based on the following observations and considerations. (i) The reaction of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2$ (I) with iodine in dichloromethane in a molar ratio 2:1 gives solely $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2]^+$ (II). (ii) Treatment of $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2]^+$ (II) with a large excess of iodide ions regenerates the neutral complex $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PRP(C_6H_5)_2$ (I). (iii) The reaction of $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PCH_2P(C_6H_5)_2$ (I) with a tenfold excess of iodine in dichloromethane affords solely $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(I)(C_6H_5)_2PCH_2P(C_6H_5)_2]^+$ (III) based on infrared evidence, whereas the corresponding reaction involving $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PCH_2P(C_6H_5)_2]$(anion) (II) gives $[(\pi\text{-}C_5H_5)Fe(CO)_2L]$(anion) (IV) [L = adduct of $(C_6H_5)_2PCH_2P(C_6H_5)_2$] as well as $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(I)(C_6H_5)_2PCH_2P(C_6H_5)_2]$(anion) (III) in approximate relative yields 1:2. (iv) The reaction of $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2$ with iodine to afford $(\pi\text{-}C_5H_5)Fe(CO)_2I$ has previously been shown to involve the bridged iodo species $[\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2I]^+$ as an intermediate, and nucleophilic attack of iodide ions on the latter yields $(\pi\text{-}C_5H_5)Fe(CO)_2I$.[19] (v) The yield of $\{(\pi\text{-}C_5H_5)Fe(CO)I\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ (V) is increased by iodinating $\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ (I) in the presence of excess iodide ions and is decreased by increasing the iodine:parent dimer molar ratio.

The inability of $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(I)(C_6H_5)_2PCH_2P(C_6H_5)_2]^+$ (III) to react with iodide ions to form $\{(\pi\text{-}C_5H_5)Fe(CO)I\}_2(C_6H_5)_2PCH_2P(C_6H_5)_2$ (V) is attributed to its stability toward rearrangement. This contrasts with the apparently high reactivity of $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(I)(C_6H_5)_2PC_2H_4P(C_6H_5)_2]^+$ (III). It should be noted that the reactions of monosubstituted derivatives of $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2$ with iodine have also been shown to afford products of the type $[(\pi\text{-}C_5H_5)Fe(CO)_2L]$(anion) resulting from asymmetric cleavage of the parent.[30]

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[30] R. J. Haines and A. L. du Preez, *Inorg. Chem.*, **8**, 1459 (1969).

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Organometallic Chemistry of the Transition Metals. XXVI. The Carbonylation of Ruthenium Diolefin Complexes[1]

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The atmospheric pressure carbonylation of the ruthenium diolefin complexes $[(\text{diene})RuCl_2]_n$ (diene = norbornadiene or bidentate benzene) under various conditions is described. Atmospheric pressure carbonylation of $[(\text{diene})RuCl_2]_n$ derivatives in the absence of an added reducing agent gives the ruthenium carbonyl chloride $[Ru(CO)_3Cl_2]_2$. This carbonyl chloride undergoes a reversible reaction with ethanol to give $[(C_2H_5OH)Ru(CO)_2Cl_2]_n$. Atmospheric pressure carbonylation of $[(\text{diene})RuCl_2]_n$ derivatives in the presence of added hydrazine gives a mixture of the ruthenium(II) ammines $[Ru(NH_3)_5L]Cl_2$ (L = CO and N_2). Atmospheric pressure carbonylation of $[(\text{diene})RuCl_2]_n$ derivatives in the presence of added hydrazine and triphenylphosphine gives not only the ruthenium(II) ammines $[Ru(NH_3)_5L]Cl_2$ (L = CO and N_2) but also the ruthenium(0) complex *trans*-$[(C_6H_5)_3P]_2Ru(CO)_3$. Atmospheric pressure carbonylation of $[(\text{diene})RuCl_2]_n$ derivatives in the presence of zinc gives variable yields of $Ru_3(CO)_{12}$; side reactions in these carbonylations lead to other products such as the norbornadiene complex $C_7H_8Ru(CO)_2(OH)_2$ and tetrametallic ruthenium carbonyl hydrides such as $H_4Ru_4(CO)_{12}$. Atmospheric pressure carbonylation of the bidentate benzene complex $[C_6H_6RuCl_2]_n$ in ethanolic lithium acetate in the presence of zinc gives a $\sim$50% yield of the tetrametallic ruthenium carbonyl hydride $H_2Ru_4(CO)_{13}$. Atmospheric pressure carbonylation of $[Ru(CO)_3Cl_2]_2$ in methanol in the presence of zinc gives $Ru_3(CO)_{12}$.

Introduction

Within the last several years dodecacarbonyltriruthenium, $Ru_3(CO)_{12}$, has become an important starting material for the preparation of numerous ruthenium complexes, particularly those containing carbonyl groups.[3] All known preparations of $Ru_3(CO)_{12}$ from common ruthenium compounds such as the hydrated chloride require elevated pressures. Thus, the generally preferred method for preparing $Ru_3(CO)_{12}$ by reductive carbonylation of hydrated ruthenium chloride with zinc in methanol solution is reported[4] to require at least 5–10 atm carbon monoxide pressure. One further disadvantage of this latter method for preparing $Ru_3(CO)_{12}$ is the apparent tendency for the zinc reducing agent, particularly if too finely divided, to reduce the ruthenium trichloride to unreactive ruthe-

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[1] (a) Part XXV: R. B. King and A. Efraty, *J. Organometal. Chem.*, **27**, 409 (1971). (b) This work was presented at the Second North American Meeting of the Catalysis Society, Houston, Texas, Feb 1971.

[2] Postdoctoral research associate, 1968–1969, 1970–1971.

[3] M. I. Bruce and F. G. A. Stone, *Angew. Chem., Int. Ed. Engl.*, **7**, 427 (1968).

[4] M. I. Bruce and F. G. A. Stone, *J. Chem. Soc. A*, 1238 (1967).

nium metal before the carbon monoxide can be introduced.

These considerations indicate the need for a new preparation of $Ru_3(CO)_{12}$, particularly one starting with the readily available hydrated ruthenium trichloride and requiring only atmospheric pressure of carbon monoxide for all of the carbonylation steps. Attractive intermediates for such preparations of $Ru_3(CO)_{12}$ appeared to be the diolefinruthenium complexes of the type $[(diene)RuCl_2]_n$ which in some cases (*e.g.*, norbornadiene) are precipitated in satisfactory to good yields when an alcoholic solution of hydrated ruthenium trichloride is stirred with the diolefin. The $[(diene)RuCl_2]_n$ complexes, because of a polymeric structure with chlorine bridges, are insoluble in unreactive organic solvents. However, they can be made to dissolve in systems of sufficient basicity to split the ruthenium–chlorine–ruthenium bridges. Furthermore, the coordinated olefin ligands in many metal–olefin complexes are readily replaced by other Lewis bases[5] including carbon monoxide in some cases.[6] For these reasons, carbonylation of $[(diene)RuCl_2]_n$ derivatives appeared to offer certain advantages over the carbonylation of ruthenium(III) halides for the preparation of ruthenium carbonyls.

