Phenylamido-complexes of Rhenium(I) and Rhenium(III)

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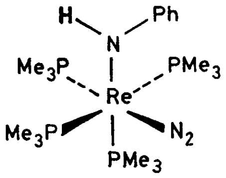
Summary The reduction of phenylimidotrichlorobis(trimethylphosphine)rhenium(V) in tetrahydrofuran by sodium amalgam under atmospheres of argon, nitrogen, hydrogen, carbon monoxide, and buta-1,3-diene, leads to new complexes in all of which there is a phenylamido-group, Re(NHPh).

It has been noted[1] that although arylimido-complexes of rhenium have long been known, few of their reactions have been studied.

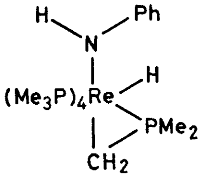
From $Re(NPh)Cl_3(PPh_3)_2$ and trimethylphosphine we have isolated $Re(NPh)Cl_3(PMe_3)_2$ and this complex, when reduced in tetrahydrofuran solution containing excess of PMe_3 by sodium amalgam, leads to a new series of phenylamido-complexes whose nature depends on the atmosphere used. All of the complexes have an Re(NHPh) group which shows an N–H stretching frequency in the i.r. spectra at *ca.* 3390 cm^{-1} and a broad resonance at *ca.* δ 2·3 in the ^1H n.m.r. spectra.

Under nitrogen we obtain the complex $Re(NHPh)(N_2)(PMe_3)_4$ (**1**) whose *X*-ray crystal structure has been determined,[2] while under argon the resulting air-sensitive complex is $ReH(NHPh)(\eta^2\text{-}CH_2PMe_2)(PMe_3)_4$, (**2**). This 8-co-ordinate rhenium(III) complex presumably arises from oxidative addition of the methyl group of PMe_3 to a rhenium(I) species. Such $\eta^2\text{-}CH_2PMe_2$ species have been recognised previously,[3] *e.g.*, in $FeH(\eta^2\text{-}CH_2PMe_2)(PMe_3)_3$.

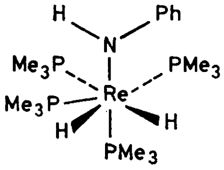
The complex (**2**) is converted into complex (**1**) by interaction with N_2, and both (**1**) and (**2**) react with hydrogen to give the 7-co-ordinate hydrido-complex $Re(H)_2(NHPh)(PMe_3)_4$ (**3**), which is readily obtained directly by reduction of $Re(NPh)Cl_3(PMe_3)_2$ under a hydrogen atmosphere.



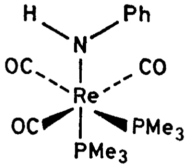
(**1**)



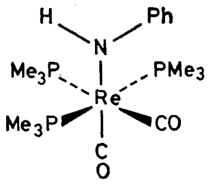
(**2**)



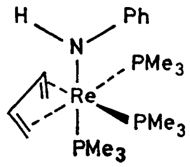
(**3**)



(**4**)



(**5**)



(**6**)

Under carbon monoxide direct reduction leads to $Re(NHPh)(CO)_3(PMe_3)_2$ (**4**) whereas interaction of the dinitrogen complex (**1**) with CO leads to $Re(NHPh)(CO)_2(PMe_3)_3$ (**5**).

Under a buta-1,3-diene atmosphere, direct reduction of $Re(NPh)Cl_3(PMe_3)_2$ leads to $Re(NHPh)(\eta^4\text{-}C_4H_6)(PMe_3)_2$ (**6**) whose *X*-ray crystal structure has also been determined.[2] This is a rare example of a rhenium–alkene complex, the only other comparable example being the hydride $Re(H)_3(\eta^4\text{-}C_4H_6)(PPh_3)_2$ recently described[4] as being formed from $ReH_7(PPh_3)_2$ on treatment with butadiene.

The ^1H and $^{31}P\{^1H\}$ n.m.r. spectra of the various compounds are all consistent with the structures shown in the diagrams.

Reductions in toluene solution lead to similar phenylamido-species.

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[1] G. La Monica and S. Cenini, *J. Chem. Soc., Dalton Trans.*, 1980, 1145.

[2] A. M. R. Galas and M. B. Hursthouse, Queen Mary College, London, personal communication.

[3] T. V. Harris, J. W. Rathke, and E. L. Muetterties, *J. Am. Chem. Soc.*, 1978, **100**, 6966; H. Schmidbauer and G. Blaschke, *Z. Naturforsch., Teil B*, 1980, **35**, 584.

[4] D. Baudry and M. Ephritikhine, *J. Chem. Soc., Chem. Commun.*, 1980, 249.