2,2'-Bipyridyl and o-Phenanthroline Carbonyl Complexes of Rhodium

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Summary Two new carbonyl complexes of rhodium, $[Rh(CO)_2\,bipy]ClO_4$ and $[Rh(CO)_2\textit{o}\text{-phen}]ClO_4$ have been prepared.

EARLIER attempts to prepare 2,2'-bipyridyl and *o*-phenanthroline carbonyl complexes of rhodium have yielded only the binuclear complex $[Rh(CO)_2Cl]_2(bipy)$. Though the formation of some mononuclear complexes was also suspected such complexes were not actually isolated.[1]

Two new carbonyl complexes of rhodium, $[Rh(CO)_2\,bipy]ClO_4$ (I) and $[Rh(CO)_2\,\textit{o}\text{-phen}]ClO_4$ (II), have now been prepared by passing carbon monoxide through an alcoholic solution of rhodium perchlorate† and the requisite amount of 2,2'-bipyridyl or *o*-phenanthroline. They separate as yellow solids and behave as 1 : 1 electrolytes in nitrobenzene. With triphenylphosphine and triphenylarsine under similar conditions it is possible to isolate yellow crystalline solids which analyse as $[Rh(CO)_2(Ph_3P)_3]ClO_4$ (III) and $[Rh(CO)_2(Ph_3As)_3]ClO_4$(IV). Compounds (I) and (II) may also be obtained, though in a state of low purity, by passing carbon monoxide through a hot alcoholic solution of rhodium trichloride‡ until the solution turns yellow and then adding, at ice temperature, an excess of sodium perchlorate followed by the calculated amount of 2,2'-bipyridyl or *o*-phenanthroline. Compounds (I) and (II) in ethanol suspension react with triphenylphosphine to give yellow solids $[Rh(CO)\,bipy(Ph_3P)_2]ClO_4$ (V) and $[Rh(CO)\,\textit{o}\text{-phen}(Ph_3P)_2]ClO_4$ (VI) respectively. The complexes (V) and (VI) may also be obtained by the addition of 2,2'-bipyridyl or *o*-phenanthroline to a solution of (III) in alcohol. Similarly $[Rh(CO)\,bipy(Ph_3As)_2]ClO_4$ has been made from either (I) or (IV).

Properties of compounds

Compound[a]	Melting or decomposition point	I.r. bands[b] (Nujol mull) ν_{CO} cm^{-1}	Volume of CO[c] released, by 20 mg. of compound (ml., corrected to S.T.P.)	Conductance[d] ($\text{ohm}^{-1}\,\text{cm.}^2\,\text{mole}^{-1}$)
$[Rh(CO)_2\,bipy]ClO_4$	200—205°	2108,2050	1·88(2·16)	30·1
$[Rh(CO)_2\,\textit{o}\text{-phen}]ClO_4$	195—200	2105,2042	1·87(2·04)	28·1
$[Rh(CO)_2(Ph_3P)_3]ClO_4$	160—162	2025,2012	0·86(0·86)	28·1
$[Rh(CO)_2(Ph_3As)_3]ClO_4$	198—199	2020,2010	0·73(0·76)	25·9
$[Rh(CO)\,bipy(Ph_3P)_2]ClO_4$	150—152	1920		29·9
$[Rh(CO)\,\textit{o}\text{-phen}(Ph_3P)_2]ClO_4$	148—153	1940		27·9
$[Rh(CO)\,bipy(Ph_3As)_2]ClO_4$	205—208	1920		28·0

[a] Carbon, hydrogen, and nitrogen analyses for all the compounds have been carried out. These values are in good agreement with values required.

[b] All compounds showed νClO_4^- at 1098 ± 3 cm^{-1}.

[c] Figures within brackets indicate volumes required.

[d] Approximately 10^{-3}M solutions in nitrobenzene at 25° were used. *Cf.* literature values for 1 : 1 electrolytes: A. Kabesh and R. S. Nyholm, *J. Chem. Soc.*, 1951, 38; L. Malatesta and L. Vallarino, *J. Chem. Soc.*, 1956, 1867; L. Vallarino, *Inorg. Chem.*, 1965, **4**, 161.

Analytical results and i.r. and conductivity data are in conformity with the above formulations for the various compounds (Table). Compounds (I), (II), (III), and (IV) react with triphenyl phosphite in excess releasing all the carbon monoxide present. Measurements of the volumes of carbon monoxide released support the formulae assigned.

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† A hot aqueous solution of a known amount of "$RhCl_3,3H_2O$" (Johnson Matthey) was treated with an excess of sodium carbonate. The precipitate was washed free from chloride and dissolved in the minimum amount of perchloric acid "(E. Merck)". The acid solution was evaporated almost to dryness and made up to a volume. Portions of this solution were used for the preparations.

‡ "$RhCl_3,3H_2O$" (Johnson Matthey).

[1] W. Hieber, H. Heusinger, and O. Vohler, *Chem. Ber.*, 1957, **90**, 2425; D. N. Lawson and G. Wilkinson, *J. Chem. Soc.*, 1965, 1900.