolar quantity of another alcohol. For 1-hexanol, amounts of gas evolved after 30 min were  $4.15 \times 10^{-3}$ ,  $0.95 \times 10^{-3}$ , and  $0.5 \times 10^{-3}$  mol for  $[\text{Ru}(\text{O}_2\text{CCF}_3)_2(\text{CO})(\text{PPh}_3)_2]$ ,  $[\text{Ru}(\text{O}_2\text{CCF}_3)(\text{NO}_3)(\text{CO})(\text{PPh}_3)_2]$ , and  $[\text{Ru}(\text{NO}_3)_2(\text{CO})(\text{PPh}_3)_2]$ , respectively.

**Reactions of carbonylbis(nitrato)bis(triphenylphosphine)ruthenium(II) and carbonylhydrido(nitrato)bis(triphenylphosphine)ruthenium(II) with carbon monoxide** have been described in the preceding paper.<sup>1</sup>

**Reaction of Carbonylbis(nitrato)bis(triphenylphosphine)ruthenium(II) with Methyldiphenylphosphine.** Methyldiphenylphosphine (0.5 mL) was added to a suspension of carbonylbis(nitrato)bis(triphenylphosphine)ruthenium (0.2 g) in ethanol (20 mL), and the

mixture was boiled under reflux for 20 min to form a clear yellow solution. The volatile material was removed under reduced pressure, and then the residual oil was covered with diethyl ether (20 mL) and left to stand for 48 h. The resultant yellow powder was filtered off, washed with diethyl ether, recrystallized from methanol–diethyl ether, and dried in vacuo to yield **carbonylbis(nitrato)tris(methyldiphenylphosphine)ruthenium** as yellow microcrystals (0.17 g, 77%).

**Reaction of Carbonylbis(nitrato)bis(triphenylphosphine)ruthenium with Trifluoroacetic Acid in Benzene.** Carbonylbis(nitrato)bis(triphenylphosphine)ruthenium (0.1 g) and trifluoroacetic acid (0.5 mL) were stirred together in benzene (20 mL) at ambient temperature for 3 h to yield a yellow solution which was subsequently evaporated to dryness under reduced pressure. The yellow residue was recrystallized from methanol, washed successively with methanol and petroleum ether, and then dried in vacuo to yield **carbonylnitrato(trifluoroacetato)bis(triphenylphosphine)ruthenium(II)** as pale yellow crystals (0.10 g, 94%).

**Reaction of Carbonylbis(nitrato)bis(triphenylphosphine)ruthenium with Trifluoroacetic Acid in Boiling Toluene.** A solution of carbonylbis(nitrato)bis(triphenylphosphine)ruthenium (0.1 g) and trifluoroacetic acid (2.0 mL) in toluene (20 mL) was boiled under reflux for 1 h and then evaporated to dryness under reduced pressure. The dark yellow residue was dissolved in 2/1 (v/v) methanol–dichloromethane (15 mL) and set aside. After 2 days, the resultant mixture of yellow and orange needles was filtered off and washed with petroleum ether to yield a ca. 50/50 mixture of the known complexes **nitrosyltris(trifluoroacetato)bis(triphenylphosphine)ruthenium** and **dicarbonylbis(trifluoroacetato)bis(triphenylphosphine)ruthenium** (combined yield 0.06 g).

**Reaction of Carbonylnitrato(trifluoroacetato)bis(triphenylphosphine)ruthenium with 1-Propanol.** A solution of carbonylnitrato(trifluoroacetato)bis(triphenylphosphine)ruthenium (0.05 g) in 1-propanol (8 mL) was boiled under reflux for 15 min. The white crystalline precipitate, which formed on cooling the mixture, was filtered off, washed with methanol and petroleum ether, and then dried in vacuo (yield 0.03 g). The product was identified as **carbonylhydridonitrato)bis(triphenylphosphine)ruthenium** by infrared spectroscopy and comparison with an authentic sample.<sup>1</sup>

**Reaction of Carbonylbis(nitrato)bis(triphenylphosphine)ruthenium(II) with Sodium acetate.** (a) In cold methanol a mixture of carbonylbis(nitrato)bis(triphenylphosphine)ruthenium (0.2 g) and sodium acetate (0.1 g) in methanol (30 mL) was stirred at ambient temperature for 15 h. The resultant pale yellow suspension was filtered off, washed successively with water, methanol, and petroleum ether, recrystallized from dichloromethane–petroleum ether and then dried in vacuo to yield **bis(acetato)carbonylbis(triphenylphosphine)ruthenium(II)** as pale yellow crystals (0.10 g, 50%).

(b) In methanol under reflux a mixture of carbonylbis(nitrato)bis(triphenylphosphine)ruthenium (0.2 g) and sodium acetate (0.1 g) in methanol (20 mL) was boiled under reflux for 2 h. After cooling of the mixture to ambient temperature, the resultant suspension was

Table I. Melting Point<sup>a</sup> and Analytical Data<sup>b</sup>

Product	Mp/°C	% C	% H	% N
[Ru(NO <sub>3</sub> ) <sub>2</sub> (CO)(PMePh <sub>2</sub> ) <sub>3</sub> ]	110–112 d	56.14 (56.22)	4.57 (4.60)	3.17 (3.28)
[Ru(NO <sub>3</sub> )(O <sub>2</sub> CCF <sub>3</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]	194–195 d	56.18 (56.52)	3.68 (3.65)	1.66 (1.69)
[Ru(O <sub>2</sub> CMe) <sub>2</sub> (CO)(PPh <sub>3</sub> ) <sub>2</sub> ]	210–212	63.52 (63.80)	5.14 (4.70)	
[RuH(O <sub>2</sub> CMe)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]	235–237	65.31 (65.62)	4.80 (4.80)	
[Ru(NO <sub>3</sub> ) <sub>2</sub> {S(O) <sub>2</sub> OMe}(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]	180–183 d	56.39 (56.28)	4.22 (4.10)	1.78 (1.72)
[Ru(NO <sub>3</sub> )(acac)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]	184–186 d	61.95 (61.90)	4.60 (4.58)	1.59 (1.71)
[RuH(acac)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]	200–201	66.31 (66.90)	5.09 (5.10)	
[Ru(NO <sub>3</sub> )(S <sub>2</sub> CH)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>1/4</sup> CH <sub>2</sub> Cl <sub>2</sub>	167–169 d	56.38 (56.42)	4.12 (3.90)	2.00 (1.72)
[Ru(S <sub>2</sub> CNMe <sub>2</sub> ) <sub>2</sub> (CO)(PPh <sub>3</sub> ) <sub>2</sub> ]	202–203	57.82 (57.75)	4.51 (4.73)	3.23 (3.13)
[Ru(S <sub>2</sub> CNMe <sub>2</sub> ) <sub>2</sub> (CO)(PPh <sub>3</sub> ) <sub>2</sub> ]	248–250			
[RuH(S <sub>2</sub> CNMe <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]	216–217	62.18 (61.93)	4.99 (4.81)	1.92 (1.81)
[Ru{S(O)CMe} <sub>2</sub> (CO)(PPh <sub>3</sub> ) <sub>2</sub> ], isomer A	269–271	61.39 (61.25)	4.59 (4.51)	
[Ru{S(O)CMe} <sub>2</sub> (CO)(PPh <sub>3</sub> ) <sub>2</sub> ], isomer B	253–254	60.48 (61.25)	4.49 (4.51)	
[Ru(NO <sub>3</sub> )(C≡CPh)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]	206–209 d	65.33 (66.09)	4.15 (4.28)	
[Ru(NO <sub>3</sub> ){C(Ph)=CHPh}(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]	189–191 d	68.17 (68.44)	4.61 (4.62)	1.57 (1.56)

<sup>a</sup> d = decomposed. <sup>b</sup> Calculated figures in parentheses.

