CHEMICAL COMMUNICATIONS

Allylic Complexes of Rhodium

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WE have previously shown that the very convenient synthesis of allylpalladium chloride, from sodium chloropalladite, allyl chloride, and carbon monoxide reacting in aqueous methanol, proceeds via oxidative hydrolysis of co-ordinated carbon monoxide.¹ We suggested that similar oxidative hydrolysis might be a convenient route for the synthesis of other organometallic compounds and have now used it to make some allylic-rhodium complexes.

Addition of allyl chloride to a methanolic solution of rhodium chlorocarbonyl $[RhCl(CO)_2]_2$ gives no apparent reaction but on adding a little water, carbon dioxide and propene are evolved and the bridged-chloroallylrhodium(III) complex $[RhCl(all)_2]_2$ (all = C_3H_5) separates as orange-yellow prisms. With 2-methylallyl chloride reacting at 10° the corresponding 2-methylallyl

complex $[RhCl(C_4H_7)_2]_2$ forms but at 40° the major product is di- μ -chloro-bis(2,5-dimethylhexa-1,5diene)dirhodium(I) $[RhCl(C_8H_{14})]_2$ (identical with an authentic sample). The equation for the formation of the allylrhodium complex appears to be:

$$[RhCl(CO)_{2}]_{2} + 6C_{3}H_{5}Cl + 4H_{2}O =$$
$$[RhCl(C_{3}H_{5})_{2}]_{2} + 4CO_{2} + 2C_{3}H_{6} + 6HCl$$

We have also prepared the 1-methylallyl complex.

We formulate these complexes as bridged-chloro asymmetrically-bonded allylic complexes on the following evidence: (1) on treatment with methanolic potassium hydroxide² the allyl complex gives propene and the 2-methylallyl complex isobutene; (2) pyridine causes successive conversion into $[RhClpy(all)_2]$ and $[Rhpy_2(all)_2]^+$; (3) with thallous

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acetylacetonate volatile mononuclear complexes of the type [Rhacac(all)₂] (all = C_3H_5 , C_4H_7) are formed; (4) the n.m.r. spectra of the bridgedchloro- and acetylacetonato-complexes indicate asymmetrically bonded allylic ligands very similar to those found for the 2-methylallylpalladium complex $[PdCl(C_4H_7)(PPh_3)]^{3,4}$ We propose the structure (I) for the allyl complex $[RhCl(C_3H_5)_2]_2$ probably with the two carbon atoms in mutual trans-positions being further away and more weakly bonded to the rhodium than the ones in trans-positions to bridging chlorines. Treatment of the bridged chloro-complex $[RhCl(C_3H_5)_2]_2$ with cyclopentadienylthallium gives a volatile complex $[Rh(C_3H_5)_2(C_5H_5)];$ the n.m.r. spectrum of which indicates one π - and one σ - bonded allyl ligand.

When 2-methylallyl chloride reacts with carbon monoxide and $[RhCl(CO)_2]_2$ in a C_2H_5OD/D_2O mixture the 2-methylallyl complex $[RhCl(C_4H_7)_2]_2$ contains no deuterium but the isomeric diene complex $[RhCl(C_8H_{14})]_2$ is partially deuterated. It is therefore possible that formation of the diene complex requires protonation of complexed 2methylallyl to isobutene which is then inserted between the rhodium-carbon bond of another

- ¹ J. K. Nicholson, J. Powell, and B. L. Shaw, Chem. Comm., 1966, 174.
- ² H. Christ and R. Hüttel, Angew. Chem., 1963, 75, 921.
- ³ J. Powell, S. D. Robinson, and B. L. Shaw, Chem. Comm., 1965, 78.
- ⁴ R. Mason and D. R. Russell, Chem. Comm., 1966, 26.
- ⁸ R. Cramer, J. Amer. Chem. Soc., 1965, 87, 4717.

Both the 2-methylallyl and the diene complexes, $[RhCl(C_4H_7)_2]_2$ and $[RhCl(C_8H_{14})]_2$ respectively, react very rapidly with carbon monoxide to give free diene and $[RhCl(CO)_2]_2$.



Partial structure for $[RhCl(C_3H_5)_2]_2$; the complex is probably symmetrical about the Cl-bridges.

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