A New Synthesis and *X*-Ray Molecular Structure of Di-μ-carbonyltricarbonyltris(triphenylphosphine)dirhodium

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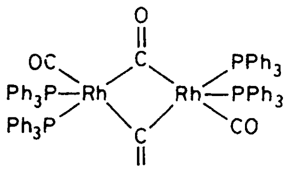
The rhodium dimer, $(CO)_2(PPh_3)Rh(\mu\text{-}CO)_2Rh(PPh_3)_2(CO)$ has been synthesized by treating anionic rhodium carbonyl complexes containing triphenylphosphine ligands with methanol; the molecular structure of this complex has been determined by single crystal *X*-ray diffraction.

In early studies of the rhodium catalysed hydroformylation of olefins, a complex which was often cited as the 'yellow dimer' was considered to be an important species in many reaction schemes [equation (1)].[1] Although this compound has been prepared by several research groups,[1,2] since it is insoluble in most common organic solvents and unstable under inert atmosphere (nitrogen or argon) or vacuum, previous efforts at a definitive characterization have been unsuccessful. Based on the i.r. spectra Wilkinson *et al.*[1a] suggested structure (**1**).

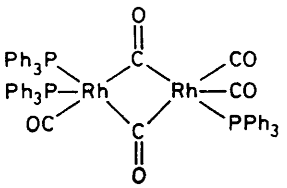
$$HRh(CO)(PPh_3)_3 \overset{CO}{\rightleftharpoons} HRh(CO)_2(PPh_3)_2 \underset{H_2}{\overset{-H_2}{\rightleftharpoons}} [Rh(CO)_2(PPh_3)_2]_2 \quad \text{yellow dimer} \qquad (1)$$

In our recent studies of anionic transition metal complexes, we have found a convenient way to prepare this complex in a crystalline form and have been able to determine its molecular structure by single crystal *X*-ray diffraction.

When $RhCl(CO)(PPh_3)_2$ was stirred in tetrahydrofuran (THF) in the presence of an excess of 1% sodium amalgam under 60 lb in^{-2} CO at 60 °C for 24 h, $Na^+[Rh(CO)_4]^-$ was formed [equation (2)].† After cooling the solution to room temperature and releasing the CO, the yellow solution was decanted and filtered. An excess of methanol was then slowly added to this yellow solution without shaking or stirring. Two layers of liquid were observed after addition of methanol. Single crystals of the yellow complex formed as the methanol diffused into the THF solution. Although this complex is unstable under nitrogen or vacuum, it is stable under a CO atmosphere. The i.r. spectra of these yellow crystals have been found to be identical to those obtained for the yellow dimer synthesized according to Wilkinson's method [Nujol, ν(CO) = 2018s, 1988vs, 1799s, and 1774vs cm^{-1}]. However, in contrast to the structure suggested for $(PPh_3)_2(CO)Rh(\mu\text{-}CO)_2Rh(CO)(PPh_3)_2$, our single crystal *X*-ray diffraction study‡ indicates that the compound is actually a dissymmetric trisphosphinepentacarbonyl dimer (**2**). The fact that this dimer contains only three triphenylphosphine ligands can probably be explained by the steric hindrance effect imposed by the ligands. This effect can be observed in the perspective view of this compound shown in Figure 1.



(**1**)



(**2**)

$$RhCl(CO)(PPh_3)_2 \xrightarrow[60\,°C]{Na\text{-}Hg,\ CO} [Rh(CO)_4]^- + 2PPh_3 + NaCl \qquad (2)$$
$$\nu(CO) = 1900\ cm^{-1}\ (\text{ref. } 4)$$

A possible mechanism for the formation of this compound is given in Scheme 1. This mechanism is supported by the fact that H_2 was observed in the gas phase (by mass spectrometric analysis) after the formation of the yellow dimer.