This paper describes our studies on the carbonylation of $[(diene)RuCl_2]_n$ derivatives and related compounds. Initially hydrazine was used as a reducing agent because of its strength and solubility. However, in most cases hydrazine was found to give ruthenium(II) ammines and nitrogen complexes rather than ruthenium(0) derivatives. Zinc was next tried as a reducing agent in view of its demonstrated value in the high-pressure preparation of $Ru_3(CO)_{12}$.[4] Using zinc as a reducing agent we were able to obtain reasonable yields of $Ru_3(CO)_{12}$ on a small scale by carbonylation of $[(diene)RuCl_2]_n$ derivatives at atmospheric pressure. However, attempts to scale up this reaction to provide relatively large quantities of $Ru_3(CO)_{12}$ have been unsuccessful apparently owing to side reactions which take place when carbon monoxide is present only at atmospheric pressure.

Experimental Section

Infrared spectra were taken in the indicated media and recorded on a Perkin-Elmer Model 621 spectrometer. Melting points were taken in capillaries and are uncorrected.

Materials.—Ruthenium trichloride trihydrate (39% ruthenium) was purchased from Englehard Industries, Newark, N. J. It was converted to the following complexes by published procedures: $[C_7H_8RuCl_2]_n$ (here and elsewhere in this paper C_7H_8 = norbornadiene),[7] $[C_6H_6RuCl_2]_n$,[8] $[Ru(CO)_2Cl_2]_n$,[9] $[(C_6H_5)_3P]_3RuCl_2$,[10] *trans*-(Pf-Pf)$_2$RuCl$_2$ (here and elsewhere in this paper Pf-Pf = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$),[11] and $[Ru(NH_3)_5N_2]Cl_2$.[12] The granular zinc used in this work was cleaned by a quick washing with concentrated hydrochloric acid.

Carbonylation Experiments (Table I).—The reactions listed in Table I were performed in an atmosphere of carbon monoxide using ordinary glass apparatus. Details of product isolation and analysis are exemplified by the specific reactions described below.

(a) **Carbonylation of $[C_7H_8RuCl_2]_n$ in the Presence of Hydrazine.**—A suspension of 0.5 g (1.9/*n* mmol) of $[C_7H_8RuCl_2]_n$ in 100 ml of ethanol was treated with 1 ml of hydrazine (either hydrazine hydrate or 95% hydrazine). The resulting mixture was boiled under reflux with stirring for 2 hr in an atmosphere of carbon monoxide. After cooling to room temperature the yellow precipitate was filtered, washed with ethanol, and then dried to give a yellow solid. The infrared spectrum of this solid in a potassium bromide pellet exhibited a strong band at 1930 cm^{-1} arising from the ν(CO) frequency in $[Ru(NH_3)_5CO]Cl$ (lit.[13] ν(CO) in $[Ru(NH_3)_5CO]Cl_2$ 1918 cm^{-1}) and a strong band at 2107 cm^{-1} arising from the ν(NN) frequency in $[Ru(NH_3)_5N_2]Cl_2$ (lit.[12] ν(NN) in $[Ru(NH_3)_5N_2]Cl_2$ 2105 cm^{-1}). The relative intensities of these two strong infrared bands varied significantly in different preparations confirming their origin from different compounds as outlined above. In addition infrared bands at ~3200 (vs, br) and 1600 (s) cm^{-1} arising from the coordinated ammonia were also observed. The yield of the $[Ru(NH_3)_5CO]Cl_2$–$[Ru(NH_3)_5N_2]Cl_2$ mixture (a meaningful parameter since the formula weights of both components are essentially equal) was ~0.5 g (92%).

A 0.2-g sample of this $[Ru(NH_3)_5CO]Cl_2$–$[Ru(NH_3)_5N_2]Cl_2$ mixture was boiled under reflux with 0.2 g of triphenylphosphine in 100 ml of ethanol. Cooling the resulting reaction mixture to room temperature gave 0.18 g of a yellow precipitate shown by its infrared spectrum to be the unchanged $[Ru(NH_3)_5CO]Cl_2$–$[Ru(NH_3)_5N_2]Cl_2$ mixture.

In another experiment a 0.3 g sample of the $[Ru(NH_3)_5CO]Cl_2$–$[Ru(NH_3)_5N_2]Cl_2$ mixture was boiled under reflux for 10 hr in 100 ml of pyridine. Cooling the resulting reaction mixture to room temperature gave 0.2 g of a yellow precipitate shown by its infrared spectrum to be the unchanged $[Ru(NH_3)_5CO]Cl_2$–$[Ru(NH_3)_5N_2]Cl_2$ mixture.

(b) **Carbonylation of the "Red Ruthenium Carbonyl Chloride" Solution[14] in the Presence of Hydrazine.**—A solution of 1.0 g (3.86 mmol) of ruthenium trichloride trihydrate in 100 ml of ethanol was boiled under reflux in a carbon monoxide atmosphere for 6 hr to give the "red ruthenium carbonyl chloride" solution.[14] While warm, this solution was treated with 10 ml of hydrazine hydrate and the mixture boiled under reflux for 1 additional hr in the carbon monoxide atmosphere. After cooling to room temperature the yellow-brown precipitate was filtered. This precipitate was dissolved in a minimum quantity of water and the filtered aqueous solution treated with excess (~100 ml) ethanol. The yellow-pink precipitate was filtered and dried to give 1.1 g (100% yield) of solid identified by its infrared spectrum to be $[Ru(NH_3)_5CO]Cl_2$ only slightly contaminated with the nitrogen complex $[Ru(NH_3)_5N_2]Cl_2$.

(c) **Carbonylation of $[C_7H_8RuCl_2]_n$ in the Presence of Both Hydrazine and Triphenylphosphine.**—A suspension of 0.6 g (2.27/*n* mmol) of $[C_7H_8RuCl_2]_n$ in 100 ml of ethanol was treated with 2 ml of 95% hydrazine and 0.8 g (3.05 mmol) of triphenylphosphine. The resulting mixture was boiled under reflux for 6 hr in a stream of carbon monoxide. After cooling to room temperature the resulting pale brown precipitate was removed by filtration and dried. This solid was extracted with toluene until no more dissolved. The toluene-insoluble residue (0.15 g, 23% yield) was shown by its infrared spectrum in the 2200–1800-cm^{-1} region to be the same type of $[Ru(NH_3)_5CO]Cl_2$–$[Ru(NH_3)_5N_2]Cl_2$ mixture as was obtained from similar experiments in the absence of triphenylphosphine. The filtered toluene solution was concentrated under vacuum until incipient crystallization. Crystallization was made complete by addition of hexane and cooling to −15°. The resulting yellow crystals were filtered and dried to give 0.25 g (16% yield) identified as *trans*-$[(C_6H_5)_3P]_2Ru(CO)_3$ by comparison of its infrared ν(CO) frequency at 1890 cm^{-1} (KBr pellet) with the ν(CO) frequency (1895 cm^{-1}) reported in the literature[15] for this compound.

(d) **Carbonylation of $[C_7H_8RuCl_2]_n$ in the Presence of Zinc.**—A mixture of 0.5 g (1.9/*n* mmol) of $[C_7H_8RuCl_2]_n$, 4.0 g (67.2 mg-atoms) of acid-washed granular zinc, and 100 ml of ethanol was boiled under reflux with magnetic stirring for 18 hr in a carbon monoxide atmosphere. The resulting orange solution

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[5] E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 2323 (1959).

[6] H. D. Kaesz, S. Winstein, and C. G. Kreiter, *J. Amer. Chem. Soc.*, **88**, 1319 (1966); R. W. Harrill and H. D. Kaesz, *ibid.*, **90**, 1449 (1968).

[7] E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 3178 (1959).

[8] G. Winkhaus and H. Singer, *J. Organometal. Chem.*, **7**, 487 (1967).

