Synthesis and Catalytic Properties of Some Carbonyltriphenylphosphine-ruthenium(II) Complexes

By **Brian R. James** * and **Larry D. Markham**, Chemistry Department, University of British Columbia, Vancouver 8, B.C., Canada
Benjamin C. Hui and **Garry L. Rempel**, Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada

The preparation of $[HRuCl(CO)_2(PPh_3)_2]$, $[RuCl_2(CO)_2(PPh_3)_2]$, $[RuCl_2(CO)(PPh_3)_2]$, and $[RuCl_2(CO)(PPh_3)_2L]$ complexes (L = *NN'*-dimethylformamide, *NN'*-dimethylacetamide, or dimethyl sulphoxide) from $[RuCl_2(PPh_3)_3]$ is reported. Analogous bromo-complexes were also synthesised. The solvent molecules (L) are co-ordinated to the metal through oxygen, and are removed by recrystallisation from methylene chloride–methanol. Under mild conditions the carbonyl complexes show low activity for homogeneous olefin hydrogenation and are ineffective for hydroformylation, but the five-co-ordinate complex $[RuCl_2(CO)(PPh_3)_2]$ is efficient as an olefin isomerisation catalyst.

PREVIOUS work from this laboratory[1] has shown that *NN'*-dimethylacetamide (dma) solutions of the complex $[RuCl_2(PPh_3)_3]$ readily absorb hydrogen according to reaction (1), and the hydrido-complex is isolable[2] as the

$$[RuCl_2(PPh_3)_3] + H_2 \rightleftharpoons [HRuCl(PPh_3)_3] + HCl \quad (1)$$

dma solvate $[HRuCl(PPh_3)_3]$,dma. In contrast to the reaction in benzene,[3] the basic dma solvent stabilises the HCl product and the equilibrium lies well to the right at ambient conditions.[4] *NN'*-Dimethylformamide (dmf) is much less suitable for the reaction since only *ca.* 0·1 mol of H_2 is absorbed per mol of complex at 35 °C and 1 atm pressure. The complex $[RuCl_2(PPh_3)_3]$ dissolves in dimethyl sulphoxide (dmso) to give bright yellow, air-stable solutions which do not react with H_2 under ambient conditions even in the presence of excess of a base such as triethylamine; these yellow solutions probably contain the $[RuCl_2(dmso)_4]$ complex.[5]

---

[1] B. R. James and L. D. Markham, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 373.

[2] B. R. James and L. D. Markham, *J. Catalysis*, 1972, **27**, 442.

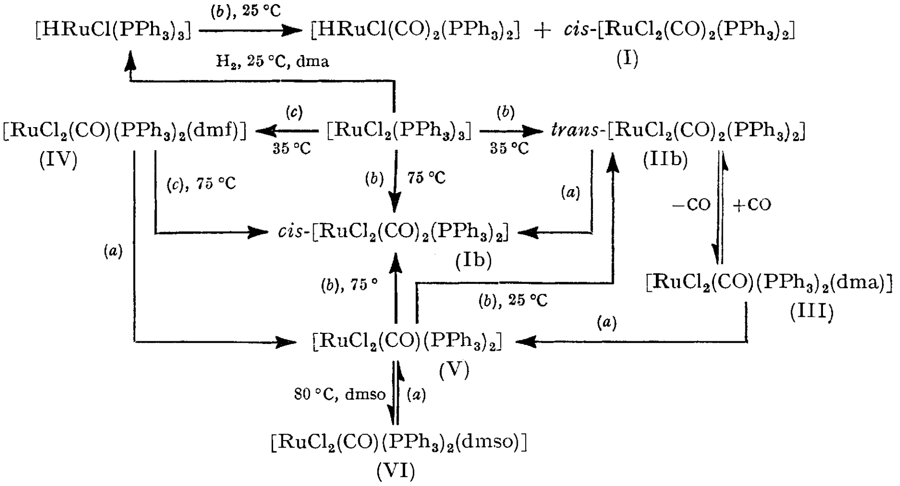
[3] P. S. Hallman, B. R. McGarvey, and G. Wilkinson, *J. Chem. Soc. (A)*, 1968, 3143.

[4] B. R. James and L. D. Markham, unpublished work.

