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-1,5-diene)dirhodium(I) $[RhCl(C_8H_{14})]_2$ (identical with an authentic sample). The equation for the formation of the allylrhodium complex appears to be:

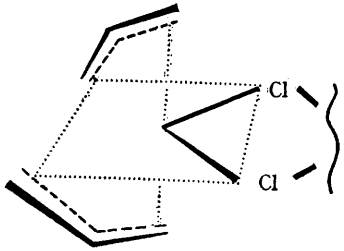
$$[RhCl(CO)_2]_2 + 6C_3H_5Cl + 4H_2O =$$
$$[RhCl(C_3H_5)_2]_2 + 4CO_2 + 2C_3H_6 + 6HCl$$

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 hydroxide[2] 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 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 bridged-chloro- 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 2-methylallyl to isobutene which is then inserted between the rhodium–carbon bond of another 2-methylallyl group. In the presence of a base such as triethylamine, diene complex formation is suppressed. The formation of diene may thus be similar to the rhodium-catalysed dimerisation of ethylene, investigated by Cramer.[5]

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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[5] R. Cramer, *J. Amer. Chem. Soc.*, 1965, 87, 4717.