[9] R. Colton and R. H. Farthing, *Aust. J. Chem.*, **20**, 1283 (1967); B. F. G. Johnson, R. D. Johnston, and J. Lewis, *J. Chem. Soc. A*, 794 (1969); M. J. Cleare and W. P. Griffith, *ibid.*, *A*, 372 (1969).

[10] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **28**, 945 (1966).

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

[12] A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *J. Amer. Chem. Soc.*, **89**, 5595 (1967).

[13] J. A. Stanko and T. W. Starinshak, *Inorg. Chem.*, **8**, 2156 (1969).

[14] J. Chatt, B. L. Shaw, and A. E. Field, *J. Chem. Soc.*, 3466 (1964).

[15] J. P. Collman and W. R. Roper, *J. Amer. Chem. Soc.*, **87**, 4008 (1965).

Table I

Carbonylation of Various Ruthenium Compounds at Atmospheric Pressure

Ruthenium compound reactant	Reducing agent	Solvent	Temp, °C	Time, hr	Product containing ruthenium
(A) No Reducing Agent Used					
$[C_7H_8RuCl_2]_n$ (2.4 g)	None	MeOH	65	20	$[Ru(CO)_3Cl_2]_2$ (2.0 g)
$[C_7H_8RuCl_2]_n$ (4.0 g)	None	EtOH	78	14	$[Ru(CO)_3Cl_2]_2$ (3.3 g)
$[C_7H_8RuCl_2]_n$ (0.7 g)	None	Toluene	110	16	$[Ru(CO)_3Cl_2]_2$ (0.6 g)
$[C_6H_6RuCl_2]_n$ (2.1 g)	None	MeOH	25	40	$[Ru(CO)_3Cl_2]_2$ (1.7 g)
$[C_6H_6RuCl_2]_n$ (0.5 g)	None	EtOH	78	12	$[Ru(CO)_3Cl_2]_2$ (0.4 g)
$[Ru(N_2)(NH_3)_5]Cl_2$	None	EtOH	78	8	$[Ru(N_2)(NH_3)_5]Cl_2$ (no reaction obsd)
(B) Hydrazine Used as Reducing Agent					
$[C_7H_8RuCl_2]_n$	N_2H_4	EtOH	78	2	$[Ru(N_2)(NH_3)_5]Cl_2 + [Ru(CO)(NH_3)_5]Cl_2$
$[C_7H_8RuCl_2]_n$	N_2H_4	CH_3CN	82	6	$[Ru(N_2)(NH_3)_5]Cl_2 + [Ru(CO)(NH_3)_5]Cl_2$
$[C_7H_8RuCl_2]_n$	N_2H_4	C_6H_6	80	3	$[Ru(N_2)(NH_3)_5]Cl_2 + [Ru(CO)(NH_3)_5]Cl_2$
$[C_6H_6RuCl_2]_n$	N_2H_4	EtOH	78	21	$[Ru(N_2)(NH_3)_5]Cl_2 + [Ru(CO)(NH_3)_5]Cl_2$
$[Ru(CO)_2Cl_2]_n$ (1.0 g)	N_2H_4	EtOH	78	16	$[Ru(CO)(NH_3)_5]Cl_2$ (1.3 g)
$RuCl_3 \cdot 3H_2O$ (1.5 g)	N_2H_4	EtOH	78	20	$[Ru(N_2)(NH_3)_5]Cl_2$ (~1.8 g) + trace of $[Ru(CO)(NH_3)_5]Cl_2$
$[Ru(N_2)(NH_3)_5]Cl_2$	N_2H_4	EtOH	78	6	$[Ru(N_2)(NH_3)_5]Cl_2$ (no reaction obsd)
$[C_7H_8RuCl_2]_n$ (1.2 g) + Ph_3P (1.1 g)	N_2H_4	EtOH	78	6	$[Ru(N_2)(NH_3)_5]Cl_2 + [Ru(CO)(NH_3)_5]Cl_2 + (Ph_3P)_2Ru(CO)_3$ (0.7 g)
$[Ru(CO)_2Cl_2]_n$ (0.6 g) + Ph_3P (1.2 g)	N_2H_4	EtOH	78	8	$[Ru(CO)(NH_3)_5]Cl_2$ (0.7 g)
$RuCl_3 \cdot 3H_2O$ (1.5 g) + Ph_3P (1.5 g)	N_2H_4	EtOH	78	6	$[Ru(N_2)(NH_3)_5]Cl_2$ (1.2 g) + trace of $[Ru(CO)(NH_3)_5]Cl_2$
$(Ph_3P)_3RuCl_2$ (0.5 g)	N_2H_4	EtOH	78	12	$[Ru(CO)(NH_3)_5]Cl_2$ (0.05 g)
$[C_7H_8RuCl_2]_n$ (0.8 g) + $Ph_2PCH_2CH_2PPh_2$ (2.3 g)	N_2H_4	EtOH	78	8	$[Ru(CO)(NH_3)_5]Cl_2$ + trace $[Ru(N_2)(NH_3)_5]Cl_2$
trans-$(Ph_2PCH_2CH_2PPh_2)_2RuCl_2$	N_2H_4	EtOH	78	6	*trans*-$(Ph_2PCH_2CH_2PPh_2)_2RuCl_2$ (no reaction obsd)
(C) Zinc Used as Reducing Agent					
$[C_7H_8RuCl_2]_n$ (0.5 g)	Zn	EtOH	78	18	$Ru_3(CO)_{12}$ (0.28 g)
$[C_7H_8RuCl_2]_n$ (5.5 g)	Zn	EtOH	78	18	$C_7H_8Ru(CO)_2(OH)_2$ (3.4 g)
$[C_7H_8RuCl_2]_n$ (0.5 g)	Zn	*i*-PrOH	82	6	$C_7H_8Ru(CO)_2(OH)_2$ (0.35 g)
$[C_7H_8RuCl_2]_n$ (0.5 g)	Zn	*tert*-BuOH	82	14	$Ru_3(CO)_{12}$ (0.06 g) + $C_7H_8Ru(CO)_2(OH)_2$ (0.42 g)
$[C_7H_8RuCl_2]_n$ (1.0 g)	Zn	THF	67	14	$Ru_3(CO)_{12}$ (0.13 g) + $C_7H_8Ru(CO)_2(OH)_2$
$[C_6H_6RuCl_2]_n$ (2.0 g)	Zn	MeOH	65	10	$Ru_3(CO)_{12}$ (0.58 g)
$[C_6H_6RuCl_2]_n$ (1.0 g)	Zn	EtOH	78	6	$Ru_3(CO)_{12}$ (0.25 g)
$[C_6H_6RuCl_2]_n$ (2.0 g)	Zn	EtOH	78	14	$Ru_3(CO)_{12}$ (0.06 g) + $H_4Ru_4(CO)_{12}$ (0.2 g)
$[C_6H_6RuCl_2]_n$ (1.5 g)	Zn–LiOAc	EtOH	78	8	$H_2Ru_4(CO)_{13}$ (0.6 g)
$[C_6H_6RuCl_2]_n$ (1.0 g)	Zn	Me_2CO	56	2	$[Ru(CO)_3Cl_2]_2$ (0.8 g)
$[C_6H_6RuCl_2]_n$ (1.0 g)	Zn	$(i\text{-}Pr)_2O$	68	10	$[C_6H_6RuCl_2]_n$ (0.8 g) recovered + $[Ru(CO)_3Cl_2]_2$
$[C_6H_6RuCl_2]_n$ (1.0 g)	Zn	Toluene	110	20	$[Ru(CO)_3Cl_2]_2$ (0.74 g)
$[Ru(CO)_3Cl_2]_2$ (2.0 g)	Zn	MeOH	25	16	$Ru_3(CO)_{12}$ (0.3 g) + recovered $[Ru(CO)_3Cl_2]_2$
$[Ru(CO)_3Cl_2]_2$ (1.5 g)	Zn	MeOH	65	1.5	$Ru_3(CO)_{12}$ (0.45 g) + $H_2Ru_4(CO)_{13}$ (0.05 g)
(D) Other Reducing Agents					
$[C_7H_8RuCl_2]_n$ (1.0 g)	Mn	MeOH	65	18	$[Ru(CO)_3Cl_2]_2$ (0.6 g)
$[C_7H_8RuCl_2]_n$ (0.4 g)	$NaBH_4$	EtOH	78	16	Pyrophoric black solid (Ru metal)
$[C_7H_8RuCl_2]_n$ (0.5 g)	H_3PO_2	EtOH	78	16	No crystalline product

