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METAL CARBONYL CHEMISTRY
IV*. THE PREPARATION OF COBALT AND RHODIUM CARBONYLS BY REDUCTIVE CARBONYLATION WITH PENTACARBONYLIRON

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SUMMARY

Octacarbonyldicobalt has been obtained in 40% yield from the reaction of cobaltous chloride and pentacarbonyliron; other cobalt salts are less effective in this reaction. The similar reaction of either anhydrous $RhCl_3$ or $[Rh(CO)_2Cl]_2$ with pentacarbonyliron has been found to give high yields of $Rh_6(CO)_{16}$ even at atmospheric pressure at the reflux temperature of methanol. Carbonylation of $[Rh(CO)_2Cl]_2$ with carbon monoxide in the presence of Ullmann copper-bronze powder or silver can be controlled to give either $Rh_6(CO)_{16}$ or $Rh_4(CO)_{12}$ almost quantitatively.

The carbonylation of transition metal salts in the presence of a variety of reducing agents has found wide application in the preparation of metal carbonyls[2]. Of particular interest is the isolated report[3] of the preparation of molybdenum and tungsten hexacarbonyls from their hexahalides and pentacarbonyliron, where the latter appears to act as both the reducing and carbonylating agent. A recent investigation[1] into the effectiveness of pentacarbonyliron as a catalyst for the hydroformylation of olefins has shown that it has little catalytic activity alone. In the presence of traces of cobalt metal or cobalt salts, however, its activity is similar to that of octacarbonyldicobalt, suggesting the possibility of a metathetical exchange of carbon monoxide between cobalt salts and pentacarbonyliron. The extension of this exchange to the preparation of cobalt and rhodium carbonyls has now been investigated.

When cobalt naphthenate and an excess of pentacarbonyliron were heated (140–150°) for 30 minutes in toluene under carbon monoxide (50 atm), octacarbonyldicobalt was obtained in an estimated yield of 43%, although the isolated yield was lower due to handling difficulties. Under similar conditions the less soluble cobalt carbonate gave only a 9% yield of the carbonyl. The highest isolated yield of octacarbonyldicobalt (40%) was obtained using cobaltous chloride in ethanol; in ether, a poor solvent for $CoCl_2$, only a very low yield (1%) was obtained, emphasising the importance of homogeneous conditions. Separate experiments showed that in the

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* For Part III see ref. 1.

absence of pentacarbonyliron no significant amounts of octacarbonyldicobalt were formed from any of the above cobalt derivatives and carbon monoxide under comparable conditions in these solvents.

Extension of this method to the preparation of rhodium carbonyls has shown that under moderate pressures of carbon monoxide (90–120 atm) anhydrous rhodium trichloride reacts with $Fe(CO)_5$ in pentane either at temperatures of 100° for a moderate time (12 h) or at 70–80° (60 h) to give high yields (Table 1) of the black rhodium carbonyl, $Rh_6(CO)_{16}$, first prepared by Hieber[4] in unspecified yield by carbonylation of $RhCl_3$ (80–230°, 200 atm CO) with silver or copper as halogen acceptor, and incorrectly[5,6] formulated as $Rh_4(CO)_{11}$. Control experiments have shown that $Rh_6(CO)_{16}$ is not obtained in the absence of pentacarbonyliron. If the proportion of $Fe(CO)_5$ to $RhCl_3$ falls to less than 2/1, only a low yield of $Rh_6(CO)_{16}$ is obtained, even under high pressures of carbon monoxide, suggesting that $Fe(CO)_5$ rather than carbon monoxide is the carbonylating agent. When short reaction times are employed, the halide $[Rh(CO)_2Cl]_2$ is the major product; this gives $Rh_6(CO)_{16}$ in 68% yield after only 6 h at 70–80° and 100 atm CO with an excess of pentacarbonyliron, suggesting that the halide is an intermediate in the formation of $Rh_6(CO)_{16}$ from $RhCl_3$. Carbon monoxide as such appears to play little part in this reaction since a similar high yield (64%) of $Rh_6(CO)_{16}$ was obtained by heating $[Rh(CO)_2Cl]_2$ under reflux for 12 h with an excess of $Fe(CO)_5$ in methanol under a slow stream of nitrogen. Pentacarbonyliron must therefore be acting as both halogen acceptor and carbonylating agent.