Table II. Spectroscopic Data

Product	$\nu(\text{MH})^a$ cm <sup>-1</sup>	$\nu(\text{CO})^a$ cm <sup>-1</sup>	$\tau_{\text{MH}}^b$	$\tau_{\text{Me}}^b$	$\delta_{\text{P}}^b$ , ppm	$J_{\text{PH}}^c$ , Hz	$^2J_{\text{PP}}^c$ , Hz
[Ru(NO <sub>3</sub> ) <sub>2</sub> (CO)(PMePh <sub>2</sub> ) <sub>3</sub> ]		1980 s		8.10 d } 8.25 t }	12.63 d } 25.33 t }	9.6 <sup>d</sup>	22.0
[Ru(NO <sub>3</sub> )(O <sub>2</sub> CCF <sub>3</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]		1982 s			51.98		
[Ru(O <sub>2</sub> CMe) <sub>2</sub> (CO)(PPh <sub>3</sub> ) <sub>2</sub> ]		1960 s		8.62	42.06		
[RuH(O <sub>2</sub> CMe)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]	2032 m	1931 s	26.5 t	9.37		19.5	
[Ru(NO <sub>3</sub> ) <sub>2</sub> {S(O) <sub>2</sub> OMe}(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]		1994 s		7.18	34.78		
[Ru(NO <sub>3</sub> )(acac)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]		1959 s		8.66 } 8.71 }	27.61		
[RuH(acac)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]	1938 m	1912 s	23.3 t	8.70 } 8.94 }		20.5	
[Ru(NO <sub>3</sub> )(S <sub>2</sub> CH)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>1/4</sup> CH <sub>2</sub> Cl <sub>2</sub>		1965 s				3.9 <sup>e</sup>	
[Ru(S <sub>2</sub> CNMe <sub>2</sub> ) <sub>2</sub> (CO)(PPh <sub>3</sub> ) <sub>2</sub> ]		1970 s		6.66 t } 7.38 d }			
[Ru(S <sub>2</sub> CNMe <sub>2</sub> ) <sub>2</sub> (CO)(PPh <sub>3</sub> ) <sub>2</sub> ]		1928 s		6.77 d } 7.18 d }			
[RuH(S <sub>2</sub> CNMe <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]	1950 m	1920 s	21.1 t	7.54		19.5	
[Ru{S(O)CMe} <sub>2</sub> (CO)(PPh <sub>3</sub> ) <sub>2</sub> ], isomer A		1942 s		8.89	43.02		
[Ru{S(O)CMe} <sub>2</sub> (CO)(PPh <sub>3</sub> ) <sub>2</sub> ], isomer B		1970 s		7.78 } 8.60 }	43.56 } 36.25 }	AB	15.0
[Ru(NO <sub>3</sub> )(C≡CPh)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]		1968 s			35.52		
[Ru(NO <sub>3</sub> ){C(Ph)=CHPh}(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]		1940 s			31.63		

<sup>a</sup> Nujol mulls. Key: m, medium; s, strong. <sup>b</sup> Singlets unless otherwise indicated. Key: d, doublet; t, triplet; AB, AB pattern. <sup>c</sup> Phosphine-hydride coupling unless otherwise indicated. <sup>d</sup> Phosphine-methyl coupling. <sup>e</sup> Phosphine-S<sub>2</sub>CH coupling.

filtered off, washed with water, methanol, and petroleum ether, and then dried in vacuo to yield **acetatocarbonylhydridobis(triphenylphosphine)ruthenium(II)** as white crystals (0.15 g, 82%).

**Reaction of Carbonylbis(nitrato)bis(triphenylphosphine)ruthenium(II) with Sulfur Dioxide in Methanol.** A slow stream of sulfur dioxide was bubbled through a solution of carbonylbis(nitrato)bis(triphenylphosphine)ruthenium (0.2 g) in 2/1 (v/v) methanol-benzene (30 mL) under reflux for 20 min. The precipitate, which deposited on cooling, was filtered off, washed successively with methanol and petroleum ether, and then dried in vacuo to yield **carbonyl(methylsulfito)(nitrato)bis(triphenylphosphine)ruthenium(II)** as pale yellow crystals (0.14 g, 67%).

**Reaction of Carbonylbis(nitrato)bis(triphenylphosphine)ruthenium(II) with Acetylacetone in the Presence of Triethylamine.** A solution of carbonyldinitratobis(triphenylphosphine)ruthenium (0.3 g), acetylacetone (0.5 mL), and triethylamine (1 mL) in benzene (20 mL) was heated under reflux for 1 h and then evaporated to dryness under reduced pressure. Methanol (10 mL) was added to the residual orange oil and the mixture was shaken for 30 min and then set aside to crystallize. The crystallized product was filtered off, washed with cold methanol and petroleum ether, and finally dried in vacuo to yield **(acetylacetonato)carbonylnitratobis(triphenylphosphine)ruthenium(II)** as yellow crystals (0.20 g, 64%).

**Reaction of Carbonylhydridonitratobis(triphenylphosphine)ruthenium(II) with Acetylacetone in the Presence of Potassium Hydroxide.** A mixture of carbonylhydridonitratobis(triphenylphosphine)ruthenium (0.1 g), potassium hydroxide (0.1 g), and acetylacetone (0.5 mL) in ethanol (20 mL) was boiled under reflux for 2.75 h and then left to crystallize. After 24 h, the precipitated product

was filtered off, washed successively with water, methanol, and petroleum ether, recrystallized from dichloromethane-methanol, and finally dried in vacuo to yield **(acetylacetonato)carbonylhydridobis(triphenylphosphine)ruthenium(II)** as white crystals (0.05 g, 48%).

**Reaction of Carbonylhydridonitratobis(triphenylphosphine)ruthenium(II) with Carbon Disulfide.** A solution of carbonylhydridonitratobis(triphenylphosphine)ruthenium (0.12 g) and carbon disulfide (0.5 mL) in benzene (20 mL) was shaken at ambient temperature for 8 h and then evaporated to dryness under reduced pressure. The residual yellow oil was dissolved in 1/1 (v/v) dichloromethane-*n*-hexane (30 mL) and set aside to crystallize. After 24 h, the precipitate was filtered off, washed with petroleum ether, and dried in vacuo to yield **carbonyl(dithioformato)nitratobis(triphenylphosphine)ruthenium(II)-dichloromethane (4/1)** as orange crystals (0.11 g, 81%).

**Reaction of Carbonylbis(nitrato)bis(triphenylphosphine)ruthenium(II) with Sodium *N,N*-Dimethyldithiocarbamate in Cold Methanol.** A suspension of carbonylbis(nitrato)bis(triphenylphosphine)ruthenium (0.1 g) in methanol (20 mL) containing sodium *N,N*-dimethyldithiocarbamate (0.1 g) was stirred at ambient temperature for 3 h. The residual solid was filtered off, washed with methanol and petroleum ether, and then dried in vacuo to yield **carbonylbis(*N,N*-dimethyldithiocarbamato)bis(triphenylphosphine)ruthenium** as dark yellow crystals (0.21 g, 91%). The product readily loses a molecule of phosphine on dissolution.

**Reaction of Carbonylbis(nitrato)bis(triphenylphosphine)ruthenium(II) with Sodium *N,N*-Dimethyldithiocarbamate in Boiling Methanol.** A suspension of carbonylbis(nitrato)bis(triphenylphosphine)ruthenium (0.1 g) in methanol (20 mL) containing sodium *N,N*-dimethyldi-

thiocarbamate (0.1 g) was boiled under reflux for 10 min. After the mixture was cooled, the yellow suspension was filtered off, washed successively with water, methanol, and petroleum ether, and then dried in vacuo to yield **carbonylbis(*N,N*-dimethyldithiocarbamato)(triphenylphosphine)ruthenium(II)** as dark yellow crystals (0.06 g, 74%).

