An η^2-Allene Complex of Rhenium Formed from an Alkyne: *X*-Ray Structure of $[\mathrm{ReCl}(\eta^2\text{-}H_2C\text{–}C\text{=}CHPh)(Ph_2PCH_2CH_2PPh_2)_2]$

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Treatment of *trans*-$[\mathrm{ReCl}(N_2)(\mathrm{dppe})_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) with $PhC{\equiv}CCH_3$ in refluxing benzene or tetrahydrofuran gives a product shown by *X*-ray analysis to be the η^2-phenylallene complex $[\mathrm{ReCl}(\eta^2\text{-}H_2C\text{–}C\text{=}CHPh)(\mathrm{dppe})_2]$.

During the course of our investigations of the properties of dinitrogen analogues at dinitrogen-binding metal sites,[1] we have embarked upon the synthesis of the series *trans*-$[\mathrm{ReCl}(XY)(\mathrm{dppe})_2]$, where the dinitrogen analogue, XY, occupies the dinitrogen site. We have already described the properties of a series of complexes where XY = isonitrile[2] and we set out to prepare a further series where XY = alkyne. (Both isonitriles and alkynes are substrates of nitrogenase). To this end, we treated *trans*-$[\mathrm{ReCl}(N_2)(\mathrm{dppe})_2]$ with, *inter alia*, $PhC{\equiv}CCH_3$ in refluxing benzene, and obtained a yellow, diamagnetic, crystalline compound (A) [ν(CC) 1610m, 1588s, and 1566m cm^{-1} (Nujol)] which analysed as the solvated expected alkyne product.

X-Ray structural analysis, however, revealed that the ligand attached to rhenium is not the alkyne, but η^2-phenylallene, produced in effect by a 1,3-migration of a proton from the methyl group of the parent alkyne. Allene complexes of the transition metals are limited in number and confined essentially to the group 8B metals;[3] thus compound (A) is the first allene compound of rhenium to be reported and, so far as we are aware, the first allene complex to be prepared by such an apparent isomerisation of an alkyne. Compound (A) was initially prepared by reaction in refluxing tetrahydrofuran (thf), but the isomorphous crystals thus obtained did not diffract so well as those from benzene, data for which are quoted here.

Crystals of (A) are large, bright orange, rectangular prisms; diffraction intensities were measured on an Enraf–Nonius CAD4 diffractometer with monochromated radiation; there were 7889 reflections with $1.5 < \theta < 22.5°$. Intensities were corrected by Lorentz–polarisation factors, for absorption, and by Bayesian methods (to ensure no negative intensities).

Crystal data: $C_{61}H_{56}ClP_4Re\cdot1.5C_6H_6$, $M = 1251.8$, monoclinic, $C2/c$ (no. 15), $a = 26.878(6)$, $b = 12.429(2)$, $c = 36.238(7)$ Å, $\beta = 92.33(2)°$, $U = 12096.2$ Å^3, $D_c = 1.375$ g cm^{-3}, $Z = 8$, $\mu(\text{Mo-}K_\alpha) = 22.2$ cm^{-1}, $\lambda(\text{Mo-}K_{\bar\alpha}) = 0.71069$ Å.†

The structure of (A) was solved from Patterson and electron-density maps; hydrogen atoms in the allene chain were identified in difference maps and set to 'ride' on their neighbouring C atoms from those locations; all other H atoms were placed in idealised positions.

There is one benzene molecule disordered over at least two sites in a general location, and a second solvent molecule, which is ordered and well defined, is situated around a centre of symmetry. Atomic co-ordinates for the disordered molecules were refined with constraints applied to the molecular bonds and angles. Refinement by large-block least-squares methods was terminated with $R = 0.057$, and $R' = 0.059$ for all reflections; reflections were weighted $w = [\sigma(F)^2 + 0.001\,28F^2]^{-1}$.