TABLE 1

USE OF PENTACARBONYLIRON AS A "REDUCTIVE CARBONYLATING" AGENT

Mole ratio	Temp. (°C)	Time (h)	CO (atm)	$[Rh(CO)_2Cl]_2$ (%)	$Rh_6(CO)_{16}$ (%)
$RhCl_3/Fe(CO)_5$					
1/3	70–80	12	90	65[a]	
1/3	70–80	60	90	10	68
1/3	110–120	12	90	7	62
1/1.5	110–120	16	120	30	4
$[Rh(CO)_2Cl]_2/Fe(CO)_5$					
1/10	70–80	6	100	[a]	68
1/*ca.* 100	65–75	12		[a]	64
1/*ca.* 100	65–75	12	1[b]	[c]	

[a] Trace quantity of $Rh_4(CO)_{12}$. [b] CO bubbled through the solution. [c] $Rh_4(CO)_{12}$ major product in this reaction.

Hexadecacarbonylhexarhodium can thus be made in good yield at atmospheric pressure in ordinary glass apparatus by this method, which has the advantage of shorter reaction times than the recently reported[7] atmospheric pressure carbonylation of $[Rh(CO)_2Cl]_2$ with carbon monoxide. Isolation of the rhodium carbonyls from the reaction mixture, readily accomplished by solvent extraction, is much easier than that of octacarbonyldicobalt. Only trace quantities of $Rh_4(CO)_{12}$ were ever observed in any of these reactions, and there was no evidence for the formation of

$Rh_2(CO)_8$. Passage of carbon monoxide through a refluxing methanol solution of $[Rh(CO)_2Cl]_2$ and an excess of pentacarbonyliron, gave $Rh_4(CO)_{12}$ as the major product, although difficulty was experienced in separating it from unchanged $[Rh(CO)_2Cl]_2$.

The high pressure synthesis of rhodium carbonyls using other halogen acceptors has also been investigated. Although similar reactions have been briefly reported previously[4], little detail and no yields were given. Table 2 shows that $Rh_6(CO)_{16}$ can be prepared in almost quantitative yield from $[Rh(CO)_2Cl]_2$ using copper, in the form of Ullmann copper-bronze powder in a copper-tube liner, as a halogen acceptor. The presence of a hydroxylic compound, such as methanol, in this reaction is essential for high yields and appears to promote the formation of $Rh_6(CO)_{16}$ in agreement with recent observations[8] on the carbonylation of rhodium trichloride trihydrate. A similar high yield of $Rh_6(CO)_{16}$ was obtained when the reaction was carried out using mixtures of carbon monoxide and hydrogen.

TABLE 2

HIGH PRESSURE CARBONYLATION OF $[Rh(CO)_2Cl]_2$ USING ULLMANN COPPER-BRONZE POWDER AND SILVER AS HALOGEN ACCEPTORS

CO (atm)	H_2 (atm)	Solvent	Temp. (°C)	Time (h)	$Rh_4(CO)_{12}$ (%)	$Rh_6(CO)_{16}$ (%)
330[a]		Pentane/ methanol	210	24		99
260[a]	70	Pentane/ methanol	210	24		98
260[a]	70	Pentane	210	24		51
330[a]			80	15	95	
330[b]			80	15	85	
330[c]			80	15	97	
330[c,d]	50		80	15	83	4

[a] Copper-bronze powder in a copper-tube liner. [b] Copper-tube liner. [c] Silver foil. [d] Trace of $HRh(CO)_4$ (see text) also formed in this reaction.