**Reaction of Carbonylhydridonitratobis(triphenylphosphine)ruthenium(II) with Sodium *N,N*-Dimethyldithiocarbamate.** A suspension of carbonylhydridonitratobis(triphenylphosphine)ruthenium (0.2 g) in methanol (20 mL) containing sodium *N,N*-dimethyldithiocarbamate (0.2 g) was stirred at ambient temperature for 12 h. The resultant pale yellow suspension was filtered off, washed with methanol and petroleum ether, recrystallized from dichloromethane-methanol, and finally dried in vacuo to yield **carbonyl(*N,N*-dimethyldithiocarbamato)hydridobis(triphenylphosphine)ruthenium(II)** as pale yellow crystals (0.20 g, 92%).

**Reactions of Carbonylbis(nitrate)bis(triphenylphosphine)ruthenium(II) with Monothioacetic Acid. (a) In Refluxing Methanol.** A mixture of carbonylbis(nitrate)bis(triphenylphosphine)ruthenium (0.1 g) and monothioacetic acid (0.5 mL) in methanol (20 mL) was boiled under reflux for 2 h. After being cooled, the mixture was filtered, and the precipitated product was washed with methanol and petroleum ether and then dried in vacuo. Recrystallization from dichloromethane-methanol gave **carbonylbis(thioacetato)bis(triphenylphosphine)ruthenium(II)** (isomer A) as bright yellow crystals (0.09 g, 87%).

**(b) In Cold Methanol.** A mixture of carbonylbis(nitrate)bis(triphenylphosphine)ruthenium (0.1 g) and monothioacetic acid (0.5 mL) in methanol (20 mL) was stirred for 7 h at ambient temperature. The resultant suspension was filtered off, washed with methanol and petroleum ether, and then dried in vacuo to yield **carbonylbis(thioacetato)bis(triphenylphosphine)ruthenium(II)** (isomer B) as a pale yellow powder (0.10 g, 97%).

**Reaction of Carbonylbis(nitrate)bis(triphenylphosphine)ruthenium(II) with Phenylacetylene.** A mixture of carbonylbis(nitrate)bis(triphenylphosphine)ruthenium (0.1 g) and phenylacetylene (0.5 mL) in ethanol (10 mL) was boiled under reflux for 15 min. After the mixture was cooled, the precipitate was filtered off, washed with ethanol and diethyl ether, and then dried in vacuo to yield **carbonylnitrate(phenylacetylido)bis(triphenylphosphine)ruthenium(II)** as yellow crystals (0.07 g, 67%).

**Reaction of Carbonylhydridonitratobis(triphenylphosphine)ruthenium(II) with Phenylacetylene.** A mixture of carbonylhydridonitratobis(triphenylphosphine)ruthenium (0.1 g) and phenylacetylene (0.5 mL) in ethanol (10 mL) was boiled under reflux for 15 min. After the mixture was cooled, the precipitate was filtered off, washed with ethanol and diethyl ether, and then dried in vacuo to yield **carbonylnitrate(phenylacetylido)bis(triphenylphosphine)ruthenium(II)** as yellow crystals (0.05 g, 44%).

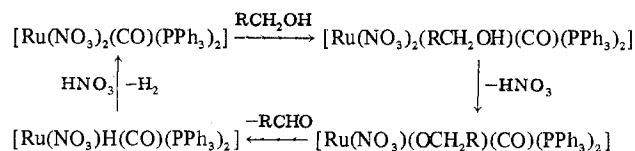
**Reactions of Carbonylbis(nitrate)bis(triphenylphosphine)ruthenium(II) with Diphenylacetylene in 1-Propanol.** A mixture of carbonylbis(nitrate)bis(triphenylphosphine)ruthenium (0.2 g) and diphenylacetylene (0.2 g) in 1-propanol (20 mL) was boiled under reflux for 2 h. After the mixture was cooled, the precipitate was filtered off, washed with methanol and petroleum ether, and then dried in vacuo to yield **carbonyl(1,2-diphenylvinyl)nitratobis(triphenylphosphine)ruthenium(II)** as bright yellow crystals (0.16 g, 73%).

**Reaction of Carbonylhydridonitratobis(triphenylphosphine)ruthenium(II) with Diphenylacetylene.** A mixture of carbonylhydridonitratobis(triphenylphosphine)ruthenium (0.2 g) and diphenylacetylene (0.2 g) in ethanol (20 mL) was boiled under reflux for 2 h. After the mixture was cooled, the precipitate was filtered off, washed successively with methanol and petroleum ether, and finally dried in vacuo to yield **carbonyl(1,2-diphenylvinyl)nitratobis(triphenylphosphine)ruthenium(II)** as bright yellow crystals (0.20 g, 84%).

## Results and Discussion

**Interconversion of  $[\text{Ru}(\text{NO}_3)_2(\text{CO})(\text{PPh}_3)_2]$  and  $[\text{RuH}(\text{NO}_3)(\text{CO})(\text{PPh}_3)_2]$ . Dehydrogenation of Alcohols.** The conversion of  $[\text{Ru}(\text{NO}_3)_2(\text{CO})(\text{PPh}_3)_2]$  to  $[\text{RuH}(\text{NO}_3)(\text{CO})(\text{PPh}_3)_2]$  by treatment with primary or secondary alcohols has been noted in the preceding paper.<sup>1</sup> The reaction, which is accompanied by aldehyde formation and is accelerated by the presence of base, is thought to proceed by a  $\beta$ -elimination mechanism similar to that previously advanced for the alcoholysis of the corresponding perfluorocarboxylates  $[\text{Ru}(\text{O}_2\text{CR}_f)_2(\text{CO})(\text{PPh}_3)_2]$ .<sup>3</sup> The latter reaction involves initial

