

Chemistry of the Metal Carbonyls. Part LIV.¹ Synthesis of Rhodium and Iridium Carbonyls

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Dodecacarbonyltettrarhodium has been prepared (60–70% yield) by treating $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ in hexane with carbon monoxide at 200 atmos. at room temperature in the presence of copper wire. The hexanuclear carbonyl $\text{Rh}_6(\text{CO})_{16}$ has been synthesized in 80–90% yield by reacting methanolic solutions of rhodium trichloride trihydrate with carbon monoxide at 40 atmos. and 60°. By varying the concentrations $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ is obtained in 80% yield. Dodecacarbonyltetrairidium has been prepared in ca. 60% yield by carbonylating a methanolic solution of iridium trichloride with carbon monoxide at 40 atmos. (60°). The mass spectrum of $\text{Rh}_6(\text{CO})_{16}$ has been measured.

THE rhodium carbonyls $\text{Rh}_4(\text{CO})_{12}$ and $\text{Rh}_6(\text{CO})_{16}$ were first prepared by treating anhydrous rhodium trichloride with carbon monoxide at 200 atmos. for several hours in the presence of a halogen-acceptor such as copper powder, silver, cadmium, or zinc.² Under these conditions, at temperatures of 50–80° the main product was $\text{Rh}_4(\text{CO})_{12}$, whereas at 80–230° the only product was $\text{Rh}_6(\text{CO})_{16}$. Yields were not quoted and separation problems arise. Recently there have been two independent brief reports of new high-yield syntheses of these rhodium carbonyls.^{3,4} Chini and Martinengo's method⁴ involves reaction between solutions of dimeric $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ and carbon monoxide in the presence of a

buffering agent. When a polar organic solvent was used, $\text{Rh}_6(\text{CO})_{16}$ was formed; however, when n-heptane was employed $\text{Rh}_4(\text{CO})_{12}$ was the major product. Herein we report our own studies.

Treatment of dimeric $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ in n-hexane with carbon monoxide at 200 atmos. in the presence of copper wire at room temperature afforded $\text{Rh}_4(\text{CO})_{12}$ in 60–70% yield. Copper(I) chloride was identified as a by-product.



The carbonyl $\text{Rh}_6(\text{CO})_{16}$ was prepared in 80–90% yield by treating a dilute methanol solution of rhodium

¹ Part LIII, T. Blackmore, J. D. Cotton, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc. (A)*, 1968, 2931.

² W. Hieber and H. Lagally, *Z. anorg. Chem.*, 1943, 251, 96.

³ S. H. H. Chaston and F. G. A. Stone, *Chem. Comm.*, 1967, 964.

⁴ P. Chini and S. Martinengo, *Chem. Comm.*, 1968, 251.

trichloride trihydrate with carbon monoxide at 40 atmos. and at 60°. No halogen-acceptor was required in this reaction. It was found that at high concentrations [e.g. $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (1.0 g.) in methanol (50 ml.)] no $\text{Rh}_6(\text{CO})_{16}$ was formed even when the carbon monoxide pressure was increased to 200 atmos.; the only product being $[\text{Rh}(\text{CO})_2\text{Cl}]_2$. This represents a convenient method of preparing tetracarbonyldichlorodirrhodium since carbonylation proceeds at pressures as low as 10 atmos. An alternative method has been described.⁵

We have also studied the synthesis of $\text{Ir}_4(\text{CO})_{12}$, first reported by Hieber and Lagally⁶ who prepared the carbonyl from the halides IrX_3 or from the haloiridates M_2IrX_6 or M_3IrX_6 ($\text{M} = \text{NH}_4, \text{K}, \text{Na}; \text{X} = \text{Cl}, \text{Br}, \text{I}$) and carbon monoxide in the presence of a halogen acceptor (Cu or Ag). High pressures (350 atmos.) and temperatures (100–140°) were used and yields were not given. In our hands this method afforded the tetranuclear iridium carbonyl in only low yield (ca. 10%) and it was difficult to separate it from residues. Others⁷ have reported good yields of the carbonyl by using temperatures of 240° and a water-insoluble form of iridium trichloride. Some $\text{Ir}_4(\text{CO})_{12}$ is also formed when a stream of carbon monoxide at atmospheric pressure is passed over $\text{IrX}_3 \cdot \text{H}_2\text{O}$ at 150°. Our synthesis, which proceeds in 70% yield, involved similar conditions to those described above for the synthesis of $\text{Rh}_6(\text{CO})_{16}$. Hydrated iridium trichloride was dissolved in methanol and treated with carbon monoxide at 40 atmos. and 60° in the absence of any halide acceptor. In order to obtain the pure product it was found necessary to treat commercially available hydrated iridium trichloride with boiling nitric acid to give a dark green