[5] B. R. James, E. Ochiai, and G. L. Rempel, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 781; I. P. Evans, A. Spencer, and G. Wilkinson, *J.C.S. Dalton*, 1973, 204.

This paper discusses the reactions of the complexes $[RuX_2(PPh_3)_3]$ and $[HRuX(PPh_3)_3]$ (X = Cl or Br) with carbon monoxide in dmf or dma. A five-co-ordinate complex, $[RuX_2(CO)(PPh_3)_2]$, has been synthesised and is an effective olefin isomerisation catalyst. The Scheme summarises a number of the reactions described for the chloro-complexes.

RESULTS AND DISCUSSION



[a] Recrystallised from CH_2Cl_2–MeOH without heating. [b] CO,dma at temperature noted. [c] CO,dmf at temperature noted.

SCHEME

We have reported briefly[1] on the rapid reaction of carbon monoxide gas with a dma solution of the complex $[HRuCl(PPh_3)_3]$ (prepared *in situ*) which yields a mixture of the complexes $[HRuCl(CO)_2(PPh_3)_2]$ and $[RuCl_2(CO)_2(PPh_3)_2]$, (I). These two *cis*-dicarbonyl products, which have very similar carbonyl stretching frequencies (Table), can be separated by recrystallisation from methylene chloride–methanol without heating. Reaction of the complex $[RuBr_2(PPh_3)_3]$ with H_2 in dma yields violet solutions containing the hydride $[HRuBr(PPh_3)_3]$ ($\lambda_{max.}$ 530 nm, ε 2 000 l mol^{-1} cm^{-1}); such solutions react with CO to give the complex $[HRuBr(CO)_2(PPh_3)_2]$. The symmetrical triplet structure of the high-field hydride resonance in the n.m.r. spectra of the dicarbonylchlorohydrido-complex [τ 14·5, *J*(PH) 19 Hz, in CH_2Cl_2] and the bromo-complex [τ 15·0, *J*(PH) 19 Hz, in CH_2Cl_2] shows that the hydride is *cis* to two equivalent phosphines as in isomer (VIIa) or (VIIb). Our previous assignment[1] of structure (VIIa) to the chlorohydrido-complex and structure (Ia) to the dichloro-complex (I) cannot be considered certain, despite the close similarity of the ν(CO) peak positions to those observed[6] for isomer (Ia) of the corresponding complexes with PEt_3 and PEt_2Ph, since in general a shift of ν(CO) to higher energy occurs with increasing aromatic substitution of the phosphine ligand.[7]*

Complex	$\tilde{\nu}$(CO) [a]/cm^{-1} Nujol	 CH_2Cl_2	Ref.
$[HRuCl(CO)_2(PPh_3)_2]$	2 042, 2 032, 1 995, 1 982	2 042, 1 983	*b*
$[HRuBr(CO)_2(PPh_3)_2]$	2 030, 1 980	2 038, 1 976	*b*
$[RuCl_2(CO)_2(PPh_3)_2]$ (I)	2 042, 1 967	2 043, 1 979	*b*
$[RuCl_2(CO)_2(PPh_3)_2]$ (Ib)	2 064, 2 001		9, *b*
$[RuCl_2(CO)_2(PPh_3)_2]$ (II)	2 005	1 997 [c]	8, *b*
$[RuCl_2(CO)(PPh_3)_2]$ (V)	1 931, 1 921	1 940	*b*
$[RuCl_2(CO)(PPh_3)_2(dma)]$ (III) [d]	1 937, 1 929	1 946	*b*
$[RuCl_2(CO)(PPh_3)_2(dmf)]$ (IV) [e]	1 928, 1 911, 1 871vw		*b*
$[RuCl_2(CO)(PPh_3)_2(dmso)]$ (VI) [f]	1 935	1 948	*b*
$[RuBr_2(CO)(PPh_3)_2]$	1 930, 1 918	1 938	*b*
$[RuBr_2(CO)(PPh_3)_2(dma)]$ [d]	1 937, 1 928	1 943	*b*
$[RuBr_2(CO)(PPh_3)_2(dmf)]$ [e]	1 927, 1 911, 1 871vw	1 934	*b*
$[RuBr_2(CO)(PPh_3)_2(dmso)]$ [f]	1 935		*b*

[a] All bands were strong, unless noted otherwise. [b] Present work. [c] In dma. [d–f] Bands due to co-ordinated solvent appear in Nujol mull at 1 610 (*d*), 1 630 (*e*), and 985, 956, and 929 cm^{-1} (*f*).