When the carbonylation reaction was carried out in the presence of Ullmann copper-bronze powder in a copper-tube liner for a shorter reaction time at a lower temperature, and in the absence of solvent, the only product was $Rh_4(CO)_{12}$ (95% yield). The yield was reduced by use of a copper-tube liner alone. The use of silver foil as a halogen acceptor in place of copper-bronze in a copper-tube liner had no significant effect upon the yield of $Rh_4(CO)_{12}$, but reduced yields were obtained with the silver foil using mixtures of carbon monoxide and hydrogen, and a small amount of $Rh_6(CO)_{16}$ was obtained from this reaction. The reduction in yield was probably due to the formation of the hydride, $HRh(CO)_4$, since on several occasions traces of yellow crystals, m.p. 0° [in accord with the only reported description[4] of $HRh(CO)_4$], were isolated from this reaction. These crystals [ν(CO) 2128 m, 2070 s, 2004 s] were unstable and decomposed above the m.p. to red crystals [ν(CO) 2087 w, 2016 s, 1996 s and 1861 m]. Although the hydride is reported to give $Rh_2(CO)_8$ (orange crystals, m.p.[4] 76°), neither of these compounds could be adequately characterised.

EXPERIMENTAL

Cobaltous chloride, cobalt naphthenate, cobalt carbonate and rhodium trichloride trihydrate were commercial samples used without further purification. Anhydrous rhodium trichloride was prepared from the trihydrate at 440° in a stream of chlorine[9], and $[Rh(CO)_2Cl]_2$ was prepared by the action of carbon monoxide on heated $RhCl_3 \cdot 3\ H_2O$[10]. Pentane in these experiments refers to Analar light petroleum (b.p. 30–40°), which was purified from peroxides and unsaturated hydrocarbons. The IR spectra were recorded on a Perkin–Elmer 21 instrument. For the reactions with rhodium compounds only typical experiments are described, and the full experimental conditions are given in Tables 1 and 2. All yields of cobalt and rhodium carbonyls are based on cobalt and rhodium respectively.

Determination of mixtures of $Co_2(CO)_8$ and $Fe(CO)_5$

The apparatus consisted of an Erlenmeyer flask (250 ml) with a magnetic stirrer, dropping funnel, a gas inlet, and an outlet connected to a gas burette (450 ml capacity); light was excluded from the apparatus[11]. A standard solution of iodine in toluene (50 g per litre) was used for each analysis, and 40 ml of this solution was taken for samples containing up to 0.6 g of total carbonyl.

A suitable aliquot (5–10 ml) of the solution to be analysed was pipetted into the flask, and toluene was added to bring the volume of the solution to *ca.* 40 ml. The system was purged with CO, the solution was stirred for 2 min, and the gas burette was read (V_1). Iodine solution was added, and the solution was stirred vigorously until the gas evolution had ceased (V_2). The system was again purged with CO, the solution stirred, and the volume (V_3) recorded. Analar pyridine (10 ml) was added, and the solution was stirred until no further gas evolution occurred (V_4). From the equations:

$$Co_2(CO)_8 + 2\ I_2 \rightarrow 2\ CoI_2 + 8\ CO$$
$$Fe(CO)_5 + I_2 \rightarrow Fe(CO)_4I_2 + CO$$
$$Fe(CO)_4I_2 + 2\ C_5H_5N \rightarrow Fe(CO)_2(C_5H_5N)_2I_2 + 2\ CO$$

the amounts of $Co_2(CO)_8$ and $Fe(CO)_5$ can be calculated as

$$Fe(CO)_5\ (g) = \tfrac{1}{2}(V_4 - V_3 \text{ at N.T.P.}) \times 0.00875$$

$$Co_2(CO)_8\ (g) = [(V_2 - V_1) - \tfrac{1}{2}(V_4 - V_3) \text{ at N.T.P.}] \times \frac{0.0171}{89.6}$$

This method was tested on known mixtures of the two carbonyls and was found to give results within 5% of the amounts known to be present.

