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Preliminary communication

PENTAMETHYLCYCLOPENTADIENYL-RHODIUM AND -IRIDIUM COMPLEXES

XXIII*. DI-μ-CARBONYLBIS(PENTAMETHYLCYCLOPENTADIENYL-RHODIUM)

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Summary

The synthesis and properties of the novel dinuclear rhodium carbonyl complex $[Rh_2(\eta^5\text{-}C_5Me_5)_2(CO)_2]$ are reported.

The current widespread interest in cyclopentadienylrhodium carbonyl cluster complexes [2—7] prompts us to communicate the preparation of a new dinuclear complex $[Rh_2(C_5Me_5)_2(CO)_2]$ (I). The cyclopentadienylcobalt analogue $[Co_2(C_5H_5)_2(CO)_2]$ has been obtained [8,9], but there has so far been no report of a corresponding rhodium complex.

We find that, although the yellow $[Rh(C_5Me_5)(CO)_2]$ can, as described [10], be sublimed unchanged at 10^{-3} mmHg and 30—40°C, when it is heated (1 h/80—85°C) at higher pressure (10—20 mmHg) a new dark blue complex is obtained which proved to be $[Rh_2(C_5Me_5)_2(CO)_2]$ (I).

Complex I was characterised by elemental analysis (Found: C, 49.7; H, 5.4. $C_{22}H_{30}O_2Rh_2$ calcd.: C, 49.6; H, 5.7%), by its mass spectrum which indicated it to be dinuclear (*m/e* 532 $[Rh_2(C_5Me_5)_2(CO)_2]^+$, 504 $[Rh_2(C_5Me_5)_2(CO)]^+$, and 476 $[Rh_2(C_5Me_5)_2]^+$), as well as by ^1H and ^{13}C NMR spectroscopy (^1H NMR ($CDCl_3$), δ at 1.65 ppm (s, C_5Me_5); ^{13}C NMR (C_6D_6) δ 9.3 ($C_5\underline{Me}_5$) and 101.1 ppm (d, J(C—Rh) 6 Hz; $\underline{C}_5Me_5$)). The IR spectrum showed a strong ν(CO) band at 1732 cm^{-1}, consistent with the presence of bridging carbonyls. The IR spectrum of $[Co_2(C_5H_5)_2(CO)_2]$ showed ν(CO) at 1790 cm^{-1} [8] and, by analogy, we formulate I as shown with a rhodium—rhodium double bond. The colour arises from a charge-transfer band at 582 nm (in dichloromethane).

Complex I is stable to air in the solid for a day but decomposes very rapidly in solution on exposure to air to give a mixture, the water-soluble component of which showed a strong broad band in the IR spectrum at 1602 cm^{-1} consistent with the presence of a bidentate carbonato complex [11]. An analogous

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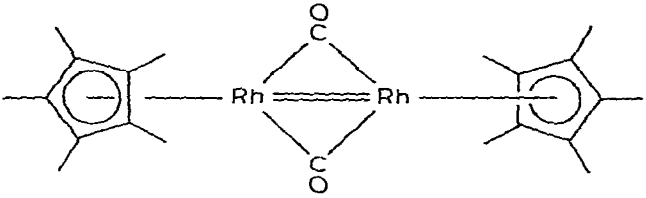
*For part XXII see ref. 1.



(I)

material was obtained by reaction of [$Rh_2(C_5Me_5)_2Cl_4$] and silver carbonate in water.

When complex I was treated with CO (3 h/20°C/1 atm) in toluene the solution turned from dark blue to brown. Evaporation of the solvent left a brown solid, the IR spectrum of which showed the presence of ca. 30% [$Rh(C_5Me_5)(CO)_2$] together with (ca. 5%) I and other materials showing ν(CO) at 1793 and 1947 cm^{-1}.

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