Reaction of a solution or suspension of the complex $[RuCl_2(PPh_3)_3]$ in dma with 1 atm CO at 35 °C resulted in rapid uptake of 2·0 mol of gas per mol of ruthenium, the final solution product being the known[8] yellow *trans*-dicarbonyl complex (II) having ν(CO) at 1 997 cm^{-1} in dma. When this reaction was carried out at 75 °C the product was the more stable white *cis*-dicarbonyl complex, (Ib) [ν(CO) 2 064, 2 001 cm^{-1}], which has been prepared by several groups;[9] this complex was also obtained on recrystallisation of the *trans*-dicarbonyl complex (II) from methylene chloride–methanol with heating. dma Solutions of (II) are not

---

* *Note added in proof:* A recent study by Fahey (*J. Org. Chem.*, 1973, **38**, 80) reports the proton-decoupled ^{13}C n.m.r. spectrum of the *cis*-isomer (Ib), and shows that this complex has configuration (Ia). This implies that complex (I) and the chlorohydrido-complex have configuration (VIIb). This study and a recent abstract (D. R. Fahey, *6th Internat. Conf. Organometallic Chem.*, Amherst, 1973, Abstract 59) report the use of complex (Ib) for hydrogenation of olefins at elevated temperatures and pressures.

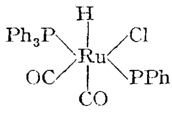
[6] J. Chatt, B. L. Shaw, and A. E. Field, *J. Chem. Soc.*, 1964, 3466.

[7] P. John, *Chem. Ber.*, 1970, **103**, 2178.

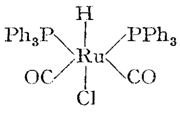
[8] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1966, **28**, 945.

[9] N. Ahmad, S. D. Robinson, and M. F. Uttley, *J.C.S. Dalton*, 1972, 843 and references therein.

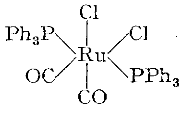
stable *in vacuo* and quite readily evolve 1 mol CO per ruthenium atom; the i.r. peak at 1 997 cm^{-1} disappeared in *ca.* 5 min and was replaced by that of a monocarbonyl complex at 1 925 cm^{-1}. This process was readily reversed on subsequent treatment with CO. Concentration of dma solutions of complex (II) *in vacuo* resulted in deposition of the monocarbonyl as the yellow complex [$RuCl_2(CO)(PPh_3)_2$(dma)], (III). The carbonyl stretching frequency due to co-ordinated dma [ν(CO) at 1 610 cm^{-1}] was some 50 cm^{-1} lower than that for the free solvent, indicating co-ordination to the metal through oxygen.[10] Complex (III) was also isolated from dma solutions of the complex [$RuCl_2(PPh_3)_3$] at 25 °C after some time, *via* slow decarbonylation of the solvent.



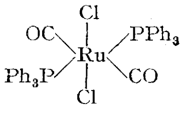
(VIIa)



(VIIb)



(Ia)



(II)

During the mild carbonylation reaction to give complex (II), we[1] and others[8] have observed a solution intermediate having a single carbonyl stretch at *ca.* 1 920 cm^{-1}, that has been assigned to another *trans*-isomer with both *cis*-chloride and -phosphine ligands. This intermediate is, however, almost certainly the monocarbonyl complex. The extreme lability of the CO ligand *trans* to another CO in complex (II) is in agreement with observations that *trans*-dicarbonyl complexes are generally much less stable than the corresponding *cis*-isomers because of the strong π-acceptor property of co-ordinated CO.[6] The i.r. spectrum of a dma solution of either of the *cis*-dicarbonyl complexes (I) or (Ib) was unchanged after several hours *in vacuo*.