Although the mass spectra of several polynuclear transition metal carbonyls have been described⁹ that of $\text{Rh}_6(\text{CO})_{16}$ has not been reported.¹⁰ We have recorded the spectrum (see Table) which shows the characteristic stepwise loss of CO groups from the hexanuclear cluster. The most stable ion was $\text{Rh}_6(\text{CO})_{10}^+$ which represents the loss of one CO group per rhodium atom in the cluster. Peaks assigned to Rh_5^+ and Rh_5C^+ were the only ions of significant abundance which provided evidence for the fragmentation of the Rh_6 cluster. An intense CO^+ peak indicated decomposition of the hexanuclear rhodium carbonyl in the mass spectrometer.¹¹

EXPERIMENTAL

Dodecacarbonyltetrarhodium.—A glass-liner which contained a hexane solution (75 ml.) of tetracarbonyldichlorodirrhodium (1.0 g.) and fine copper wire (35 g.; 45 S.W.G.) was placed in a 1 l. autoclave and treated with carbon monoxide (200 atmos.) at room temperature for 4 days. The deep red solution produced was decanted from the copper wire and cooled to -10° . The product (0.5 g., 52%) was recrystallised from hexane [Found: C, 19.45. Calc. for $\text{Rh}_4(\text{CO})_{12}$: C, 19.3%]. $\nu_{\text{max.}}$ (CO), 2075s, 2070s, 2062sh, 2044m, 2016w, 1978w, and 1885s cm^{-1} (n-hexane) [lit.,¹² 2074s, 2068s, 2061sh, 2043m, and 1885s cm^{-1} (light petroleum)].

Hexadecacarbonylhexarhodium.—A 1-l. autoclave was charged with rhodium trichloride trihydrate (1.0 g.) and aqueous methanol (90%, 200 ml.). The autoclave was pressurised with carbon monoxide (40 atmos.) at 60° for 4 days. The black crystalline product was removed from the autoclave with a jet of methanol, filtered off, washed with hot hexane, and dried *in vacuo* to afford the product (0.6 g., 88%) [Found: C, 18.25; O, 24.85; Rh, 56.85. Calc. for $\text{Rh}_6(\text{CO})_{16}$: C, 18.05; O, 24.0; Rh, 57.95%]. $\nu_{\text{max.}}$ (CO), 2075s, 2060sh, 2044m, 1811m, br cm^{-1} (carbon tetrachloride) [lit.,¹² 2073, 2026, and 1800 cm^{-1} (KBr disc)].

Tetracarbonyldichlorodirrhodium.—The 1-l. stainless-steel autoclave containing a glass-liner was charged with rhodium trichloride trihydrate (1.0 g.), methanol (50 ml.), and carbon monoxide (25 atmos.). The reaction vessel was maintained at 60° for 36 hr. The pale yellow solution obtained was evaporated (40°) to a small volume (ca. 5 ml.). Anhydrous sodium sulphate (30 g.) was added and the product was extracted with hot hexane (3×50 ml.). The solution was dried further (Na_2SO_4 ; 30 g.) filtered, and cooled to -10° to give orange crystals (0.6 g., 80%); these were dried *in vacuo* and identified by their i.r. spectrum,¹³ $\nu_{\text{max.}}$ (CO), 2103w, 2087s, 2078w, 2030s, and 2003w cm^{-1} (n-hexane).

Dodecacarbonyltetrairidium.—Commercial, hydrated iridium trichloride was treated with concentrated nitric acid and the mixture was heated to complete dryness on a steam-bath. The black crystalline residue (1.0 g.) was

⁹ M. I. Bruce, *Adv. Organometallic Chem.*, 1968, **6**, 273; and refs. cited therein; J. Lewis and B. F. G. Johnson, *Accounts Chem. Res.*, 1968, **1**, 245.