## Scheme I



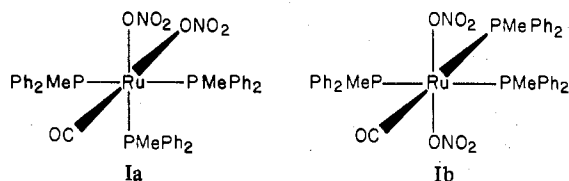
solvation by alcohol; the formation of alcohol solvates has been established by analytical and spectroscopic data<sup>3</sup> and has been confirmed by an X-ray diffraction study performed on the methanol solvate  $[\text{Ru}(\text{O}_2\text{CCF}_3)_2(\text{MeOH})(\text{CO})(\text{PPh}_3)_2]$ .<sup>4</sup> In contrast, the bis(nitrate) complex  $[\text{Ru}(\text{NO}_3)_2(\text{CO})(\text{PPh}_3)_2]$  does not form an isolable methanol solvate, presumably because the nitrate anion has greater chelating power than the perfluorocarboxylate anions and can compete more effectively with alcohols for the sixth coordination site on the ruthenium.<sup>5</sup> However, this observation does not preclude the involvement of alcohol solvates in low concentrations as intermediates in the solvolysis sequence. The reverse reaction, conversion of  $[\text{RuH}(\text{NO}_3)(\text{CO})(\text{PPh}_3)_2]$  to  $[\text{Ru}(\text{NO}_3)_2(\text{CO})(\text{PPh}_3)_2]$ , can be achieved by treatment of the former complex with dilute nitric acid. This reaction, combined with the alcoholysis step, completes a cycle for the catalytic dehydrogenation of primary and secondary alcohols to aldehydes and ketones, respectively. This cycle, which is outlined in Scheme I, is directly analogous to that previously observed for the corresponding perfluorocarboxylate complexes.<sup>3</sup> Since the nitrate complexes  $[\text{Ru}(\text{NO}_3)_2(\text{CO})(\text{PPh}_3)_2]$  and  $[\text{RuH}(\text{NO}_3)(\text{CO})(\text{PPh}_3)_2]$  have the same stereochemistry as their perfluorocarboxylate analogues, the detailed catalytic scheme previously given for the perfluorocarboxylate complexes<sup>3</sup> is also applicable to the corresponding nitrate system. In view of the apparent parallel between the activity of  $[\text{Ru}(\text{O}_2\text{CCF}_3)_2(\text{CO})(\text{PPh}_3)_2]$  and  $[\text{Ru}(\text{NO}_3)_2(\text{CO})(\text{PPh}_3)_2]$  as alcohol dehydrogenation catalysts, the catalytic efficiencies of these species and the mixed complex  $[\text{Ru}(\text{NO}_3)(\text{O}_2\text{CCF}_3)(\text{CO})(\text{PPh}_3)_2]$  were compared. Hydrogen evolution data for the three catalysts, obtained under standardized conditions (see Experimental Section and ref 3), show that catalyst efficiency declines by a factor of ca. 10 in the sequence  $[\text{Ru}(\text{O}_2\text{CCF}_3)_2(\text{CO})(\text{PPh}_3)_2] \gg [\text{Ru}(\text{NO}_3)(\text{O}_2\text{CCF}_3)(\text{CO})(\text{PPh}_3)_2] > [\text{Ru}(\text{NO}_3)_2(\text{CO})(\text{PPh}_3)_2]$ . This result is in accord with our observations that nitrate competes with methanol more favorably than does perfluorocarboxylate in the alcohol solvation process (see above) and that alcoholysis of the "mixed" complex  $[\text{Ru}(\text{NO}_3)(\text{O}_2\text{CCF}_3)(\text{CO})(\text{PPh}_3)_2]$  leads to exclusive formation of  $[\text{RuH}(\text{NO}_3)(\text{CO})(\text{PPh}_3)_2]$  rather than  $[\text{RuH}(\text{O}_2\text{CCF}_3)(\text{CO})(\text{PPh}_3)_2]$ . The much greater efficiency of  $[\text{Ru}(\text{O}_2\text{CCF}_3)_2(\text{CO})(\text{PPh}_3)_2]$  relative to  $[\text{Ru}(\text{NO}_3)(\text{O}_2\text{CCF}_3)(\text{CO})(\text{PPh}_3)_2]$  probably reflects the fact that in the latter complex the alcohol has to compete with the nitrate anion—a stronger chelating agent than the perfluorocarboxylate anion—in order to enter the coordination sphere and initiate the dehydrogenation process. 1-Hexanol was selected for the comparative study because it gives a convenient rate of dihydrogen evolution under our standard conditions. However, essentially similar data have been collected for other alcohols including 1-heptanol, 1-octanol, benzyl alcohol, and cyclohexanol. For optimum dihydrogen evolution the catalysis should be promoted by addition of the corresponding free acid (ca. 12 mol/mol of catalyst).<sup>3</sup> However, in order to avoid possible side reactions arising from the oxidizing power of nitric acid, free acid was omitted from these reactions.

**Reactions with Carbon Monoxide.** The complex  $[\text{Ru}(\text{NO}_3)_2(\text{CO})(\text{PPh}_3)_2]$  is readily carbonylated by carbon monoxide in boiling benzene or ethanol to afford  $[\text{Ru}(\text{NO}_3)_2(\text{CO})_2(\text{PPh}_3)_2]$  in good yield. This product is identical with the complex obtained from the reaction of  $[\text{Ru}(\text{CO})_3-$

(PPh<sub>3</sub>)<sub>2</sub>] with nitric acid in boiling ethanol.<sup>1</sup> The absence of hydridic species from the products obtained on carbonylating [Ru(NO<sub>3</sub>)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>] in boiling ethanol indicates that carbonylation takes precedent over the alcoholysis reaction. The carbonylation product itself is not susceptible to alcoholysis. However, the alcoholysis product [RuH(NO<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>] is readily carbonylated under mild conditions to yield [RuH(NO<sub>3</sub>)(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] and, on more prolonged reaction, [Ru(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>]. Stereochemical assignments for these carbonylation products are given in the preceding paper.<sup>1</sup>

**Reactions with Tertiary Phosphines.** The complexes [Ru(NO<sub>3</sub>)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>] and [RuH(NO<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>] both declined to add a third molecule of triphenylphosphine. The behavior of [RuH(NO<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>] in this respect is unexpected since the analogous complex [RuH(O<sub>2</sub>(CCF<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>] is readily converted to [RuH(O<sub>2</sub>CCF<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>3</sub>] under similar conditions.<sup>2</sup> The nitrate and trifluoroacetate ligands have similar steric properties—the latter is marginally more bulky than the former—therefore, the difference in behavior must reflect the greater chelating power of nitrate relative to trifluoroacetate referred to above.

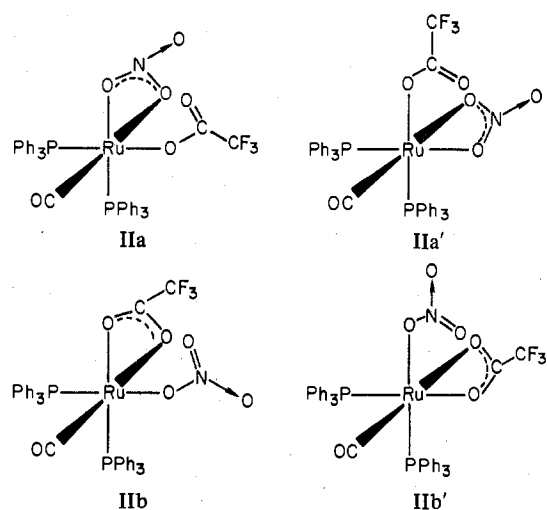
Both complexes, [Ru(NO<sub>3</sub>)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>] and [RuH(NO<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>], reacted readily with the smaller and more basic phosphines PMe<sub>2</sub>Ph and PMePh<sub>2</sub>. However, the yellow oils obtained from these reactions were reluctant to crystallize, and only one product [Ru(NO<sub>3</sub>)<sub>2</sub>(CO)(PMePh<sub>2</sub>)<sub>3</sub>] was obtained in pure crystalline form. The NMR data for this product [<sup>1</sup>H NMR Ph:Me proton ratio 10:3, methyl resonance—doublet plus triplet (virtual coupling); <sup>31</sup>P NMR doublet (δ = 12.63 ppm) and triplet (δ = 25.33 ppm), J<sub>pp</sub> = 22 Hz] confirm the proposed stoichiometry and are indicative of stereochemistry Ia or Ib.



The carbonyl frequency [ $\nu(\text{CO})$  1980 cm<sup>-1</sup>] is typical of carbonyl trans to nitrate in ruthenium(II) chemistry—the related complex [Ru(NO<sub>3</sub>)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>] has a  $\nu(\text{CO})$  value of 1986 cm<sup>-1</sup>—and thus favors stereochemistry Ia. Moreover, this geometry is in keeping with that of the precursor [Ru(NO<sub>3</sub>)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>].

**Reaction of [Ru(NO<sub>3</sub>)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>] with Trifluoroacetic Acid.** The bis(nitrate) [Ru(NO<sub>3</sub>)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>] reacts with trifluoroacetic acid in cold benzene to yield the “mixed” complex [Ru(NO<sub>3</sub>)(O<sub>2</sub>CCF<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>] in essentially quantitative yield as a pale yellow air-stable crystalline solid. The infrared spectrum of the product displays a carbonyl absorption at 1982 cm<sup>-1</sup> and bands attributable to nitrate and trifluoroacetate (1710, 1570, 1450, 1275 cm<sup>-1</sup>). The <sup>31</sup>P NMR spectrum (298 K) consists of a singlet (δ = 51.98 ppm) which decoalesces at lower temperatures to form an AB pattern. The spectroscopic data are indicative of a labile dynamic equilibrium, analogous to those found for the related complexes [Ru(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>]<sup>7</sup> and [Ru(NO<sub>3</sub>)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>]<sup>8</sup>, involving exchange between equivalent structures IIa and IIa' or IIb and IIb'.