was filtered and the filtrate concentrated to give 0.28 g (~69% yield) of orange crystalline $Ru_3(CO)_{12}$, which was identified by its infrared spectrum in the $\nu(CO)$ region.

Various attempts to scale up this preparation of $Ru_3(CO)_{12}$ gave completely different results. Thus a mixture of 5.5 g (20.8/*n* mmol) of $[C_7H_8RuCl_2]_n$, 20 g (306 mg-atoms) of granular zinc, and 500 ml of ethanol was boiled under reflux with magnetic stirring for 18 hr in a carbon monoxide atmosphere. The resulting solution was filtered hot and then evaporated at 25° (40 mm). The residue was washed with water and then recrystallized from a mixture of chloroform and pentane to give 3.4 g (58% yield) of a yellow solid consisting mainly of $C_7H_8Ru(CO)_2(OH)_2$. A dichloromethane solution of this crude material was chromatographed on a alumina column. The small yellow band initially appearing on the column was eluted with hexane. Concentration of this eluate gave a small amount (0.06 g, 1.4% yield) of orange crystalline $Ru_3(CO)_{12}$. Further development and elution of the chromatogram with a mixture of dichloromethane and methanol gave a much larger yellow band. Evaporation of this eluate gave 2.4 g (41% yield) of yellow $C_7H_8Ru(CO)_2(OH)_2$, mp 235–238° dec. The compound $C_7H_8Ru(CO)_2(OH)_2$ was found to be diamagnetic by a magnetic susceptibility measurement of the solid compound on an Alpha Scientific Faraday balance.

The same product was obtained if isopropyl or *tert*-butyl alcohol was substituted for the ethanol solvent. Essentially the same results were also obtained if 3.8 g of $[C_7H_8RuCl_2]_n$ was carbonylated in the presence of excess zinc in 800 ml of ethanol. *Anal.* Calcd for $C_9H_{10}RuO_4$: C, 38.2; H, 3.5; O, 22.6; Cl, 0.0; Zn, 0.0. Found on two independent preparations in ethanol solution: C, 38.8, 38.6; H, 3.7, 3.9; O, 22.1, 21.6; Cl, 0.7; Zn, 0.8. Found on a preparation in isopropyl alcohol solution: C, 37.6; H, 3.4.

Infrared Spectrum (KBr Pellet).—$\nu(OH)$ frequency at 3455 (w, br) cm^{-1} (also observed in a Nujol mull); $\nu(CH)$ frequencies at 2975 (m), 2948 (m, sh), 2908 (w, sh), 2875 (w), and 2813 (vw) cm^{-1}; $\nu(CO)$ frequencies at 2058 (s, sh), 2044 (vs), and 1963 (vvs) cm^{-1} in KBr or at 2047 (vs) and 1970 (vs) cm^{-1} in chloroform solution; other bands at 1625 (m), 1541 (m), 1443 (w), 1420 (vw), 1400 (vw), 1375 (w), 1337 (w), 1264 (vw), 1222 (vw), 1063 (m), 1037 (m), 1023 (m, sh), 1003 (w, sh), 922 (vw), 866 (vw, sh), 843 (vw), 793 (vw), 708 (w), 650 (w), 582 (vw), and 480 (m) cm^{-1}.

(e) **Preparation of $[Ru(CO)_3Cl_2]_2$.**—A suspension of 2.4 g (9.1/*n* mmol) of $[C_7H_8RuCl_2]_n$ in 100 ml of methanol was boiled under reflux for 20 hr, with magnetic stirring in a carbon monoxide atmosphere. Solvent was removed from the filtered reaction mixture at ~25° (40 mm) to give 2.0 g (86% yield) of yellow solid $[Ru(CO)_3Cl_2]_2$. Further purification was effected by sublimation at 150° (1 mm). The sublimed $[Ru(CO)_3Cl_2]_2$ exhibited

ν(CO) frequencies at 2146 (s), 2138 (s), 2090 (vs), 2070 (vs), 2020 (w), and 2005 (w) cm^{-1} in chloroform solution (lit.[4] values: 2144 (vs), 2138 (vs, sh), 2084 (vs), 2063 (vs, sh), 2021 (m), 2016 (w), and 2009 (w, sh) cm^{-1}).

(f) **Conversion of $[C_6H_6RuCl_2]_n$ to $Ru_3(CO)_{12}$.**—A mixture of 2.0 g (8.0/n mmol) of $[C_6H_6RuCl_2]_n$, 16.0 g (245 mg-atoms) of zinc, and 200 ml of methanol was boiled under reflux for 10 hr with magnetic stirring in a carbon monoxide atmosphere. After cooling to room temperature the resulting suspension of the orange solid was decanted away from the unreacted zinc. The orange solid was separated from the solution by filtration and then dried to give 0.9 g of crude $Ru_3(CO)_{12}$. After recrystallization from a mixture of chloroform and methanol 0.58 g (34% yield) of orange crystalline $Ru_3(CO)_{12}$ was obtained. This product was identified by the ν(CO) frequencies at 2065 (s), 2035 (s), and 2012 (m) cm^{-1} in carbon tetrachloride solution (lit.[1] ν(CO) in CCl_4 solution 2061 (s), 2032 (s), and 2015 (m) cm^{-1}).

(g) **Conversion of $[Ru(CO)_3Cl_2]_2$ to $Ru_3(CO)_{12}$.**—A mixture of 1.5 g (2.92 mmol) of $[Ru(CO)_3Cl_2]_2$, 10 g (153 mg-atoms) of zinc, and 100 ml of methanol was boiled under reflux in a carbon monoxide atmosphere for 1.5 hr. The suspension was decanted away from the unreacted zinc and solvent removed at 25° (40 mm). The residue was extracted with chloroform and the filtered chloroform solution evaporated at 25° (40 mm). The residue was washed with methanol to give 0.45 g (36% yield) of orange crystalline $Ru_3(CO)_{12}$ identified as above from its infrared spectrum.

Removal of solvent from the methanol washings followed by sublimation of the residue at 110–130° (1.0 mm) gave 0.05 g (4.5% yield) of a red sublimate of $H_2Ru_4(CO)_{13}$.