Solutions or suspensions of the complex [$RuCl_2(PPh_3)_3$] in dmf absorbed only 1 mol of CO per mol of complex at 35 °C and 1 atm to give a yellow monocarbonyl complex [$RuCl_2(CO)(PPh_3)_2$(dmf)], (IV); at 75 °C a second mol of CO slowly reacted with this complex to give the *cis*-dicarbonyl complex [$RuCl_2(CO)_2(PPh_3)_2$], (Ib). The reason for the much more facile absorption of the second mol of CO in the dma solution is not clear, since the co-ordinating strengths of dma and dmf appear to be very similar.[11]

A dmf solution of $RuCl_3,3H_2O$, which had been reduced previously by reaction with 1 atm H_2 at 80 °C for 24 h, precipitated complex (IV) on addition of excess of triphenylphosphine; in this case the carbonyl complex must arise *via* decarbonylation of the solvent.[12] Complex (IV) was also precipitated on adding 1 atm CO at 25 °C to a dmf solution of $RuCl_3,3H_2O$ containing excess of phosphine; (IV) similarly precipitated if the $RuCl_3$–PPh_3–dmf solution was pretreated for 12 h at 70 °C with 1 atm H_2, when small amounts of the violet hydrido-complex were present. Treatment of a dmf solution of $RuCl_3,3H_2O$ with H_2 at 80 °C for much longer periods (*ca.* 60 h) yielded brown solutions which probably[13] contain ruthenium(I). Addition of acetic acid–sodium acetate, and then triphenylphosphine, led to formation of the dimeric ruthenium(I) complex [$Ru(O_2CMe)(CO)_2$-$PPh_3]_2$, which has been prepared previously by Lewis and his co-workers[14] using $Ru_3(CO)_{12}$ as starting material.

The co-ordinated dma and dmf ligands in complexes (III) and (IV), respectively, were removed by recrystallisation from methylene chloride–methanol, and the five-co-ordinate yellow complex [$RuCl_2(CO)(PPh_3)_2$], (V), was formed. When complex (III), (IV), or (V) was dissolved in dmso at 80 °C, the product recovered on concentrating the solution was [$RuCl_2(CO)(PPh_3)_2$-(dmso)], (VI); recrystallisation again removed co-ordinated dmso. The i.r. spectrum of complex (VI) showed peaks due to dmso at 985, 956, and 929 cm^{-1} (Nujol), indicating that the sulphoxide ligand is co-ordinated through oxygen,[5] as for the dma and dmf complexes.

Complex (V) apparently isomerised in methylene chloride solution with the original 1 940 cm^{-1} carbonyl band being gradually replaced by a rather broad band at 1 970 cm^{-1}; however, only the original isomer precipitated from solution on addition of methanol. In one instance, a yellow crystalline product having a sharp carbonyl band at 1 977 cm^{-1} (Nujol) and no co-ordinated solvent was obtained after treatment of complex (III) with hot acetone, but attempts to reproduce this synthesis gave isomer mixtures. Solutions of complex (V) showed no reaction toward O_2 under mild conditions. Very slow uptake of H_2 occurred in dma at 40 °C and 1 atm, probably accompanied by solvent decarbonylation, since the product (identified by its i.r. spectrum) was [$HRuCl(CO)_2(PPh_3)_2$]. Treatment of a dma solution of complex (V) with CO at room temperature yielded the six-co-ordinate *trans*-dicarbonyl complex (II); at 75 °C, the complex (Ib) was formed.

Catalytic Properties.—Our synthetic studies on these ruthenium carbonyl complexes arose from interest in their potential use as catalysts for carbonylation (and decarbonylation) reactions.[15] The [$HRuCl(CO)_2(PPh_3)_2$] complex, for example, is related to the well known[16] rhodium(I) hydroformylation catalyst [$HRh(CO)_2$-$(PPh_3)_2$] {formed from [$HRh(CO)(PPh_3)_3$] in solution

---

[10] A. J. Carty, *Canad. J. Chem.*, 1966, **44**, 1881.

[11] V. Gutmann, 'Co-ordination Chemistry in Non-Aqueous Solvents,' Springer–Verlag, New York, 1968, pp. 19–34.

[12] A. Rusina and A. A. Vlcek, *Nature*, 1965, **206**, 275.

[13] B. R. James, R. S. McMillan, and E. Ochiai, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 239.

[14] G. R. Crooks, G. Gamlen, B. F. G. Johnson, J. Lewis, and I. G. Williams, *J. Chem. Soc.* (*A*), 1969, 2761.