In order to distinguish between these isomer pairs, it is necessary to invoke chemical evidence. Alcoholysis reactions in complexes of the form [RuX<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>] (X = NO<sub>3</sub><sup>1</sup> or O<sub>2</sub>CCF<sub>3</sub><sup>3</sup>) have been shown to involve cleavage of Ru—O bonds trans to PPh<sub>3</sub> rather than carbonyl. Therefore, the conversion of [Ru(NO<sub>3</sub>)(O<sub>2</sub>CCF<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>] to [RuH(NO<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>] rather than [RuH(O<sub>2</sub>CCF<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>] by solvolysis with alcohols indicates that the nitrate rather than the



carboxylate ligand occupies the site trans to the carbonyl group. This, in turn, implies that the dynamic equilibrium process occurring is IIa = IIa' rather than IIb = IIb'. Our previous observation (see above) that the relative chelating power sequence is NO<sub>3</sub><sup>-</sup> > O<sub>2</sub>CCF<sub>3</sub><sup>-</sup> is also in accord with this conclusion. A kinetic and mechanistic investigation of the dynamic equilibrium process occurring in this and related fluxional molecules will be reported elsewhere.<sup>8</sup>

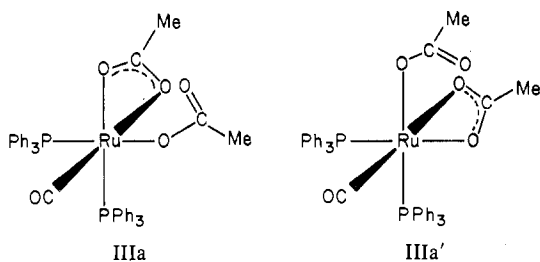
The action of trifluoroacetic acid on [Ru(NO<sub>3</sub>)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>] in boiling toluene yielded orange and yellow crystals which were identified by their infrared spectra as the known complexes [Ru(O<sub>2</sub>CCF<sub>3</sub>)<sub>3</sub>(NO)(PPh<sub>3</sub>)<sub>2</sub>] and [Ru(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], respectively, but were not separated as analytically pure products. In this connection it is noteworthy that the action of nitric acid on benzene solutions of [RuH<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>3</sub>] produced a mixture of [Ru(NO<sub>3</sub>)<sub>3</sub>(NO)(PPh<sub>3</sub>)(OPPh<sub>3</sub>)] and [Ru(NO<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>].<sup>1</sup> This latter reaction, involving formation of a dicarbonyl product in the absence of an obvious carbonyl source, strongly implies the occurrence of an intermolecular carbonyl transfer step at some stage in these processes.

**Reaction of [Ru(NO<sub>3</sub>)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>] with Acetic Acid and/or Sodium Acetate.** Acetic acid, unlike its trifluoro analogue, failed to react with [Ru(NO<sub>3</sub>)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>] in the cold or in boiling toluene. However, complete conversion of [Ru(NO<sub>3</sub>)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>] to [Ru(O<sub>2</sub>CMe)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>] was readily achieved using sodium acetate in cold methanol. Addition of free acetic acid to lower the pH and thereby suppress any tendency for a base-promoted alcoholysis and β-elimination sequence to occur did not appear necessary since no evidence for the formation of hydridic materials was observed.<sup>9</sup>

However, under more vigorous conditions alcoholysis and subsequent β-elimination reactions do occur. Thus, treatment of [Ru(NO<sub>3</sub>)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>] with sodium acetate in boiling methanol led to formation of the hydride [Ru(O<sub>2</sub>CMe)H(CO)(PPh<sub>3</sub>)<sub>2</sub>] in high yield. Here again the sodium acetate apparently functions as a base since [Ru(O<sub>2</sub>CMe)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>] and its bis(nitrate) precursor are resistant to attack by methanol alone under similar conditions.

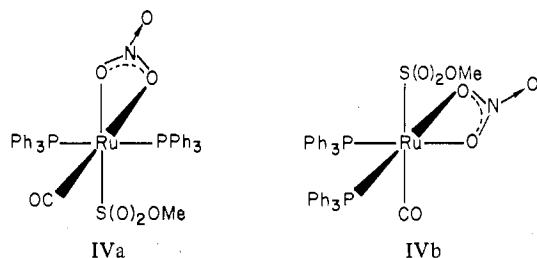
Spectroscopic data for the product [Ru(O<sub>2</sub>CMe)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>] are identical with those previously reported for a sample prepared from [Ru(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>] and sodium acetate–acetic acid buffer in methanol and are indicative of the fluxional structure (IIIa = IIIa').<sup>2</sup> A detailed investigation of the molecular dynamics of this structure will be reported elsewhere.<sup>7</sup>

The complex [Ru(O<sub>2</sub>CMe)H(CO)(PPh<sub>3</sub>)<sub>2</sub>] has previously been shown<sup>2</sup> to have a stereochemistry (trans phosphines) analogous to that reported for [RuH(NO<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>].<sup>1</sup>



### Reaction of $[\text{Ru}(\text{NO}_3)_2(\text{CO})(\text{PPh}_3)_2]$ with Sulfur Dioxide in Boiling Methanol.

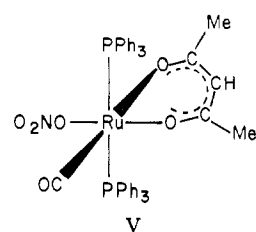
Pale yellow, air-stable crystals of stoichiometry  $[\text{Ru}(\text{O}_2\text{SMe})(\text{NO}_3)(\text{CO})(\text{PPh}_3)_2]$ , obtained on treatment of  $[\text{Ru}(\text{NO}_3)_2(\text{CO})(\text{PPh}_3)_2]$  with sulfur dioxide in methanol, showed bands ( $\nu(\text{SO}_2)$  1240 and 1100  $\text{cm}^{-1}$ ) significantly different from those recorded for the related monodentate O-coordinated or bidentate O,O'-coordinated methyl sulfito complexes (1085–1050 and 1000–820  $\text{cm}^{-1}$ ).<sup>11</sup> The product is therefore formulated as an S-bonded methyl sulfito derivative  $[\text{Ru}\{\text{S}(\text{O})_2\text{OMe}\}(\text{NO}_3)(\text{CO})(\text{PPh}_3)_2]$  formed by "insertion" of sulfur dioxide in the Ru–OMe bond of an intermediate methoxy complex. A directly analogous complex  $[\text{Ru}\{\text{S}(\text{O})_2\text{OMe}\}(\text{O}_2\text{CCF}_3)(\text{CO})(\text{PPh}_3)_2]$  has been similarly obtained from  $[\text{Ru}(\text{O}_2\text{CCF}_3)_2(\text{CO})(\text{PPh}_3)_2]$ .<sup>2</sup> A closely related platinum complex  $[\text{Pt}\{\text{S}(\text{O})_2\text{OMe}\}_2(\text{PPh}_3)_2]$  likewise prepared from  $[\text{Pt}(\text{O}_2\text{CCF}_3)_2(\text{PPh}_3)_2]$  has also been formulated as a derivative of S-coordinated methyl sulfite on the basis of similar infrared data (1270 and 1100  $\text{cm}^{-1}$ ).<sup>12</sup> The <sup>31</sup>P NMR spectrum of the new complex  $[\text{Ru}\{\text{S}(\text{O})_2\text{OMe}\}(\text{NO}_3)(\text{CO})(\text{PPh}_3)_2]$  [ $\delta = 34.78$  singlet] indicates the presence of two equivalent phosphine ligands and thus supports two possible structures IVa and IVb. We are not able to say positively which stereochemistry is correct but we favor IVa on steric grounds. An analogous structure was proposed for the complex  $[\text{Ru}\{\text{S}(\text{O})_2\text{OMe}\}(\text{O}_2\text{CCF}_3)(\text{CO})(\text{PPh}_3)_2]$  on the basis of similar reasoning.<sup>2</sup>



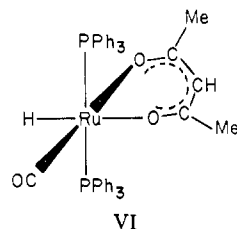
### Reaction of $[\text{Ru}(\text{NO}_3)_2(\text{CO})(\text{PPh}_3)_2]$ with Acetylacetonone.