(h) **Conversion of $[C_6H_6RuCl_2]_n$ to $H_2Ru_4(CO)_{13}$.**—A mixture of 1.5 g (6.0/n mmol) of $[C_6H_6RuCl_2]_n$, 6.0 g (92 mg-atoms) of zinc, 1.6 g (24.3 mmol) of lithium acetate, and 200 ml of ethanol was boiled under reflux for 8 hr in a carbon monoxide atmosphere. The reaction mixture was filtered. Solvent was removed from the brown filtrate at ~25° (40 mm). A brown oil remained. This was treated with 100 ml of water. The oil solidified. The solid was removed by filtration and dried. It was crystallized from a mixture of chloroform and hexane to give 0.8 g of an orange solid indicated by its infrared spectrum to be mainly $H_2Ru_4(CO)_{13}$. Sublimation of this solid at 100–110° (0.02 mm) gave 0.6 g (52% yield) of a red solid. The infrared spectrum of this solid in the ν(CO) region (cyclohexane solution) exhibited bands at 2082 (s), 2062 (s), 2055 (s), 2031 (m), 2025 (s), 2012 (w), and 1868 (w) cm^{-1}. The proton nmr spectrum of this solid in $CDCl_3$ solution exhibited high-field singlet resonances at τ 18.6 and 27.5. This indicates this product to be a mixture of the two reported[16] isomers of $H_2Ru_4(CO)_{13}$.

Reaction of $[Ru(CO)_2Cl_2]_n$ with Ammonia.—A mixture of 0.7 g (3.07/n mmol) of $[Ru(CO)_2Cl_2]_n$, 50 ml of concentrated aqueous ammonium hydroxide (~29% NH_3), and 100 ml of ethanol was stirred for 6 hr at room temperature. Solvent was then removed at ~25° (40 mm). The resulting brown-red solid was crystallized from a mixture of ethanol and water to give 0.3 g (34% yield) of a pink-yellow solid identified as $[Ru(NH_3)_5CO]Cl_2$ by the infrared ν(CO) frequency at 1930 (s) cm^{-1} (KBr pellet) and by bands at ~3200 (vs, br) and 1620 (m) cm^{-1} arising from the coordinated ammonia.

Reactions of Ruthenium Carbonyl Chlorides with Hydrazine.—A mixture of 0.5 g (2.19/n mmol) of $[Ru(CO)_2Cl_2]_n$, 5 ml of hydrazine hydrate, and 50 ml of ethanol was boiled under reflux for 4 hr. The resulting white solid was removed by filtration. Crystallization of this solid from a mixture of water and ethanol gave 0.6 g (96% yield) of a white solid identified as $[Ru(NH_3)_5CO]Cl_2$ by the infrared ν(CO) frequency and the infrared bands from the coordinated ammonia.

A mixture of 0.3 g (0.58 mmol) of $[Ru(CO)_3Cl_2]_2$, 5 ml of hydrazine hydrate, and 50 ml of ethanol was boiled under reflux for 2 hr. The white precipitate was removed by filtration and purified by crystallization from a mixture of water and ethanol to give 0.25 g (75% yield) of white $[Ru(NH_3)_5CO]Cl_2$ identified by its infrared spectrum and elemental analyses. *Anal.* Calcd for $CH_{15}Cl_2N_5ORu$: C, 4.2; H, 5.3; N, 24.2. Found: C, 3.2; H, 5.6; N, 22.2.

Reaction of $[C_7H_8RuCl_2]_n$ with Hydrazine.—A mixture of 0.4 g (1.51/n mmol) of $[C_7H_8RuCl_2]_n$, 5 ml of hydrazine hydrate, and 100 ml of ethanol was boiled under reflux for 30 hr. A yellow solid separated. This was removed by filtration and dried to give 0.32 g (74% yield) of $[Ru(NH_3)_5N_2]Cl_2$ identified by its infrared ν(NN) frequency at 2110 (vs) cm^{-1} and by infrared bands at ~3200 (vs, br) and 1610 (s) cm^{-1} arising from the coordinated ammonia. *Anal.* Calcd for $Cl_2H_{15}N_7Ru$: Cl, 24.9; H, 5.3; N, 34.4. Found: Cl, 24.6; H, 6.2; N, 34.1.

A similar reaction between $[C_7H_8RuCl_2]_n$ and excess hydrazine hydrate in aqueous solution at room temperature failed to give any $[Ru(NH_3)_5N_2]^{2+}$ or other Ru–N_2 complexes.

Reaction of $[Ru(CO)_3Cl_2]_2$ with Ethanol.—A mixture of 1.5 g (2.93 mmol) of $[Ru(CO)_3Cl_2]_2$ and 150 ml of ethanol was boiled under reflux for 36 hr. Solvent was removed from the resulting reaction mixture at ~25 (40 mm). A methanol solution of the resulting complex was decolorized with charcoal. The filtered methanol solution was concentrated and treated with diethyl ether to give 0.4 g (25% yield) of yellow solid $[(C_2H_5OH)Ru(CO)_2Cl_2]_n$. *Anal.* Calcd for $C_4H_6Cl_2O_3Ru$: C, 17.5; H, 2.2; Cl, 25.9; O, 17.5. Found: C, 17.7; H, 1.8; Cl, 26.3; O, 16.7.

Infrared Spectrum (KBr Pellet).—ν(OH) frequency at 3270 (s, br) cm^{-1}; ν(CH) frequencies at 3000 (vw) and 2986 (w) cm^{-1}; ν(CO) frequencies at 2080 (vs), 2015 (vs, sh), and 2005 (vs) cm^{-1} in a KBr pellet or at 2085 (vs) and 2010 (vs) cm^{-1} in chloroform solution; other bands at 1600 (w, br), 1405 (m), 1259 (w), 1085 (m), 1025 (s), 877 (m), 630 (w), 567 (w), 558 (w), 490 (m), 482 (m), and 451 (w) cm^{-1}.

Upon drying at 80° (0.1 mm) the $[(C_2H_5OH)Ru(CO)_2Cl_2]_n$ lost its ethanol to form $[Ru(CO)_2Cl_2]_n$.

Discussion

The carbonylation of $[(\text{diene})RuCl_2]_n$ (diene = norbornadiene or bidentate benzene) complexes in warm alcohol at atmospheric pressure resulted in the replacement of the coordinated olefins with carbon monoxide. This reaction is thus analogous to the reported[6] atmospheric pressure carbonylation of certain (diene)Mo$(CO)_4$ derivatives (diene = bidentate 1,3,5-cyclooctatriene or cyclooctatetraene) to give $Mo(CO)_6$. The product from the atmospheric pressure carbonylation of the $[(\text{diene})RuCl_2]_n$ complexes was the ruthenium carbonyl chloride $[Ru(CO)_3Cl_2]_2$ previously[4] obtained by the carbonylation of ruthenium trichloride at elevated pressures (~10 atm). The carbonylation of the $[(\text{diene})RuCl_2]_n$ complexes may thus be represented by the equation

$$(2/n)[(\text{diene})RuCl_2]_n + 6CO \longrightarrow [Ru(CO)_3Cl_2]_2 + 2(\text{diene})$$

where diene = norbornadiene or bidentate benzene. The presence of the carbon monoxide is essential to the stability of $[Ru(CO)_3Cl_2]_2$ in boiling ethanol. In the absence of carbon monoxide $[Ru(CO)_3Cl_2]_2$ loses one carbonyl group for each ruthenium atom to give the ethanol complex $[(C_2H_5OH)Ru(CO)_2Cl_2]_n$; this ethanol complex could be isolated in the pure state as a yellow crystalline solid. The infrared spectrum of $[(C_2H_5OH)Ru(CO)_2Cl_2]_n$ exhibited the expected two ν(CO) frequencies for a dicarbonyl in addition to a strong ν(OH) frequency from the coordinated ethanol. Reaction of $[(C_2H_5OH)Ru(CO)_2Cl_2]_n$ with carbon monoxide in boiling ethanol regenerates the carbonyl chloride $[Ru(CO)_3Cl_2]_2$ indicating the existence of the equilibrium

$$[Ru(CO)_3Cl_2]_2 + 2C_2H_5OH \rightleftharpoons (2/n)[(C_2H_5OH)Ru(CO)_2Cl_2]_n + 2CO$$

In addition, the complex $[(C_2H_5OH)Ru(CO)_2Cl_2]_n$ loses the coordinated ethanol at 80° (0.1 mm) to form $[Ru(CO)_2Cl_2]_n$. Once isolated, $[(C_2H_5OH)Ru(CO)_2Cl_2]_n$ was sparingly soluble in organic solvents.