[15] B. R. James, *Inorg. Chim. Acta Rev.*, 1970, **4**, 73.

[16] C. K. Brown and G. Wilkinson, *J. Chem. Soc.* (*A*), 1970, 2753 and references therein.

under CO}, which is active under mild conditions. The ruthenium complex, however, is not an effective catalyst under conditions that we have tried so far. For example, after 12 h at 70 °C, a 0·5M-solution of oct-1-ene in dma containing 4×10^{-3}M-$[HRuCl(CO)_2(PPh_3)_2]$ showed less than 1 mol of gas uptake per mol of catalyst using 1 atm of CO–H_2 (1 : 1); a $1{\cdot}3 \times 10^{-3}$M-solution of the same complex in dimethylacetamide–hex-1-ene (1 : 1) showed no detectable product (g.l.c.) after 26 h at 100 °C under 4 atm each of H_2 and CO. Although ruthenium complexes are not generally very efficient for homogeneous olefin hydroformylation, five-co-ordinate complexes of the type $[Ru(CO)_3(PPh_3)_2]$ have been found to be effective.[15] The presently studied chlorohydrido-complex appears to remain six-co-ordinate in solution, even in co-ordinating solvents, and this is undoubtedly a major factor governing its low activity. Addition of Lewis acids such as triethylaluminium has been used to remove a co-ordinated phosphine ligand with creation of a vacant co-ordination site in some cobalt phosphine complexes,[17] although we have not yet studied the effect of such cocatalysts in the ruthenium systems.

The previously noted [1] slow gas uptake at 80 °C and 1 atm CO–H_2 by a dma solution of methyl vinyl ketone containing the complex $[HRuCl(CO)_2(PPh_3)_2]$ was found to be a hydrogenation reaction; the tendency shown by α,β-unsaturated ketones to give the saturated carbonyl product under hydroformylation conditions was first noted by Adkins and Krsek.[18] The fact that the complex does catalyse hydrogenation suggests that more strongly co-ordinating olefins (methyl vinyl ketone as compared to oct-1-ene) may compete for a co-ordination site at the catalyst centre.

dma Solutions of the complexes $[RuCl_2(CO)(PPh_3)_2]$ and (Ib) (2×10^{-3}M) were both inactive for hydrogenation of oct-1-ene (1·0M) and maleic acid (0·1M) at 35 °C under 1 atm H_2. Under the same conditions but using $[HRuCl(PPh_3)_3]$ as catalyst, the initial hydrogenation rates for the two substrates are $2{\cdot}0 \times 10^{-3}$ and $1{\cdot}5 \times 10^{-5}$ mol l^{-1} s^{-1}, respectively.[4] At 80 °C and 1 atm, a dma solution containing $5{\cdot}7 \times 10^{-3}$M-complex (I) catalyses the hydrogenation of 2·5M-methyl vinyl ketone to ethyl methyl ketone at a linear rate of $2{\cdot}6 \times 10^{-5}$ mol l^{-1} s^{-1}. Introduction of π-acceptor carbonyl groups into ruthenium complexes is commonly found to decrease activity for hydrogenation.[15]

Despite its inactivity as a hydrogenation catalyst, the complex $[RuCl_2(CO)(PPh_3)_2]$ was found to be efficient for catalytic olefin isomerisation. A solution of equal volumes of oct-1-ene and benzene–ethanol (1 : 1) containing $1{\cdot}1 \times 10^{-2}$M-complex was found to contain 95% internal olefins (mostly oct-2-ene) and 5% terminal olefin after 1 h at 70 °C under an atmosphere of nitrogen. G.l.c. analysis indicated that stepwise isomerisation was occurring resulting in oct-2-ene, oct-3-ene, and oct-4-ene. The same solution after 14 h had reached what appeared to be an equilibrium composition and contained oct-4-, -3-, and -2-ene, in decreasing amounts, with no oct-1-ene. Thermodynamic data are not available for the oct-3- and -4-ene isomers and it is not clear if the isomer composition is thermodynamically controlled. The catalyst was recovered unchanged after separation from the solution and recrystallisation from CH_2Cl_2–MeOH. No increase in isomerisation rate was observed when the reaction was repeated under an atmosphere of H_2 instead of N_2, and no octane was produced in either case. The catalyst appeared to be almost totally insoluble in neat oct-1-ene at 100 °C; yet oct-1-ene (3·5 cm^3) containing the monocarbonyl complex (0·035 g) in suspension was 65% isomerised after 12 h under an atmosphere of N_2 at 100 °C.