Treatment of  $[\text{Ru}(\text{NO}_3)_2(\text{CO})(\text{PPh}_3)_2]$  with acetylacetonone in benzene solution gave an oil whose infrared spectrum was indicative of incomplete reaction. However, decreasing the acidity of the reaction medium by the addition of triethylamine resulted in the precipitation of  $[\text{Ru}(\text{acac})(\text{NO}_3)(\text{CO})(\text{PPh}_3)_2]$  as yellow air-stable crystals. The infrared spectrum of the product displays absorption bands characteristic of O,O'-chelated acetylacetonone (1570 and 1525  $\text{cm}^{-1}$ ),<sup>12</sup> nitrate (1470 and 1270  $\text{cm}^{-1}$ ), and carbonyl ligands (1959  $\text{cm}^{-1}$ ). The proton NMR spectrum ( $\tau_{\text{Me}}$  8.66 and 8.71;  $\tau_{\text{CH}}$  5.95) is indicative of acetylacetonate coordinated trans to a pair of dissimilar ligands, and the <sup>31</sup>P NMR spectrum [ $\delta = 27.61$  singlet] therefore implies that the phosphine ligands are mutually trans. Stereochemistry V is the only one fully consistent with these data.

Attempts to recrystallize  $[\text{Ru}(\text{acac})(\text{NO}_3)(\text{CO})(\text{PPh}_3)_2]$  from methanol in the presence of residual traces of triethylamine yielded the solvolysis and  $\beta$ -elimination product  $[\text{Ru}(\text{acac})\text{H}(\text{CO})(\text{PPh}_3)_2]$ . This hydride was also obtained from the reaction of an ethanolic suspension of  $[\text{RuH}(\text{NO}_3)(\text{CO})(\text{PPh}_3)_2]$  with acetylacetonone in the presence of base.

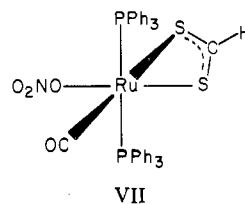


The infrared spectrum of this product displays bands attributable to O,O'-chelated acetylacetonate (1595 and 1508  $\text{cm}^{-1}$ ),<sup>12</sup> carbonyl (1912  $\text{cm}^{-1}$ ), and hydride (1938  $\text{cm}^{-1}$ ) ligands. The high-field proton NMR spectrum consists of a triplet [ $\tau_{\text{MH}}$  23.3;  $^2J_{\text{PH}} = 20.5$  Hz] indicative of magnetically equivalent <sup>31</sup>P nuclei. The low-field proton NMR spectrum contains resonances at  $\tau$  8.7 and 8.94 attributable to the methyl groups of an asymmetrically bound acetylacetonone ligand. These data establish VI as the only feasible stereochemistry.



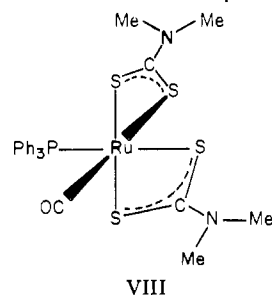
### Reaction of $[\text{RuH}(\text{NO}_3)(\text{CO})(\text{PPh}_3)_2]$ with Carbon Disulfide.

Carbon disulfide reacted readily with  $[\text{RuH}(\text{NO}_3)(\text{CO})(\text{PPh}_3)_2]$  in benzene solution to afford orange, air-stable crystals of stoichiometry  $[\text{Ru}(\text{S}_2\text{CH})(\text{NO}_3)(\text{CO})(\text{PPh}_3)_2]$ . The infrared spectrum of this product displays bands attributable to dithioformate [1225 (vw) and 920  $\text{cm}^{-1}$ ],<sup>14</sup> nitrate (1485 and 1275  $\text{cm}^{-1}$ ), and carbonyl (1965  $\text{cm}^{-1}$ ) ligands. The low-field proton NMR signal of the dithioformate ligand is a triplet  $\tau_{\text{CH}}$  0.5;  $^4J_{\text{PH}} = 3.9$  Hz. The low value of the coupling  $^4J_{\text{PH}}$  clearly implies that the dithioformate ligand is cis rather than trans to the two equivalent phosphine ligands<sup>14</sup> and thus establishes VII as the only feasible stereochemistry for the complex.

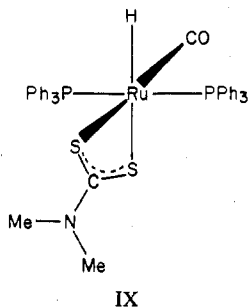


### Reaction of $[\text{Ru}(\text{NO}_3)_2(\text{CO})(\text{PPh}_3)_2]$ and $[\text{RuH}(\text{NO}_3)(\text{CO})(\text{PPh}_3)_2]$ with Sodium N,N-Dimethyldithiocarbamate.

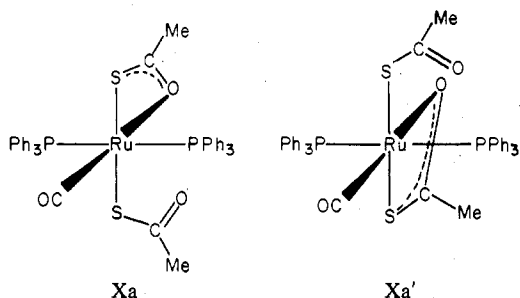
A solution of sodium N,N-dimethyldithiocarbamate in boiling methanol reacts with  $[\text{Ru}(\text{NO}_3)_2(\text{CO})(\text{PPh}_3)_2]$  to yield air-stable yellow crystals of stoichiometry  $[\text{Ru}(\text{S}_2\text{CNMe}_2)_2(\text{CO})(\text{PPh}_3)_2]$ . Infrared and <sup>1</sup>H NMR spectra establish that the product is identical with that obtained by the reaction of sodium N,N-dimethyldithiocarbamate with  $[\text{RuCl}(\text{O}_2\text{CMe})(\text{CO})(\text{PPh}_3)_2]$ <sup>15</sup> and, therefore, has stereochemistry VIII. Treatment of  $[\text{Ru}(\text{NO}_3)_2(\text{CO})(\text{PPh}_3)_2]$  with sodium



*N,N*-dimethyldithiocarbamate in cold methanol affords a yellow powder of stoichiometry  $[\text{Ru}(\text{S}_2\text{CNMe}_2)_2(\text{CO})(\text{PPh}_3)_2]$ . This product, which presumably contains a monodentate dithiocarbamate ligand, readily loses a molecule of phosphine to form  $[\text{Ru}(\text{S}_2\text{CNMe}_2)_2(\text{CO})(\text{PPh}_3)]$  on attempted recrystallization. This process is accompanied by a shift in  $\nu(\text{CO})$  from 1970 to 1928  $\text{cm}^{-1}$ . Because of the stability of the Ru-S bonds, these dithiocarbamate complexes are not susceptible to alcoholysis. However, the hydride  $[\text{Ru}(\text{S}_2\text{CNMe}_2)\text{H}(\text{CO})(\text{PPh}_3)_2]$  is readily obtained by the reaction of  $[\text{RuH}(\text{NO}_3)(\text{CO})(\text{PPh}_3)_2]$  with sodium dimethyldithiocarbamate in cold methanol and is identical with the complex of stereochemistry IX previously prepared from  $[\text{RuClH}(\text{CO})(\text{PPh}_3)_3]$  in a similar manner.<sup>15</sup>