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[16] B. F. G. Johnson, J. Lewis, and I. G. Williams, *J. Chem. Soc. A*, 901 (1970).

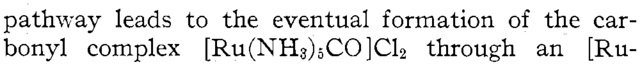
Therefore its molecular weight could not be determined.

Our objective in devising new routes to $Ru_3(CO)_{12}$ and other ruthenium(0) derivatives led to a study of the carbonylation of $[(diene)RuCl_2]_n$ complexes in the presence of strong reducing agents. In the earliest studies of this type hydrazine was used since it is both soluble and known[17] to effect similar reductions such as platinum(II) to platinum(0). Carbonylation of $[C_7H_8RuCl_2]_n$ at atmospheric pressure in the presence of hydrazine as a reducing agent yielded a solid product which gave variable analyses but which exhibited strong infrared bands at 1930 and 2107 cm^{-1} in addition to infrared bands around 3200 and 1600 cm^{-1} which arise from coordinated ammonia. The relative intensities of the strong 1930- and 2107-cm^{-1} bands in this product varied somewhat in different preparations. However, all other features of the infrared spectrum of its product were the same in different samples prepared by performing the carbonylation of $[C_7H_8RuCl_2]_n$ in the radically different solvents benzene, acetonitrile, and ethanol. The reaction solvent is therefore not incorporated as a ligand in this ruthenium complex. Comparison of the infrared spectrum and other properties of this product obtained from the carbonylation of $[C_7H_8RuCl_2]_n$ in the presence of hydrazine with those reported for the known compounds $[Ru(NH_3)_5N_2]Cl_2$[12] and $[Ru(NH_3)_5CO]Cl_2$[13] suggests that this carbonylation product is a mixture of these two compounds with the infrared band at 1930 cm^{-1} being assigned to the $\nu(CO)$ frequency in $[Ru(NH_3)_5CO]Cl_2$ and the infrared band at 2107 cm^{-1} being assigned to the $\nu(NN)$ frequency in $[Ru(NH_3)_5N_2]Cl_2$.

The reaction of $[C_7H_8RuCl_2]_n$, hydrazine, and carbon monoxide appears to proceed by two parallel pathways (Scheme I). The first pathway leads to the formation of the nitrogen complex $[Ru(NH_3)_5N_2]Cl_2$ without involvement of the carbon monoxide. Indeed, the nitrogen complex $[Ru(NH_3)_5N_2]Cl_2$ can be prepared by heating $[C_7H_8RuCl_2]_n$ with hydrazine hydrate in ethanol in the absence of carbon monoxide. The second pathway leads to the eventual formation of the carbonyl complex $[Ru(NH_3)_5CO]Cl_2$ through an $[Ru(CO)_3Cl_2]_2$ intermediate. The presence of a ruthenium carbonyl chloride intermediate is suggested not only by the carbonylation of $[C_7H_8RuCl_2]_n$ in the absence of hydrazine to give $[Ru(CO)_3Cl_2]_2$ as described above but also by the separately demonstrated reaction of $[Ru(CO)_3Cl_2]_2$ with hydrazine in boiling ethanol to give the carbonyl complex $[Ru(NH_3)_5CO]Cl_2$. The distinctness of these two pathways in Scheme I is indicated by the separately demonstrated failure of pure $[Ru(NH_3)_5N_2]Cl_2$ to undergo carbonylation in boiling ethanol to give $[Ru(NH_3)_5CO]Cl_2$ even in the presence of hydrazine.

Scheme I

Reaction of $[(diene)RuCl_2]_n$ Complexes with Hydrazine and Carbon Monoxide in Boiling Ethanol



The reaction between the ruthenium(II) derivative $[C_7H_8RuCl_2]_n$, hydrazine, and carbon monoxide gives only other ruthenium(II) derivatives, *i.e.*, $[Ru(NH_3)_5N_2]Cl_2$ and $[Ru(NH_3)_5CO]Cl_2$. Thus, in this reaction hydrazine is not effective in converting a ruthenium(II) derivative to a ruthenium(0) derivative. In order to find conditions where hydrazine might reduce a ruthenium(II) complex to a ruthenium(0) complex, the reductive carbonylations of $[C_7H_8RuCl_2]_n$ with hydrazine were repeated in the presence of certain tertiary phosphines. The reductive carbonylation of a mixture of $[C_7H_8RuCl_2]_n$ and triphenylphosphine with hydrazine gave the same toluene-insoluble mixture of $[Ru(NH_3)_5CO]Cl_2$ and $[Ru(NH_3)_5N_2]Cl_2$ as was obtained in the absence of triphenylphosphine. In addition, however, a toluene-soluble compound was also obtained. This latter compound exhibited a single strong $\nu(CO)$ frequency at 1895 cm^{-1} indicating it to be the known[15] ruthenium(0) derivative *trans*-$[(C_6H_5)_3P]_2Ru(CO)_3$. Thus in the presence of both triphenylphosphine and carbon monoxide the ruthenium(II) derivative $[C_7H_8RuCl_2]_n$ can be reduced to a ruthenium(0) derivative. The reductive carbonylation of the triphenylphosphine–ruthenium(II) complex $[(C_6H_5)_3P]_3RuCl_2$[10] with hydrazine was also investigated. In this case the only isolable ruthenium complex was the carbonyl $[Ru(NH_3)_5CO]Cl_2$ identified by its characteristic $\nu(CO)$ frequency. None of the nitrogen complex $[Ru(NH_3)_5N_2]Cl_2$ was obtained. Apparently, the presence of coordinated triphenylphosphine inhibits the reaction of ruthenium(II) derivatives with hydrazine to give the nitrogen complex $[Ru(NH_3)_5N_2]Cl_2$. The triphenylphosphine ligands may block coordination positions that are needed for the necessarily complex process of generating a coordinated N_2 ligand from hydrazine.

The carbonylation of ruthenium complexes in the presence of the chelating ditertiary phosphine $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (abbreviated as Pf-Pf) was investigated also using hydrazine as the reducing agent. Addition of Pf-Pf to $[C_7H_8RuCl_2]_n$ in ethanol prior to carbonylation at the boiling point in the presence of hydrazine had no effect, since the only ruthenium compounds which could be isolated from the reaction were $[Ru(NH_3)_5N_2]Cl_2$ and $[Ru(NH_3)_5CO]Cl_2$. The complex *trans*-$(Pf\text{-}Pf)_2RuCl_2$ was recovered unchanged when subjected to carbonylation in boiling ethanol in the presence of hydrazine. The failure for *trans*-$(Pf\text{-}Pf)_2RuCl_2$ to form ammines when treated with hydrazine even in the presence of carbon monoxide may arise from difficulties in displacing the bidentate chelating Pf-Pf ligands.