Reactions of cobalt and rhodium salts with pentacarbonyliron

(*a*). *Cobaltous chloride.* Anhydrous cobaltous chloride (7.6 g, 60 mmole), pentacarbonyliron (24.0 g, 123 mmole) and dry ethanol (50 ml) were heated at 110–120° for 30 min under carbon monoxide (60 atm). The ethanol solvent was removed under vacuum, and the residue was extracted with pentane (50 ml). The extract was filtered, and cooled (0°) overnight to give octacarbonyldicobalt (4.0 g, 11.7 mmole, 40%), m.p. 51°, (lit.[12] m.p. 51°); the IR spectrum was identical to that reported[13]. No reaction occurred in the absence of pentacarbonyliron.

(*b*). *Cobalt naphthenate* (*cobalt* 10% *w/w*). Under similar conditions cobalt naphthenate (20.0 g, 50 mmole) and pentacarbonyliron (8.0 g, 40 mmole) in toluene (50 ml) gave octacarbonyldicobalt (2.6 g, 7.6 mmole, 43 %) estimated by the gasometric technique described. Sublimation of the residue obtained after evaporation of the toluene gave orange crystals of octacarbonyldicobalt. No reaction occurred in the absence of pentacarbonyliron.

(*c*). *Cobalt carbonate*. When cobalt carbonate (2.0 g, 17 mmole), pentacarbonyliron (6.0 g, 30 mmole) and toluene (50 ml) were heated at 140° for 4 h under an initial pressure of 110 atm of CO and H_2 (ratio 1/1), analysis of the reaction mixture gave octacarbonyldicobalt (0.36 g, 1.5 mmole, 9 %). In the absence of pentacarbonyliron the yield of octacarbonyldicobalt was only 1 %.

(*d*). *Rhodium trichloride*. Anhydrous rhodium trichloride (2.0 g, 9.57 mmole), pentacarbonyliron (6.83 g, 35.4 mmole) and dry pentane (100 ml) were heated at 110–115° for 12 h under carbon monoxide (90 atm); filtration of the solution and evaporation of the solvent to low volume gave red crystals of tetracarbonyl-μ-dichlorodirhodium (0.015 g, 0.038 mmole, 7 %), m.p. 125° (lit.[12] m.p. 125°). The IR spectrum was identical to that reported. Extraction of the residue with boiling chloroform and evaporation of the extract gave black crystals of hexadecacarbonylhexarhodium (1.0 g, 0.94 mmole, 60 %), m.p. 238–242° with decomposition (lit.[4] m.p. 235°), identified by IR spectroscopy[5] and elemental analysis. (Found: C, 18.3; H, 0.1; Rh, 57.7. $C_{16}O_{16}Rh_6$ calcd.: C, 18.0; H, 0.0; Rh, 58.0 %.)

(*e*). *Tetracarbonyl-μ-dichlorodirhodium*. (*i*). *High pressure synthesis*. Tetracarbonyl-μ-dichlorodirhodium (1.30 g, 3.34 mmole), pentacarbonyliron (6.4 g, 32 mmole) and dry pentane (100 ml) were heated at 70–80° for 6 h under carbon monoxide (100 atm). The reaction mixture was worked up as described in (*d*) above to give recovered tetracarbonyl-μ-dichlorodirhodium (0.043 g, 0.09 mmole, 3 %) and hexadecacarbonylhexarhodium (0.70 g, 0.66 mmole, 68 %). (*ii*). *Low pressure synthesis*. Tetracarbonyl-μ-dichlorodirhodium (1.0 g, 2.59 mmole), pentacarbonyliron (45 g, 200 mmole) and methanol (30 ml) were refluxed under a slow stream of nitrogen for 12 h. The solvent was evaporated and the residue extracted with cold pentane. Removal of the solvent from the pentane extract gave a mixture (0.026 g) shown by IR spectroscopy to be mainly $[Rh(CO)_2Cl]_2$ and a trace of $Rh_4(CO)_{12}$. Extraction of the residue with boiling chloroform gave hexadecacarbonylhexarhodium (0.51 g, 0.48 mmole, 64%).

