A Phenylazo-complex of Rhenium(III): the Structure of $Re(N_2C_6H_5)Cl_2[P(CH_3)_2C_6H_5]_3$

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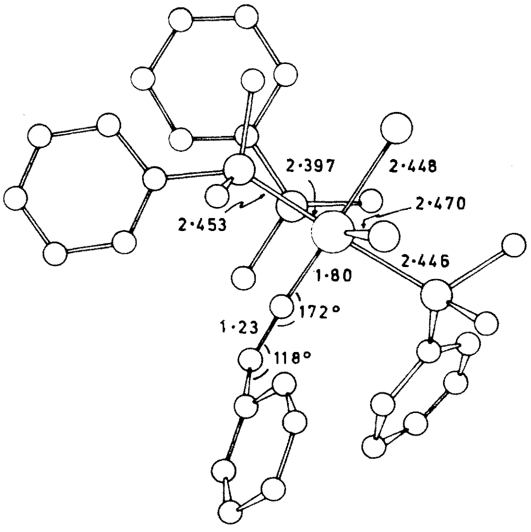
Summary The synthesis and stereochemistry of $Re(N_2C_6H_5)Cl_2(PMe_2Ph)_3$ are described, with particular emphasis on the geometry of the phenylazo-ligand and the metal–nitrogen bond length.

mer-$ReCl_3(PMe_2Ph)_3$ reacts with phenylhydrazine in refluxing ethanol to give two rhenium complexes; an orange complex (A) analysing for $C_{22}H_{30}Cl_2N_3P_2Re$, and a red complex (B) $C_{30}H_{38}Cl_2N_2P_3Re$. (A) is possibly a phenylhydrazine–nitridorhenium(V) complex with *trans*-phosphine ligands (from ^1H n.m.r. and i.r. spectral measurements). When treated with dimethylphenylphosphine (A) is converted into (B) in moderate yield. (B) shows no i.r. absorptions due to ν (NH) and signals due to N–H are not observed in the ^1H n.m.r. spectrum. (B) is now shown to be a phenylazo-derivative of rhenium(III), $ReCl_2(N_2Ph)(PMe_2Ph)_3$, with the structure shown in the Figure.

The bond lengths result from a least-squares refinement of the 3028 diffractometer-observed reflexion intensities for which $I_{obs} > 5\sigma(I_{obs})$—further refinement is continuing with the 3934 absorption corrected data for which $I_{obs} > 3\sigma(I_{obs})$; the present e.s.d.'s in the bond lengths average 0·004 Å (Re-P and Re–Cl) and 0·01 Å for bonds between the lighter atoms.



FIGURE

A comparison of the bond lengths in the present complex with those in *mer*-$ReCl_3(PMe_2Ph)_3$[1] shows the corresponding parameters to be identical within experimental error. Thus, the metal–phosphorus (P-*trans* to P) bond lengths average 2·458 Å in the trichloride and 2·449 Å in the phenylazo-derivative while the Re–P and Re–Cl bonds *trans* to one another are respectively 2·401 and 2·454 Å in the trichloride and 2·397 and 2·470 Å here. With an Re–Cl bond length of 2·448 Å *trans* to the phenylazo-ligand, it follows that the phenylazo-ligand has a *trans*-bond-lengthening effect which is only slightly less than that of a tertiary phosphine, whereas the nitride ion has a much larger *trans*-bond-weakening effect.[2]

The present analysis is clearly of interest in relation to the arylazo-compounds of platinum(II) which have been discussed by Parshall[3] and to the several studies of metal–nitrogen multiple bonds by Ibers *et al.*[4] Parshall provided spectroscopic evidence for 'substantial interaction' of metal orbitals with the azo-π-orbitals. The Re–N bond length of 1·80 Å is identical, within experimental error, to that in $ReNCl_2(PEt_2Ph)_3$[2] but 0·1 Å longer than those in three rhenium–imino-complexes.[4] The shortening by about 0·25 Å of the Re–N bond length in the azo-complex from the sum of single-bond covalent radii is consistent with the suggestion that the bond has a fair amount of π-bond character and the Re–N–N bond angle may also be rationalised in this way. The observed N–N bond length of 1·23 Å, identical with that for example in $H_3C{-}N{=}N{-}CH_3$,[5] suggests to us that the phenylazo-ligand is a σ- and π-donor[6] with respect to the rhenium(III) ion, whereas the evidence[3] that it is a σ-donor and π-acceptor with respect to platinum(II) is convincing.

Bright and Ibers[4] have summarised evidence in favour of the view that the metal–nitrogen bond lengths are sensitive to intramolecular steric effects. There is evidence for ligand–ligand overcrowding in the present complex for the *cis*-P–Re–P bond angles are typically 95° while the N–Re–Cl angle is 102°. One can also see that the metal-to-ligand bond lengths, *cis* to the phenylazo-ligand and nitride ion, are *ca.* 0·03 Å longer in the nitrido-complex,[2] but it is not certain that this result can be related simply to the differing steric and/or electronic effects of the methyl and ethyl substituents on the tertiary phosphine ligands. The quantitative distinction between the σ- and π-bonding properties of the two nitrogen ligands is evidenced in their very different *trans*-bond-weakening properties. The present result usefully supplements the list of metal–nitrogen bond lengths[4] and one notes that in two dichloro-metal complexes the metal–nitrogen bond length is 1·80 Å, in three trichloro-complexes 1·70 Å, and in two pentachloro-complexes is 1·60 Å (all ± 0·01 Å and referring to six-co-ordinate species only). It is difficult to avoid the conclusion that the total charge requirements of the metals in their various oxidation states play a substantial role in determining the extent to which a given nitrogen ligand forms multiple bonds with the metal.

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