The use of hydrazine as a reducing agent in the carbonylation of $[(diene)RuCl_2]_n$ derivatives thus does not provide a promising route for the preparation of $Ru_3(CO)_{12}$. In a further attempt to develop an improved preparation of $Ru_3(CO)_{12}$ some atmospheric pressure carbonylations of $[(diene)RuCl_2]_n$ derivatives were carried out in ethanol solution in the presence of zinc, a satisfactory reducing agent for the preparation of $Ru_3(CO)_{12}$ by the carbonylation of $RuCl_3 \cdot 3H_3O$ at elevated pressures. Initially, this procedure appeared very promising since yields of up to ~70% of $Ru_3(CO)_{12}$ were obtained upon carbonylation *at atmospheric pressure* of the norbornadiene complex $[C_7H_8$-

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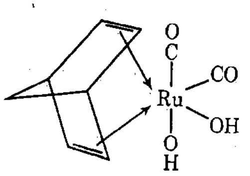
[17] L. Malatesta and C. Cariello, *J. Chem. Soc.*, 2323 (1958).

$RuCl_2]_n$ on a 0.5-g scale in the presence of excess acid-washed metallic zinc. However, when an attempt was made to scale up this reaction, the yield of $Ru_3(CO)_{12}$ decreased drastically at the expense of a yellow solid of stoichiometry $C_7H_8Ru(CO)_2(OH)_2$. The presence of two strong ν(CO) frequencies of approximately equal relative intensities supports formulation of this compound as a dicarbonyl. Furthermore, the same ruthenium compound was obtained when isopropyl or *tert*-butyl acohol was substituted for the ethanol solvent indicating that the alkyl group of the alcohol was not incorporated in the product. The diamagnetism of $C_7H_8Ru(CO)_2(OH)_2$ indicates that the ruthenium is in an even oxidation state. Unfortunately, $C_7H_8Ru(CO)_2(OH)_2$ was too insoluble in appropriate solvents for observation of its nmr spectrum to confirm directly the presence of a nonbornadiene ligand. In addition its volatility was too low for a mass spectrum to be obtained. All of these data suggest formulation of $C_7H_8Ru(CO)_2(OH)_2$ as an octahedral ruthenium(II) derivative of structure I or a geometrical isomer thereof. Attempts to replace the hydroxyl groups in $C_7H_8Ru(CO)_2(OH)_2$ with chlorine atoms by treatment with thionyl chloride led instead to decomposition.



I

The formation of $C_7H_8Ru(CO)_2(OH)_2$ thus appears to make the reductive carbonylation at atmospheric pressure of $[C_7H_8RuCl_2]_n$ with zinc an unsatisfactory method for the preparation of $Ru_3(CO)_{12}$ in quantity. Part of the difficulty may arise from the fact that the bonds between ruthenium and the chelating diolefin norbornadiene are not broken under these reaction conditions. This problem can be circumvented if a $[(diene)RuCl_2]_n$ complex with a more weakly bonded diolefin can be substituted for the norbornadiene complex $[C_7H_8RuCl_2]_n$. For this purpose the bidentate benzene complex[8] $[C_6H_6RuCl_2]_n$ was selected because the resonance stability of free benzene should make coordinated benzene more readily displaced from its complexes than coordinated norbornadiene. The reductive carbonylation of $[C_6H_6RuCl_2]_n$ in ethanol solution with zinc gave $Ru_3(CO)_{12}$. However, the reaction time was found to be very critical since if the period of carbonylation was too long, the yield of $Ru_3(CO)_{12}$ decreased drastically in favor of the tetrametallic ruthenium carbonyl hydride[16] $H_4Ru_4(CO)_{12}$. The infrared spectrum of the $H_4Ru_4(CO)_{12}$ obtained in the reaction exhibited ν(CO) frequencies in CCl_4 solution at 2082 (m), 2070 (s), 2031 (m), 2025 (m), and 2010 (w) cm^{-1} and a high-field nmr resonance in $CDCl_3$ solution at τ 27.5 in accord with the properties recently[18] reported for this complex (ν(CO) 2081 (s), 2067 (vs), 2029 (m), 2024 (s), and 2009 (w) cm^{-1}; τ(Ru–H) 28.0). The formation of $H_4Ru_4(CO)_{12}$ in this reaction suggests that $Ru_3(CO)_{12}$ is unstable in boiling ethanol solution in 1 atm of carbon monoxide at least in the presence of the zinc chloride by-product. This is consistent with the reported[16] reaction of $Ru_3(CO)_{12}$ with boiling di-*n*-butyl ether to give tetrametallic hydrides of the types $H_4Ru_4(CO)_{12}$ and $H_2Ru_4(CO)_{13}$ even in the absence of added acids, bases, or metal halides.

In order to improve the yield of $Ru_3(CO)_{12}$ obtained in the reductive carbonylation of $[C_6H_6RuCl_2]_n$ with zinc, conditions to effect this reaction must be found where $Ru_3(CO)_{12}$ is not converted to the tetrametallic hydrides. Use of boiling methanol rather than boiling ethanol as the solvent for the reductive carbonylation of $[C_6H_6RuCl_2]_n$ with zinc improves somewhat the yield of $Ru_3(CO)_{12}$ probably because of the lower boiling point of methanol (65°) relative to ethanol (78°). When the carbonylation of $[C_6H_6RuCl_2]_n$ is performed in the presence of zinc in nonhydroxylic solvents such as acetone, diisopropyl ether, or toluene, the zinc does not enter into the reaction; instead the ruthenium(II) carbonyl chloride $[Ru(CO)_3Cl_2]_2$ is formed. The use of a hydroxylic solvent such as an alcohol thus appears to be essential in the reductive carbonylation of ruthenium halides with zinc. Carbonylation of $[C_6H_6RuCl_2]_n$ using manganese rather than zinc as the metallic reducing agent gave only $[Ru(CO)_3Cl_2]_2$ even in boiling methanol; the manganese thus did not enter into the reaction.

The reductive carbonylation of $[C_6H_6RuCl_2]_n$ with zinc was also performed in boiling ethanol in the presence of lithium acetate. In this case the major ruthenium carbonyl product was the tetrametallic hydride $H_2Ru_4(CO)_{13}$.[16] This reaction appears to be of some value for the efficient preparation of $H_2Ru_4(CO)_{13}$ from hydrated ruthenium trichloride through $[C_6H_6RuCl_2]_n$ without the need to go through $Ru_3(CO)_{12}$ as an intermediate.