Lyons [19] has reported the recovery of a monocarbonyl complex analogous to $[RuCl_2(CO)(PPh_3)_2]$ but having the sixth co-ordination site occupied by a conjugated olefin, following some isomerisation reactions using $[RuCl_2(PPh_3)_3]$ as catalyst. A $[RuCl_2(CO)(PPh_3)_2]$ complex, proposed as the active catalytic species, was thought to arise from reaction of $[RuCl_2(PPh_3)_3]$ with peroxide impurities in the olefins. The present studies show that such a five-co-ordinate complex can be readily synthesised and that it is an active isomerisation catalyst.

A plausible mechanism for the isomerisation involves conversion of a $[RuCl_2(CO)(PPh_3)_2(\text{olefin})]$ complex into a chlorohydrido-species, ethanol possibly being the hydride source, followed by reversible hydride addition–elimination *via* an alkyl species. Lack of hydrogenation implies that oxidative addition of molecular hydrogen to the alkyl species does not compete effectively with reverse formation of the hydride–olefin species [equation (2)]. Wells and his co-workers [20] have suggested that

$$\begin{aligned} &\mathrm{HRu(olefin)} \rightleftharpoons \mathrm{Ru(alkyl)} \overset{\mathrm{H_2}}{\nrightarrow} \\ &\qquad \mathrm{H_2Ru(alkyl)} \longrightarrow \mathrm{HRu} + \mathrm{alkane} \qquad (2) \end{aligned}$$

for some related hydrogen-isotope redistribution reactions catalysed by the complex $[RuCl_2(PPh_3)_3]$ in benzene, the necessary hydride might arise *via* intramolecular hydrogen transfer from *ortho* positions of the phosphine ligands.

The monocarbonyl complexes such as (IV) were found to be efficient under mild conditions for hydrogenation of alk-1-enes in methanol solution on addition of sodium tetrahydroborate; a dihydrido-intermediate such as $[H_2Ru(CO)(PPh_3)_2(\text{solvent})]$ [21] may be the active catalyst.

Dibromocarbonyl complexes were prepared by methods analogous to those used for the corresponding chloro-complexes. I.r. data for all the complexes are given in the Table. All the monocarbonyl complexes

---

[17] M. Hidai, Y. Kuse, T. Hikita, Y. Uchida, and A. Misono, *Tetrahedron Letters*, 1970, 1715.

[18] H. Adkins and G. Krsek, *J. Amer. Chem. Soc.*, 1949, **71**, 3051.

[19] J. E. Lyons, *J. Org. Chem.*, 1971, **36**, 2497; *Chem. Comm.*, 1971, 562.

[20] B. Hudson, D. E. Webster, and P. B. Wells, *J.C.S. Dalton*, 1972, 1204.

[21] J. J. Levison and S. D. Robinson, *J. Chem. Soc.* (*A*), 1970, 2947.

are yellow, the bromo-complexes being somewhat duller than the chloro-analogues. CH_2Cl_2 solution i.r. spectra of the $[RuX_2(CO)(PPh_3)_2L]$ complexes (X = Cl or Br; L = dma, dmf, or dmso) were recorded immediately after dissolution. After several minutes at 25 °C, dissociation of the solvent ligands was observed; for example, a band at 1 643 cm^{-1} due to co-ordinated dmf was gradually replaced by a band due to free dmf at 1 673 cm^{-1}.

EXPERIMENTAL

Ruthenium trichloride $RuCl_3,3H_2O$ was obtained on loan from Johnson, Matthey Ltd., and triphenylphosphine was purchased from Strem Chemicals. The solvents *NN'*-dimethylacetamide and *NN'*-dimethylformamide (Fisher Scientific) and dimethyl sulphoxide (Baker Scientific) were certified grade, and were stored on Linde 4-A molecular sieves. Prepurified grade hydrogen and C.P. grade carbon monoxide were obtained from Matheson Co. The complexes $[RuCl_2(PPh_3)_3]$ and $[RuBr_2(PPh_3)_3]$ were prepared from $RuCl_3,3H_2O$ using the method of Stephenson and Wilkinson.[8] Solutions of these complexes were prepared on a small scale (1—4 cm^3 solvent) *in vacuo*, the complex being added to thoroughly degassed solvent.