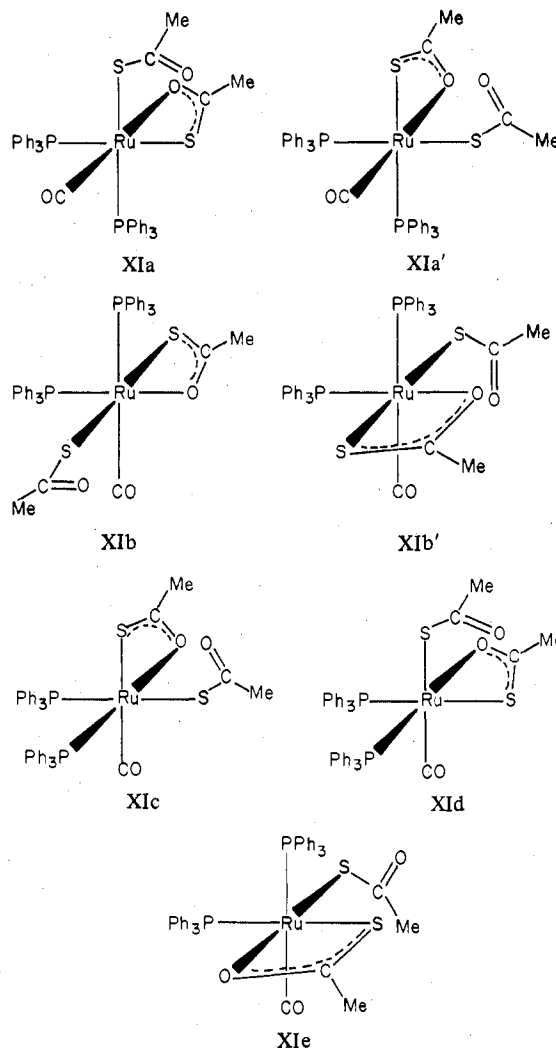


**Reaction of  $[\text{Ru}(\text{NO}_3)_2(\text{CO})(\text{PPh}_3)_2]$  with Thioacetic Acid.** Thioacetic acid reacts with  $[\text{Ru}(\text{NO}_3)_2(\text{CO})(\text{PPh}_3)_2]$  in boiling methanol to afford a product of stoichiometry  $[\text{Ru}\{\text{S}(\text{O})\text{CMe}_2(\text{CO})(\text{PPh}_3)_2\}]$  (isomer A). The stereochemistry of this product can be deduced from the chemical and spectroscopic evidence as follows. The  $^{31}\text{P}$  NMR spectrum shows a temperature-independent singlet, and the  $^1\text{H}$  NMR spectrum of the methyl (thioacetate) groups consists of a singlet which decoalesces to two equal resonances at low temperature. These spectra indicate the presence of a pair of mutually trans phosphine ligands and a fluxional system, respectively. Since ruthenium(II) has a greater affinity for sulfur than for oxygen, it seems probable that both thioacetate ligands are coordinated through sulfur and that the fluxional behavior arises from competition between the two oxygen donor atoms for the remaining coordination site. Stereochemistry X is the only one which is consistent with the NMR data and at the same time provides scope for a fluxional process ( $\text{Xa} \rightleftharpoons \text{Xa}'$ ). A kinetic and mechanistic study of this process will be given elsewhere.<sup>8</sup>



Treatment of  $[\text{Ru}(\text{NO}_3)_2(\text{CO})(\text{PPh}_3)_2]$  with thioacetic acid in cold methanol afforded a second isomer of stoichiometry  $[\text{Ru}\{\text{S}(\text{O})\text{CMe}_2(\text{CO})(\text{PPh}_3)_2\}]$  (isomer B), which has spectroscopic properties substantially different from those of isomer A and which readily converts into the latter on recrystallization from dichloromethane-methanol. The  $^{31}\text{P}$  spectrum of isomer B consists of a temperature-independent AB pattern, and the  $^1\text{H}$  NMR spectrum exhibits two temperature-independent singlets ( $\tau$  7.78 and 8.60) attributable to the methyl groups of two nonequivalent thioacetic ligands. In attempting to assign the stereochemistry of isomer B, we once more assume

that the thioacetate ligands will coordinate to ruthenium through sulfur rather than oxygen. If we then exclude structure  $\text{Xa} \rightleftharpoons \text{Xa}'$ , which has already been assigned to isomer A, and structures involving trans phosphine ligands, which are eliminated on the basis of the  $^{31}\text{P}$  NMR data, five possible stereochemical arrangements (XIa-e) remain for isomer B.

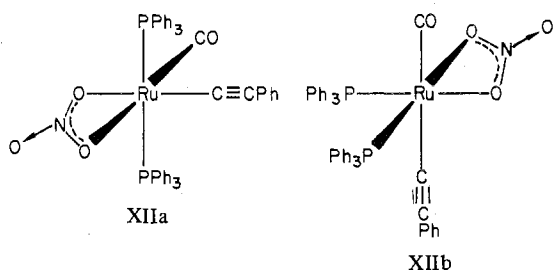


Two of these (XIa and XIb) might reasonably be expected to display fluxional behavior—similar to that observed for isomer A—involving interconversion of equivalent structures [ $\text{XIa} \rightleftharpoons \text{XIa}'$  and  $\text{XIb} \rightleftharpoons \text{XIb}'$ , respectively] by interchange of monodentate and bidentate thioacetate ligands and are, therefore, not consistent with the temperature-independent nature of the  $^1\text{H}$  and  $^{31}\text{P}$  NMR data. Of the three remaining structures, two (XIc and XIe) retain the basic stereochemistry of the precursor  $[\text{Ru}(\text{NO}_3)_2(\text{CO})(\text{PPh}_3)_2]$  whereas the third does not. Therefore, given the mild conditions used to obtain isomer B, we conclude that it probably possesses stereochemistry XIc or XIe.<sup>16</sup>

**Reactions of  $[\text{Ru}(\text{NO}_3)_2(\text{CO})(\text{PPh}_3)_2]$  and  $[\text{RuH}(\text{NO}_3)(\text{CO})(\text{PPh}_3)_2]$  with Phenylacetylene.** Bright yellow, air-stable crystals of stoichiometry  $[\text{Ru}(\text{NO}_3)(\text{C}\equiv\text{CPh})(\text{CO})(\text{PPh}_3)_2]$  were obtained by treating  $[\text{Ru}(\text{NO}_3)_2(\text{CO})(\text{PPh}_3)_2]$  with phenylacetylene in boiling ethanol or benzene. The same product was obtained from the reaction of  $[\text{RuH}(\text{NO}_3)(\text{CO})(\text{PPh}_3)_2]$  with phenylacetylene in ethanol. The reaction of  $[\text{Ru}(\text{NO}_3)_2(\text{CO})(\text{PPh}_3)_2]$  with phenylacetylene in ethanol may involve the formation of a hydride intermediate  $[\text{RuH}(\text{NO}_3)(\text{CO})(\text{PPh}_3)_2]$  by alcoholysis. However, in benzene solution direct substitution of  $\text{NO}_3^-$  by  $\text{C}\equiv\text{CPh}^-$  must occur. The acetylide product  $[\text{Ru}(\text{NO}_3)(\text{C}\equiv\text{CPh})(\text{CO})-$

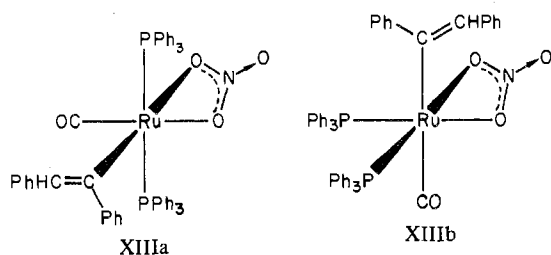
(PPh<sub>3</sub>)<sub>2</sub>] displayed no tendency to undergo "insertion" reactions with excess phenylacetylene. In this respect it differs from the corresponding trifluoroacetate system where reaction of [RuH(O<sub>2</sub>CCF<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>] or [Ru(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>] with phenylacetylene gave the vinylic product [Ru(O<sub>2</sub>CCF<sub>3</sub>){C(Ph)=CH-C≡CPh}(CO)(PPh<sub>3</sub>)<sub>2</sub>].<sup>17,18</sup> Presumably the difference in behavior reflects the greater reluctance of bidentate nitrate to surrender a coordination site to the incoming acetylene and thereby facilitate the "insertion" step.