¹⁰ B. F. G. Johnson, J. Lewis, I. G. Williams, and J. M. Wilson, *J. Chem. Soc. (A)*, 1967, 341.

¹¹ S. Pignataro and F. P. Lossing, *J. Organometallic Chem.*, 1968, **11**, 571.

¹² W. Beck and K. Lottes, *Chem. Ber.*, 1961, **94**, 2578.

¹³ C. W. Garland and J. R. Wilt, *J. Chem. Phys.*, 1962, **36**, 1094.

Mass spectrum of $\text{Rh}_6(\text{CO})_{16}^+$

Ion	A	Ion	A
$\text{Rh}_6(\text{CO})_{16}^+$	57	Rh_5C^+	13
$\text{Rh}_6(\text{CO})_{15}^+$	36	Rh_5^+	91
$\text{Rh}_6(\text{CO})_{14}^+$	32	Rh_4C^+	10
$\text{Rh}_6(\text{CO})_{13}^+$	23	Rh_4^+	27
$\text{Rh}_6(\text{CO})_{12}^+$	24	$\text{Rh}_4(\text{CO})_{10}^{2+}$	15
$\text{Rh}_6(\text{CO})_{11}^+$	72	$\text{Rh}_4(\text{CO})_9^{2+}$	10
$\text{Rh}_6(\text{CO})_{10}^+$	100	$\text{Rh}_4(\text{CO})_8^{2+}$	13
$\text{Rh}_6(\text{CO})_9^+$	93	$\text{Rh}_4(\text{CO})_7^{2+}$	13
$\text{Rh}_6(\text{CO})_8^+$	72	$\text{Rh}_4(\text{CO})_6^{2+}$	23
$\text{Rh}_6(\text{CO})_7^+$	64	$\text{Rh}_4(\text{CO})_5^{2+}$	21
$\text{Rh}_6(\text{CO})_6^+$	59	$\text{Rh}_4(\text{CO})_4^{2+}$	21
$\text{Rh}_6(\text{CO})_5^+$	60	$\text{Rh}_4(\text{CO})_3^{2+}$	19
$\text{Rh}_6(\text{CO})_4^+$	64	$\text{Rh}_4(\text{CO})_2^{2+}$	17
$\text{Rh}_6(\text{CO})_3^+$	60	$\text{Rh}_4(\text{CO})^{2+}$	13
$\text{Rh}_6(\text{CO})_2^+$	55	Rh_3^{2+}	13
$\text{Rh}_6(\text{CO})^+$	46		

* Recorded using an AEI MS9 mass spectrometer with an ionising energy of 70 ev, accelerating voltage 4 kv, trap-current of 300 μA and ion-chamber temperature of 150°.

crystalline form of the chloride which was completely soluble in methanol.

⁵ J. A. McCleverty and G. Wilkinson, *Inorg. Synth.*, 1966, **8**, 211.

⁶ W. Hieber and H. Lagally, *Z. anorg. Chem.*, 1940, **245**, 321.

⁷ N. S. Imyanitov and D. M. Rudkovskii, *J. Gen. Chem. (U.S.S.R.)*, 1963, **33**, 1041.

⁸ W. Hieber, H. Lagally, and A. Mayr, *Z. anorg. Chem.*, 1941, **246**, 138.

dissolved in warm water (15 ml.) and the dark green solution was added to the 1-l. autoclave. Methanol (200 ml.) and sodium hydrogen carbonate (1.0 g.) were added and the autoclave was charged with carbon monoxide (40 atmos.). The mixture was heated at 60° for 36 hr. The yellow crystalline product ⁶ obtained was separated by decantation and by sweeping out the autoclave with a jet of absolute alcohol. After filtration, and being washed in turn with 0.5N-hydrochloric acid (50 ml.), absolute alcohol (50 ml.),

and methylene chloride (50 ml.), the crystals (0.45 g., 57%) were dried *in vacuo* [Found: C, 13.33; H, 0.0; Cl, 0.0. Calc. for Ir₄(CO)₁₂: C, 13.05%], $\nu_{\max}(\text{CO})$, 2071s, 2064sh, 2032m, and 2018w cm.⁻¹ (cyclohexane).

We thank the U.S. Air Force of Scientific Research for support of the work described, and Johnson Matthey Co. Ltd for a loan of rhodium and iridium chlorides.

[8/1373 Received, September 23rd, 1968]