When carbon monoxide was bubbled through the refluxing solution instead of nitrogen the major product, as identified by IR spectroscopy, was dodecacarbonyltetrarhodium, but isolation of this product from unreacted $[Rh(CO)_2Cl]_2$ was difficult; no $Rh_6(CO)_{16}$ was detected in this reaction.

Reactions of rhodium compounds with Ullmann copper-bronze powder and silver

The experiments using Ullmann copper-bronze powder were carried out in an open glass tube which fitted inside a copper tube in a stainless steel autoclave. The experiments using silver foil were carried out in an open glass tube lined with silver foil in an autoclave; no copper-tube liner was used in these experiments.

(*a*). *Preparation of dodecacarbonyltetrarhodium*. Tetracarbonyl-μ-dichlorodirhodium (0.98 g, 2.5 mmole) mixed with dry Ullmann copper-bronze powder, was heated at 80° for 15 h under carbon monoxide (330 atm). The autoclave was vented, the solid residue was extracted with cold pentane, and the extract was filtered and evaporated to give dodecacarbonyltetrarhodium (0.89 g, 1.19 mmole, 95%) which decomposed at 150° (lit.[4] m.p. 150° with decomposition). The compound was identified by IR spectroscopy[5] and elemental analysis. (Found: C, 19.4; H, 0.1; Rh, 55.1. $C_{12}O_{12}Rh_4$ calcd.: C, 19.2; H, 0.0; Rh, 54.9%.) Extraction of the residue with boiling chloroform gave only a trace of $Rh_6(CO)_{16}$.

(*b*). *Preparation of hexadecacarbonylhexarhodium.* Tetracarbonyl-μ-dichlorodirhodium (1.13 g, 2.91 mmole) in pentane (100 ml) and methanol (5 ml) was mixed with Ullmann copper-bronze powder and heated at 210° for 24 h under carbon monoxide (330 atm). After venting the autoclave the residue was extracted with boiling chloroform. Removal of the solvent from the extract gave hexadecacarbonylhexarhodium (1.02 g, 0.96 mmole, 99%).

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REFERENCES

1 B. L. Booth, H. Goldwhite and R. N. Haszeldine, *J. Chem. Soc., C*, (1966) 1447.

2 J. C. Hileman, *Metal Carbonyls*, in W. L. Jolly (Ed.), *Preparative Inorganic Reactions*, Interscience, New York, 1964, p. 77.

3 A. N. Nesmeyanov, K. N. Anisimov, E. P. Mikheev, V. L. Volkov and Z. P. Valueva, *Zh. Neorg. Khim.*, 4 (1959) 249, 503; *Russ. J. Inorg. Chem.*, 4 (1959) 107, 228.

4 W. Hieber and H. Lagally, *Z. Anorg. Chem.*, 251 (1943) 96.

5 W. Beck and K. Lottes, *Chem. Ber.*, 94 (1961) 2578.

6 E. R. Corey, L. F. Dahl and W. Beck, *J. Amer. Chem. Soc.*, 85 (1963) 1202.

7 P. Chini and S. Martinengo, *Chem. Commun.*, (1968) 251.

8 S. H. H. Chaston and F. G. A. Stone, *Chem. Commun.*, (1967) 964.

9 J. W. Mellor, *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol XIII, Longmans, London, 1956.

10 J. A. McCleverty and G. Wilkinson, *Inorg. Syn.*, 8 (1966) 211.

11 M. Orchin and I. Wender, *Anal. Chem.*, 21 (1949) 875; H. W. Sternberg, M. Orchin and I. Wender, *Anal. Chem.*, 24 (1952) 174.

12 I. Wender, H. Greenfield and M. Orchin, *J. Amer. Chem. Soc.*, 73 (1951) 256; I. Wender, H. W. Sternberg, S. Metlin and M. Orchin, *Inorg. Syn.*, 5 (1957) 190.

13 I. Wender, H. W. Sternberg and M. Orchin, in P. H. Emmett (Ed.), *Catalysis*, Vol. 5, Reinhold, New York, 1957, p. 73.