This work suggests that the ruthenium(II) carbonyl chloride $[Ru(CO)_3Cl_2]_2$ can be prepared efficiently by the carbonylation at atmospheric pressure of $[(diene)RuCl_2]_n$ complexes in the absence of a strong reducing agent but that the ruthenium(0) carbonyl $Ru_3(CO)_{12}$ cannot be prepared efficiently by the reductive carbonylation at atmospheric pressure of $[(diene)RuCl_2]_n$ complexes because of side reactions. Appreciably superatmospheric pressures of carbon monoxide thus appear to be necessary to inhibit the destruction of $Ru_3(CO)_{12}$ in side reactions which reduce the yield. Another possible approach to the efficient preparation of $Ru_3(CO)_{12}$ at atmospheric carbon monoxide pressure appeared to be the reductive carbonylation of $[Ru(CO)_3Cl_2]_2$ which has three carbonyl groups for each ruthenium atom and hence should undergo reductive carbonylation under much milder conditions than the $[(diene)RuCl_2]_n$ complexes which contain no carbonyl groups. The reductive carbonylation of $[Ru(CO)_3Cl_2]_2$ with zinc proceeded slowly in methanol even at room temperature to give an 18% yield of $Ru_3(CO)_{12}$ after 16 hr with the concurrent recovery of some unchanged $[Ru(CO)_3Cl_2]_2$. The yield of $Ru_3(CO)_{12}$ was increased to 36% by carrying out the reductive carbonylation of $[Ru(CO)_3Cl_2]_2$ with zinc in boiling methanol for a relatively short period, but even under these conditions a small yield (4.5%) of the tetrametallic hydride $H_2Ru_4(CO)_{13}$ was also obtained.

In summary, the conversion of $RuCl_3 \cdot 3H_2O$ to $Ru_3(CO)_{12}$ without using carbon monoxide at superatmo-

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(18) H. D. Kaesz, S. A. R. Knox, J. W. Koepke, and R. B. Saillant, *Chem. Commun.*, 477 (1971).

spheric pressures can best be done by the three-step sequence

$$\mathrm{RuCl_3 \cdot 3H_2O} + 1,3\text{-}\mathrm{C_6H_8} \longrightarrow [\mathrm{C_6H_6RuCl_2}]_n \quad (\mathrm{C_6H_8} = 1,3\text{-cyclohexadiene}) \qquad (1)$$

$$(2/n)[\mathrm{C_6H_6RuCl_2}]_n + 6\mathrm{CO} \longrightarrow [\mathrm{Ru(CO)_3Cl_2}]_2 + 2\mathrm{C_6H_6} \qquad (2)$$

$$3[\mathrm{Ru(CO)_3Cl_2}]_2 + 6\mathrm{CO} + 6\mathrm{Zn} \longrightarrow 2\mathrm{Ru_3(CO)_{12}} + 6\mathrm{ZnCl_2} \qquad (3)$$

Combination of steps 2 and 3 into a single step is less satisfactory since under conditions where the coordinated diolefin ligands in $[(\mathrm{diene})\mathrm{RuCl_2}]_n$ complexes can be replaced by carbon monoxide, the ultimate product $\mathrm{Ru_3(CO)_{12}}$ undergoes appreciable decomposition with the tetrametallic ruthenium carbonyl hydrides (*e.g.*, $\mathrm{H_4Ru_4(CO)_{12}}$) among the decomposition products.

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The Chemistry of Methyltitanium Trichloride. II. Variable-Temperature Nuclear Magnetic Resonance and Infrared Spectra of Some Complexes of Methyltitanium Trichloride and of Titanium Tetrachloride with Unsymmetrical Bidentate Ligands

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The pseudooctahedral complexes of methyltitanium trichloride with the unsymmetrical bidentate ligands methyl β-dimethylaminoethyl ether, methyl β-methylthioethyl ether, and methyl β-dimethylaminoethyl sulfide are precipitated on mixing hexane solutions of methyltitanium trichloride and the appropriate ligand. They are intensely colored solids, extremely sensitive to atmospheric oxygen and moisture and thermally unstable, decomposing gradually on storage *in vacuo* at room temperature. The nmr spectra of the complexes show that, in solution, they prefer to adopt that meridional configuration in which the harder ligand atom lies trans to the titanium–methyl group. In their ir spectra, the complexes all show bands in the 450–490-cm^{-1} region, which are assigned to ν(Ti–C). These bands are absent from the ir spectra of the corresponding complexes of titanium tetrachloride, which we have also prepared and characterized (mainly to assist in the assignment of nmr data). By contrast to the foregoing, the product isolated from the reaction of methyltitanium trichloride with *N,N,N′,N′*-tetramethyl-*o*-aminobenzylamine (B) is a titanium(III) derivative which can be formulated as $\mathrm{TiCl_3 \cdot B}$.

Introduction

In the course of investigations directed toward the elucidation of detailed mechanisms for the action of Ziegler-type catalysts, we have reported,[1] on the basis of the results of a variable-temperature nmr study, that the pseudooctahedral complexes of methyltitanium trichloride with the symmetrical bidentate ligands $\mathrm{CH_3OCH_2CH_2OCH_3}$, $\mathrm{(CH_3)_2NCH_2CH_2N(CH_3)_2}$, and $\mathrm{CH_3SCH_2CH_2SCH_3}$ prefer to adopt a mer configuration (I) at low temperatures. At room temperature, the ligand–methyl groups of each complex give rise to a single peak in the nmr spectrum due to the operation of what we have referred to as a primary exchange process, which could involve, *e.g.*, opening and reclosure of the chelate ring, or a twist mechanism. No evidence could be found in the low-temperature spectra for the presence of fac isomer (II) (Figure 1). Indeed the observation that the chemical shift of the titanium–methyl group in each complex remained virtually constant (within 0.02 ppm) throughout the temperature range (+27 to −100°) in which the complexes were examined would suggest that the fac isomer does not participate in the exchange process occurring at the higher temperatures to any significant extent.

The present report is concerned principally with the preparation, properties, and variable-temperature nmr spectra of the complexes (III–V, respectively) of methyltitanium trichloride with the unsymmetrical bidentate ligands $\mathrm{CH_3OCH_2CH_2N(CH_3)_2}$, $\mathrm{CH_3OCH_2CH_2SCH_3}$, and $\mathrm{(CH_3)_2NCH_2CH_2SCH_3}$. An attempt to prepare the complex of methyltitanium trichloride with $o\text{-}\mathrm{C_6H_4[CH_2N(CH_3)_2]N(CH_3)_2}$ led to the isolation of a 1:1 complex of this ligand with titanium trichloride (VI). We have also prepared the complexes (VII–X, respectively) of these four ligands and of $\mathrm{(CH_3)_2NCH_2CH_2N(CH_3)_2}$ (XI)[2] with titanium tetrachloride. It was hoped that, as a result of this study, we might be able to answer two questions. (i) If, as our earlier investigations suggest, the complexes of methyltitanium trichloride adopt a mer configuration, which of the two possible mer configurations (*vide infra*) would be preferred? (ii) What is the mechanism of the primary exchange process referred to above?

Experimental Section

Spectra.—Nmr spectra were run on methylene chloride solutions of the complexes in sealed tubes using a Varian Associates HA100 instrument. Samples were prepared and chemical shift (τ) values were determined as described previously.[1]

Ir spectra were recorded on Nujol mulls using a Perkin-Elmer 225 spectrometer. The samples were prepared under dry nitrogen in an evacuable drybox and placed between thin polythene sheets supported between cesium iodide plates.

Analyses.—Carbon, halogen, and nitrogen analyses were performed by the departmental analyst. Titanium and chlorine were determined as outlined previously.[1]

Starting Materials.—The treatment of solvents (hexane and dichloromethane) and titanium tetrachloride and the preparation of dimethylzinc were carried out as before.[1]

$\mathrm{CH_3OCH_2CH_2N(CH_3)_2}$ was obtained by reaction of β-dimethyl-

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[1] R. J. H. Clark and A. J. McAlees, *J. Chem. Soc. A*, 2026 (1970).

[2] R. Tabacchi, L. Vuitel, and A. Jacot-Guillarmod, *Helv. Chim. Acta*, **53**, 1495 (1970).