The structure of (A) is shown in Figure 1, with important bond dimensions. The Re atom is six-co-ordinate, the two diphosphine ligands forming approximately rectangular co-

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† *Data for crystal from thf*: $C_{61}H_{56}ClP_4Re\cdot1.5C_4H_8O$, $M = 1242.8$, monoclinic, space group $C2/c$ (no. 15), $a = 26.793(5)$, $b = 12.368(5)$, $c = 36.182(7)$ Å, $\beta = 92.22(1)°$, $U = 11980.6$ Å^3, $D_c = 1.378$ g cm^{-3}, $Z = 8$, $\mu(\text{Mo-}K_\alpha) = 22.5$ cm^{-1}. $R = 0.094$ and $R' = 0.113$ for all 5529 reflections with $1.5 < \theta < 20°$. The atomic co-ordinates for both structures are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K. Requests should quote the full literature citation.

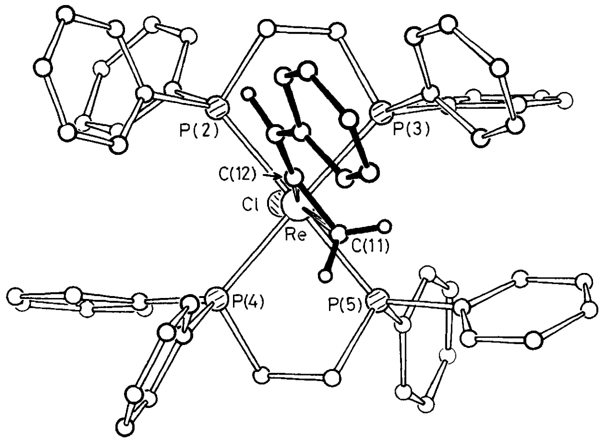

Figure 1. Structure of $[\mathrm{ReCl}\{\eta^2\text{-}\mathrm{H_2C{-}C{=}CH(Ph)}\}(\mathrm{dppe})_2]$. Selected molecular dimensions (with e.s.d.s in parentheses) are: Re–C(11) 2.181(6), Re–C(12) 2.087(6), Re–P(2) 2.454(2), Re–P(3) 2.413(2), Re–P(4) 2.424(2), Re–P(5) 2.470(2), Re–Cl 2.469(2), C(11)–C(12) 1.41(1), C(12)–C(13) 1.32(1), C(13)–C(14) 1.47(1) Å; P(2)–Re–P(5) 165.9(1), P(3)–Re–P(4) 177.4(1), C(11)–C(12)–C(13) 134.5(6), C(12)–C(13)–C(14) 127.4(6)°.

ordination about the equator, with the phenylallene and chlorine groups at opposite poles. The four P atoms do not make a good plane, but rather a shallow tetrahedron; the Re atom is not within this tetrahedron, but removed slightly towards the allene bond. The Re–P distances show a spread in values, with the distances to P(3) and P(4) (those on the same side of the tetrahedron as the Re and allene group) rather shorter than those to P(2) and P(5). These distortions result primarily from steric interactions of the bulky phosphine ligands and from the alignment of the phenylallene group.

The ligating allene atoms lie approximately parallel to the P(2)· · · P(5) vector and in the plane of these P atoms and the Cl atom. Indeed the whole phenylallene ligand is not bent far from this plane; the angle between the normals to the phenyl group of this ligand and the P,P,Cl plane is 14.7(3)°. Similar alignment of the allene carbon atoms is found in square-planar allene complexes of platinum[3] where the η^2-allene has a long C–C distance [*ca.* 1.48 Å, *cf.* 1.41(1) Å in (A)] and a short distance between the other two allenic carbons [*ca.* 1.33 Å, *cf.* 1.32(1) Å in (A)]. This type of bonding implies considerable σ-bond character in the rhenium–C_2 system, and represents one extreme form of allene ligation. The other extreme is where the η^2-C_2 distance is relatively short (*ca.* 1.37 Å) and in this case the η^2-C_2 group lies perpendicular to the metal–coligand plane (square-planar system).[3]

The ligating allene atoms in (A) are bisected precisely by the plane through P(3), P(4), and Cl: the Re–C(11) distance is marginally longer than Re–C(12) where the carbon atom has sp^2 hybridisation.

This alkyne–allene conversion is clearly related to the well known base-catalysed isomerisation of alkynes, which occurs *via* an allene intermediate.[4] To what extent the rhenium is involved in the above proton transfer is not clear, but will be investigated.

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