Microanalyses were performed by Mr. P. Borda of this Department, or by Galbraith Laboratories, Knoxville, Tennessee. M.p.s were determined in evacuated capillary tubes on a Gallenkamp apparatus, and are uncorrected. I.r. spectra were recorded as Nujol mulls or in solution using a Perkin-Elmer 457 grating spectrometer, and were calibrated with polystyrene film. N.m.r. spectra of the hydrido-complexes were recorded in dma and in CH_2Cl_2 solution, using a Varian T-60 spectrometer. The gas-uptake experiments were studied using a constant-pressure apparatus described previously.[22]

Bromodicarbonylhydridobis(triphenylphosphine)ruthenium(II).—Dibromotris(triphenylphosphine)ruthenium(II) was dissolved with shaking in dma (0·04 g cm^{-3}) under 1 atm of hydrogen at 25 °C. After 30 min, the hydrogen was removed and replaced by a hydrogen–carbon monoxide (1 : 1), whereupon the violet solution immediately became yellow (n.m.r., symmetrical triplet at τ 15·3). A white solid was precipitated on concentration of the solution at 25 °C. The *product* was washed with dma to remove the remaining yellow colour, recrystallised from methylene chloride–methanol without heating, washed with methanol, and dried *in vacuo* (40%) (Found: C, 59·6; H, 4·1; Br, 9·9. Calc. for $C_{38}H_{31}BrO_2P_2Ru$: C, 59·8; H, 4·1; Br, 10·5%).

Dicarbonylchlorohydridobis(triphenylphosphine)ruthenium(II).—Dichlorotris(triphenylphosphine)ruthenium(II) was dissolved with shaking in dma (0·04 g cm^{-3}) under 1 atm hydrogen at 25 °C. After 30 min, the hydrogen was replaced by hydrogen–carbon monoxide (1 : 1), the violet solution immediately becoming yellow on shaking (n.m.r., symmetrical triplet at τ 14·6). The white solid which precipitated on concentrating the solution also contained variable amounts of dicarbonyldichlorobis(triphenylphosphine)ruthenium(II). The solid was washed with dma to remove the yellow colour which was present; careful recrystallisation from methylene chloride–methanol was used to separate the chlorohydrido-*product*, which was washed with methanol and dried *in vacuo* (10%) (Found: C, 62·0; H, 4·3; Cl, 4·8. Calc. for $C_{38}H_{31}ClO_2P_2Ru$: C, 63·6; H, 4·3; Cl, 4·9%).

Dicarbonyldichlorobis(triphenylphosphine)ruthenium(II), (I).—Dichlorotris(triphenylphosphine)ruthenium(II) was dissolved with shaking in dma (0·04 g cm^{-3}) under 1 atm hydrogen at 25 °C. After 30 min, the hydrogen was removed and replaced by carbon monoxide; to the resulting yellow solution was added an equal volume of methanol. The yellowish crude product which precipitated was recrystallised from methylene chloride–methanol without heating, giving a white *solid* (40%), m.p. 230—235 °C (Found: C, 60·2; H, 4·2; Cl, 9·1. Calc. for $C_{38}H_{30}Cl_2O_2P_2Ru$: C, 60·6; H, 4·0; Cl, 9·4%).

Carbonyldichloro(dimethylformamide)bis(triphenylphosphine)ruthenium(II), (IV).—A dark brown suspension (0·1 g cm^{-3}) of dichlorotris(triphenylphosphine)ruthenium(II) in dmf was treated with 1 atm carbon monoxide at 25 °C, the colour rapidly becoming yellow. An equal volume of diethyl ether was added to the suspension, the liquid was decanted off, and the yellow *product* was washed with diethyl ether and dried *in vacuo* (80%), m.p. 188—192 °C (Found: C, 59·4; H, 4·7; Cl, 9·3; N, 1·8. Calc. for $C_{40}H_{37}Cl_2NO_2P_2Ru$: C, 60·3; H, 4·6; Cl, 8·9; N, 1·8%). The *bromo-analogue* was prepared similarly, m.p. 178—181 °C (Found: C, 54·0; H, 4·3; N, 1·5. Calc. for $C_{40}H_{37}Br_2NO_2P_2Ru$: C, 54·2; H, 4·2; N, 1·6%).