The acetylide complex is assigned either stereochemistry XIIa or XIIb on the basis of spectroscopic data. The <sup>31</sup>P



NMR spectrum consists of a singlet, and the infrared spectrum displays bands at 2120 and 1968 cm<sup>-1</sup> attributable to  $\nu(\text{C}\equiv\text{C})$  and  $\nu(\text{CO})$ , respectively. Since the phosphine ligands are obviously equivalent and the  $\nu(\text{CO})$  frequency is typical of carbonyl trans to nitrate rather than acetylide, the complex probably has stereochemistry XIIa. This stereochemistry is also in keeping with that preferred by related ruthenium(II) complexes of similar stoichiometry (see above).

**Reactions of [RuH(NO<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>] and [Ru(NO<sub>3</sub>)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>] with Diphenylacetylene.** The complexes [RuH(NO<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>] and [Ru(NO<sub>3</sub>)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>] both react with diphenylacetylene in ethanol to afford the 1,2-diphenylvinyl product [Ru{C(Ph)=CHPh}(NO<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>] as air-stable bright yellow crystals. The reaction of the latter precursor with diphenylacetylene presumably proceeds via the alcoholysis product [RuH(NO<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>] since there is no evidence of a direct reaction between [Ru(NO<sub>3</sub>)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>] and diphenylacetylene in benzene. The spectroscopic properties of the new vinyl complex [ $\nu(\text{CO})$  1940,  $\nu(\text{C}=\text{C})$  1580 cm<sup>-1</sup>; <sup>31</sup>P NMR  $\delta$  = 31.63 ppm (singlet)] are consistent with the probable stereochemistry XIIIa but do not entirely exclude the alternative XIIIb.



On the basis of steric considerations,<sup>19</sup> we tentatively assign cis stereochemistry to the diphenylvinyl ligand. However, we are unable to locate the NMR signal of the vinylic proton and thereby confirm the proposed geometry. Therefore, this assignment must be treated with caution, particularly since

recent work on the "insertion" of diphenylacetylene into the metal-hydrogen bonds of [RuH(NO)(PPh<sub>3</sub>)<sub>3</sub>] and [MH-(CO)(PPh<sub>3</sub>)<sub>3</sub>] (M = Rh or Ir) has yielded trans vinylic products.<sup>20</sup>

**Registry No.** Ru(NO<sub>3</sub>)<sub>2</sub>(CO)(PMePh<sub>2</sub>)<sub>3</sub>, 66255-74-1; Ru(NO<sub>3</sub>)(O<sub>2</sub>CCF<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>, 66289-67-6; Ru(O<sub>2</sub>CMe)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>, 61990-12-3; RuH(O<sub>2</sub>CMe)(CO)(PPh<sub>3</sub>)<sub>2</sub>, 50661-73-9; Ru(NO<sub>3</sub>)(S(O)<sub>2</sub>OMe)(CO)(PPh<sub>3</sub>)<sub>2</sub>, 66255-66-1; Ru(NO<sub>3</sub>)(acac)(CO)(PPh<sub>3</sub>)<sub>2</sub>, 66255-73-0; RuH(acac)(CO)(PPh<sub>3</sub>)<sub>2</sub>, 61951-11-9; Ru(NO<sub>3</sub>)(S<sub>2</sub>CH)(CO)(PPh<sub>3</sub>)<sub>2</sub>, 66255-72-9; Ru(S<sub>2</sub>CNMe<sub>2</sub>)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>, 66255-71-8; Ru(S<sub>2</sub>CNMe<sub>2</sub>)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>, 56870-60-1; RuH(S<sub>2</sub>CNMe<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>, 56800-88-5; Ru(S(O)CMe)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>, isomer A, 66289-66-5; Ru(S(O)CMe)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>, isomer B, 66255-70-7; Ru(NO<sub>3</sub>)(C≡CPh)(CO)(PPh<sub>3</sub>)<sub>2</sub>, 66255-69-4; Ru(NO<sub>3</sub>)(C(Ph)=CHPh)(CO)(PPh<sub>3</sub>)<sub>2</sub>, 66255-68-3; Ru(NO<sub>3</sub>)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>, 66255-67-2; RuH(NO<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>, 66255-84-3; PMePh<sub>2</sub>, 1486-28-8; HO<sub>2</sub>CCF<sub>3</sub>, 76-05-1; propanol, 5723-77-3; NaO<sub>2</sub>CMe, 127-09-3; SO<sub>2</sub>, 7446-09-5; acetylacetone, 123-54-6; CS<sub>2</sub>, 75-15-0; NaS<sub>2</sub>CNMe<sub>2</sub>, 128-04-1; HS(O)CMe, 507-09-5; HC≡CPh, 536-74-3; PhC≡CPh, 501-65-5.

## References and Notes

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- (2) A. Dobson and S. D. Robinson, *Inorg. Chem.*, **16**, 1321 (1977).
- (3) A. Dobson and S. D. Robinson, *Inorg. Chem.*, **16**, 137 (1977).
- (4) M. B. Hursthouse, personal communication.
- (5) Other evidence discussed later in this paper amply supports our conclusion that nitrate is able to compete successfully with trifluoroacetate as a chelate ligand.
- (6) Only Ru-OC(O)CF<sub>3</sub> bonds trans to phosphine appear to be susceptible to alcoholysis.
- (7) C. J. Creswell, A. Dobson, and S. D. Robinson, *Inorg. Chem.*, in preparation; A. Dobson, S. D. Robinson, and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, 370 (1975).
- (8) C. J. Creswell, P. B. Critchlow, M. Preece, N. S. Sridhara, and S. D. Robinson, *Inorg. Chem.*, in preparation.
- (9) The complex [Ru(O<sub>2</sub>CMe)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>] has previously been prepared by treatment of [Ru(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>] with sodium acetate in cold methanol.<sup>2</sup> However, the product obtained in this manner is frequently contaminated with [Ru(O<sub>2</sub>CMe)H(CO)(PPh<sub>3</sub>)<sub>2</sub>] formed by a base-promoted alcoholysis and  $\beta$ -elimination sequence in which the sodium acetate functions as the base. Addition of free acetic acid to lower the pH and suppress the alcoholysis reaction leads to a good yield of pure [Ru(O<sub>2</sub>CMe)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>].
- (10) A more detailed analysis of these spectra and a kinetic and mechanistic investigation of the dynamic equilibrium process are given in a forthcoming paper.<sup>3</sup>
- (11) A. Wojcicki, *Adv. Organomet. Chem.*, **12**, 31 (1974), and references therein.
- (12) D. M. Barlex and R. D. W. Kemmitt, *J. Chem. Soc., Dalton Trans.*, 1436 (1972).
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- (15) P. B. Critchlow and S. D. Robinson, *J. Chem. Soc., Dalton Trans.*, 1367 (1975).
- (16) In theory the nonequivalent structures XIc and XI d could also interconvert by rapid monodentate-bidentate monothiocarboxylate interchange. However, the NMR spectra do not show any evidence of this process and we, therefore, conclude that one of the structures is significantly more stable than the other.
- (17) A. Dobson and S. D. Robinson, unpublished results.
- (18) The exact structure and stereochemistry of the ligand "C(Ph)=CH-C≡CPh" are still in doubt. An X-ray diffraction study is being undertaken by Dr. M. B. Hursthouse, Queen Mary College, London.
- (19) For an example of the steric influence of auxiliary ligands on the "insertion" of disubstituted acetylenes into ruthenium-hydrogen bonds see T. Blackmore, M. I. Bruce, F. G. A. Stone, R. E. Davis, and A. Garza, *Chem. Commun.*, 852 (1971); J. L. Davidson, M. Green, F. G. A. Stone, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 286 (1975).
- (20) R. A. Sanchez-Delgado and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 804 (1977).