Dihydrido-complexes of Osmium

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Summary The synthesis of *cis*-[OsH_2L_4] and *cis*-[$OsH_2(CO)L_3$] (L = tertiary phosphine or arsine) from [OsH_4L_3] are described, and the conversion of [$OsH_4(PEtPh_2)_3$] into a new dinitrogen complex [$OsH_2(N_2)(PEtPh_2)_3$].

METAL polyhydrido-complexes in general show a substitution pattern in which two hydride ligands may be replaced, directly or indirectly, by a single ligand molecule such as monotertiary phosphine, dinitrogen, or carbon monoxide. Recently, a large number of osmium tetrahydrido-complexes [OsH_4L_3] (L = tertiary phosphine or arsine) have been reported,[1,2] and these can be protonated to give [OsH_5L_3]$^+$. A hexahydrido-complex [$OsH_6(PMe_2Ph)_2$] has also been prepared.[1] We now report two series of dihydrido-complexes.

[OsH_4L_3] reacts with an excess of L in refluxing toluene during 24 h to give [OsH_2L_4] (L = PMe_2Ph, PEt_2Ph, $AsEt_2Ph$, $PMePh_2$, $PEtPh_2$, or $AsEtPh_2$). The complexes are generally air-stable, white, and crystalline, and in toluene solution show one band in the i.r. spectra in the region 1940—2000 cm^{-1} attributable to ν(Os–H). Similarly, under 1 atm pressure of carbon monoxide in refluxing toluene during 18 h [OsH_4L_3] yields [$OsH_2(CO)L_3$] (L = PMe_2Ph, PEt_2Ph, $PMePh_2$, $PEtPh_2$, or $AsEtPh_2$). The carbonyls are also air-stable, and in solution the i.r. spectra show two bands in the region 1840—1940 cm^{-1}. These are due to ν(C≡O) and ν(Os–H), possibly coupled.

The ^1H n.m.r. spectra of the compounds in the metal hydride region seem very similar to those of [$MH_2(PF_3)_4$] (M = Ru or Os),[3] [$RuH_2(PMe_2Ph)_4$],[4] and [$RuH_2(CO)(PMePh_2)_3$].[4] It is likely that all our dihydrido-complexes similarly have the hydride ligands in the *cis*-configuration.

Dinitrogen is capable of replacing two hydride ligands in some polyhydrido-complexes, *e.g.*, [$CoH_3(PPh_3)_3$], which yields [$CoH(N_2)(PPh_3)_3$].[5] The osmium tetrahydrides do not react with dinitrogen, even at a pressure of 150 atm. However, they do react with toluene-*p*-sulphonyl azide, a reagent which has been used in organic chemistry to replace two active hydrogen atoms from a methylene group by a diazo-group.[6] Only in one case, [$OsH_2(N_2)(PEtPh_2)_3$], was it possible to isolate a crystalline product. This compound has ν(N≡N) at 2085 cm^{-1} and ν(Os–H) at 1925 cm^{-1} (Nujol mull). It decomposes fairly rapidly at 20°, even under dinitrogen, and all the other homologues appeared to be even less stable.

ν(N≡N) in [$FeH_2(N_2)(PEtPh_2)_3$][7] is found at 2055 cm^{-1} and in [$FeH_2(N_2)(PPh_3)_3$][8] at 2074, 2053, and 2049 cm^{-1} (solid-state splitting). In [$RuH_2(N_3)PPh_3)_3$][9] it is found at 2147 cm^{-1}. These values all refer to Nujol mulls. ν(N≡N) does not vary much with the phosphine, but because the order of stability of these dinitrogen complexes is apparently Fe > Ru > Os, then ν(N≡N) does not show any reliable correlation with thermal or oxidative stability.

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