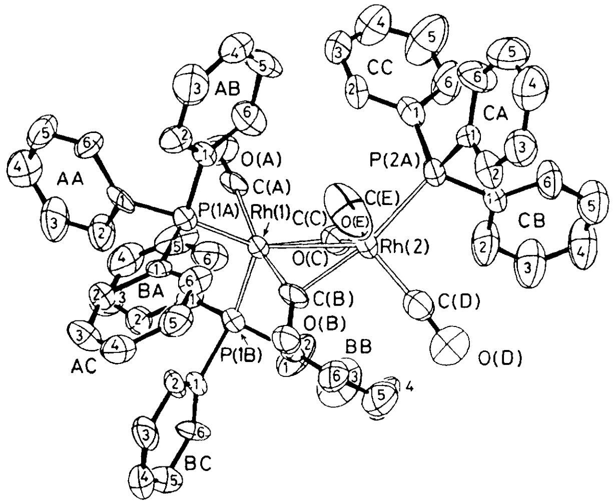


Figure 1. A perspective view of the structure of $[Rh_2(CO)_5(PPh_3)_3]$. Principal bond lengths (Å): Rh(1)–Rh(2), 2.769; Rh(1)–C(A), 1.949; Rh(1)–C(B), 1.939; Rh(1)–C(C), 2.034; Rh(1)–P(1A), 2.402; Rh(1)–P(1B), 2.369; Rh(2)–C(B), 2.090; Rh(2)–C(C), 2.008; Rh(2)–C(D), 1.858; Rh(2)–C(E), 1.862; and Rh(2)–P(2A), 2.387.

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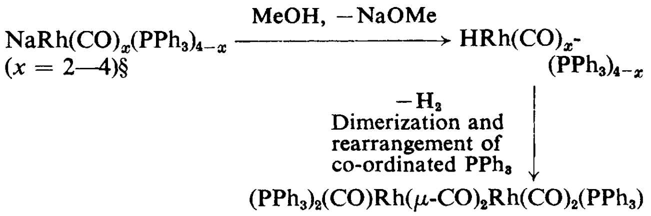
† Although Collman *et al.* suggested that $[Rh(CO)_2(PPh_3)_2]^-$ was the product under these conditions,[3] a high pressure i.r. study revealed that only $[Rh(CO)_4]^-$ was formed.

‡ *Crystal data* for (**2**): $C_{59}H_{45}O_5P_3Rh_2$, $M = 1132.74$, monoclinic, $a = 15.289(4)$, $b = 16.943(3)$, $c = 20.625(5)$ Å, $\beta = 72.67(2)°$, space group $P2_1/n$, $Z = 4$. The structure was solved by Patterson heavy atom methods and refined by a block diagonal least squares procedure to a discrepancy factor of 0.092 based on 3892 observed data. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



$$\begin{tikzcd}
\mathrm{NaRh(CO)}_x\mathrm{(PPh_3)}_{4-x}\ (x = 2\text{—}4)\S \arrow[r, "\mathrm{MeOH},\ -\mathrm{NaOMe}"] & \mathrm{HRh(CO)}_x\text{-}\mathrm{(PPh_3)}_{4-x} \arrow[d, "{-\mathrm{H_2}\ \text{Dimerization and rearrangement of co-ordinated } \mathrm{PPh_3}}"'] \\
& \mathrm{(PPh_3)_2(CO)Rh(\mu\text{-}CO)_2Rh(CO)_2(PPh_3)}
\end{tikzcd}$$

(2)

Scheme 1

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§ On release of CO, an i.r. study revealed that two Rh species are present. The major species is $[\mathrm{Rh(CO)_4}]^-$ (*ca.* 90%). The other species is $[\mathrm{Rh(CO)_3(PPh_3)}]^-$ (*ca.* 10%). The structure of $[\mathrm{Rh(CO)_3(PPh_3)}]^-$ has been determined by single crystal *X*-ray diffraction.[5] Although $[\mathrm{Rh(CO)_2(PPh_3)_2}]^-$ has not been observed at this stage, we can not exclude the possibility of its existence at a very low concentration.