Carbonyldichloro(dimethylacetamide)bis(triphenylphosphine)ruthenium(II), (III).—Dichlorotris(triphenylphosphine)ruthenium(II) in dma (0·02 g cm^{-3}) was treated with carbon monoxide by shaking under 1 atm of the gas at 25 °C for 10 min. The bright yellow solution was reduced to small volume by pumping, and the resulting yellow *precipitate* was washed with diethyl ether and dried *in vacuo* (80%), m.p. 143—145 °C (Found: C, 60·3; H, 5·1; N, 2·1. Calc. for $C_{41}H_{39}Cl_2NO_2P_2Ru$: C, 60·7; H, 4·9; N, 1·7%). The *bromo-analogue* was prepared similarly, m.p. 139—141 °C (Found: C, 53·4; H, 4·7; N, 2·1. Calc. for $C_{41}H_{39}Br_2NO_2P_2Ru$: C, 54·7; H, 4·4; N, 1·6%).

Carbonyldichlorobis(triphenylphosphine)ruthenium(II), (V).—Carbonyldichloro(dimethylformamide)bis(triphenylphosphine)ruthenium(II) was recrystallised from hot methylene chloride–methanol; the yellow *product* was washed with diethyl ether and dried *in vacuo* (70%), m.p. 259—263 °C (Found: C, 60·3; H, 4·3; Cl, 9·1; *M* (in benzene) 743. Calc. for $C_{37}H_{30}Cl_2OP_2Ru$: C, 61·3; H, 4·1; Cl, 9·8%; *M* 724). The *bromo-analogue* was prepared similarly, m.p. 171—175 °C (Found: C, 54·4; H, 4·1. Calc. for $C_{37}H_{30}Br_2OP_2Ru$: C, 54·7; H, 3·7%).

Carbonyldichloro(dimethylsulphoxide)bis(triphenylphosphine)ruthenium(II), (VI).—Carbonyldichlorobis(triphenylphosphine)ruthenium(II) was dissolved in dmso (0·02 g cm^{-3}) at 70 °C, and the solvent was reduced to small volume by pumping. The resulting yellow *precipitate* was washed with methanol and diethyl ether, and dried *in vacuo* at 60 °C (80%), m.p. 160—165 °C (Found: C, 56·6; H, 4·5. Calc. for $C_{39}H_{36}Cl_2O_2P_2RuS$: C, 58·4; H, 4·5%). The *bromo-analogue* was prepared similarly, m.p. 174—178 °C (Found: C, 53·3; H, 4·4. Calc. for $C_{39}H_{36}Br_2O_2P_2RuS$: C, 52·5; H, 4·1%).

Di-μ-acetato-tetracarbonylbis(triphenylphosphine)diruthenium(I) (*from Ruthenium Trichloride*).—$RuCl_3,3H_2O$ (0·4 g) in dmf (30 cm^3) was treated with 1 atm hydrogen at 80 °C for 60 h. Sodium acetate trihydrate (1·5 g) in acetic

---

[22] B. R. James and G. L. Rempel, *Canad. J. Chem.*, 1966, **44**, 233.

acid (10 cm^3) was added and the solution heated gently (50 °C) under an atmosphere of nitrogen for a few minutes. The solution was then cooled and filtered under an atmosphere of nitrogen into dmf (10 cm^3) containing triphenylphosphine (0·6 g). dmf Was removed by distillation under reduced pressure and the residue extracted into warm ethanol from which yellow crystals were obtained on cooling. The *crystals* (0·46 g, 65%) were filtered off and recrystallised from benzene (Found: C, 55·65; H, 3·65; P, 6·40; Ru, 21·95. Calc. for $C_{22}H_{18}O_4PRu$: C, 55·25; H, 3·80; P, 6·45; Ru. 21·15%).

We thank the National Research Council of Canada and the Universities of British Columbia and Waterloo, for financial support, and Johnson, Matthey Ltd., for loan of the ruthenium.

[3/431 *Received*, 23*rd February*, 1973]