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Preliminary communication

THE FORMATION OF ALKYNE AND ALKYNYL COMPLEXES BY REACTION OF 1-ALKYNES WITH *trans*-[M(N_2)$_2$($Ph_2PCH_2CH_2PPh_2$)$_2$] (M = Mo OR W) AND WITH [Mo($Ph_2PCH_2PPh_2$)$_3$]: X-RAY STRUCTURE OF *trans*-[Mo(C≡CPh)$_2$($Ph_2PCH_2CH_2PPh_2$)$_2$]

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Summary

Reaction of RC≡CH (R = Ph, CO_2Me or CO_2Et) with *trans*-[M(N_2)$_2$(dppe)$_2$] (M = Mo or W; dppe = $Ph_2PCH_2CH_2PPh_2$) or [Mo(dppm)$_3$] (dppm = $Ph_2PCH_2PPh_2$) gives the alkyne complexes [M(RC≡CH)$_2$(diphos)$_2$] (diphos = dppe, M = Mo, R = Ph; diphos = dppm, M = Mo, R = Ph or CO_2Me) and the alkynyl complexes *trans*-[M(C≡CR)$_2$(dppe)$_2$], [MH_2(C≡CR)$_2$(dppe)$_2$] (M = Mo or W, R = Ph, CO_2Me or CO_2Et) and *cis*-[WH(C≡CCO_2Me)(dppe)$_2$]: the X-ray structure of *trans*-[Mo(C≡CPh)$_2$(dppe)$_2$] is reported.

Alkynes are reagents of particular interest, not only because of their ability to transform at metal centres, inter alia to alkynyl (M–C≡CR) and vinylidene (M=C=CHR) compounds [1], but also because the reduction of acetylene to ethylene is an important probe of the active centre of the metallo-enzyme nitrogenase [2].

Because of our interest in the use of alternative substrates to gain knowledge of nitrogenase, we have commenced a programme of study of the behaviour of alkynes at dinitrogen-binding centres. We have previously reported the reactions of alkynes at the dinitrogen-binding centre {ReCl(dppe)$_2$}, which give the vinylidene complexes [3] [ReCl(C=CHR)(dppe)$_2$] (from RC≡CH) and the η^2-allene complex [4] [ReCl(η^2-$H_2\underbrace{C-C}$=CHPh)(dppe)$_2$] (from CH_3C≡CPh). Alkyne complex intermediates were proposed in these reactions, but were not isolated.

We now report our studies on the reactions of alkynes with the dinitrogen complexes *trans*-[Mo(N_2)$_2$(dppe)$_2$] (**A**) and with the labile complex [Mo(dppm)$_3$]

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(**B**), which give rise to alkyne and alkynyl complexes, but not vinylidene nor η^2-allene compounds.

Thus, treatment of **A** or **B** with $RC\equiv CR'$ at reflux in THF (tetrahydrofuran) gives the diamagnetic alkyne complexes *trans*-$[Mo(RC\equiv CR')_2(dppe)_2]$ and *cis*-$[Mo(RC\equiv CR')_2(dppm)_2]$ ($R = H$, $R' = CO_2Me$ or Ph; $R' = Me$, $R = Ph$) by displacement of N_2 and dppm respectively. The formulation of these compounds follows from analysis and spectroscopic data. Thus, e.g., the presence of the alkyne ligand in *trans*-$[Mo(PhC\equiv CH)_2(dppe)_2]$ and *cis*-$[Mo(HC\equiv CCO_2Me)_2(dppm)_2]$ has been confirmed by ^{13}C NMR spectroscopy. ($H\mathit{C}\equiv CR$ resonances 150.9 ppm (CD_2Cl_2) and 149.3 ppm ($CDCl_3$) respectively, relative to $SiMe_4$; doubletted in undecoupled spectra, $^1J(CH)$ 159.0 and 154.4 Hz respectively.)

The N_2-ligand is more labile in **A** than in *trans*-$[ReCl(N_2)(dppe)_2]$ **C**, and reactions of **A** with alkynes may be induced by tungsten irradiation at 20 °C, as opposed to prolonged reflux and irradiation for **C**. Under these milder conditions, oxidation of the metal occurs for **A**, to give the alkynyl complexes *trans*-$[M(C\equiv CR)_2(dppe)_2]$ (M = Mo or W, R = Ph, CO_2Me or CO_2Et), *cis*-$[WH(C\equiv CCO_2Me)(dppe)_2]$ and $[MH_2(C\equiv CR)_2(dppe)_2]$ (M = Mo or W, R = Ph, CO_2Me or CO_2Et).

These diamagnetic compounds have been characterised by analysis, their spectroscopic properties (e.g., $\nu(C\equiv C)$ in the range 2010–2040 cm^{-1}, $\delta(M-H)$ in the range -0.3 to -2.0 ppm rel. $SiMe_4$), and by X-ray crystallography for *trans*-$[Mo(C\equiv CPh)_2(dppe)_2]$, the structure of which * is shown in Figure 1, together with important bond distances and angles.

The Mo atom lies on a crystallographic centre of symmetry and its coordination pattern is essentially (*trans*) octahedral. The virtually linear alkynyl group is ca. 11° away from the normal to the plane of the four P-atoms, and the four phosphine phenyl groups on that side of the molecule each have close contacts with the $C\equiv C$

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* *Crystal data* for *trans*-$[Mo(C\equiv CPh)_2(Ph_2PCH_2CH_2PPh_2)_2]\cdot 2THF$ (THF = tetrahydrofuran): $C_{68}H_{58}MoP_4\cdot 2C_4H_8O$, i.e. $C_{76}H_{74}MoO_2P_4$, $M = 1239.3$. Trinclinic, $a = 9.928(5)$, $b = 12.086(4)$, $c = 14.794(2)$ Å, $\alpha = 108.21(2)$, $\beta = 96.77(3)$, $\gamma = 101.36(3)°$, $V = 1622.3$ Å^3. Space group $P\bar{1}$ (no. 2). $Z = 1$, $D_c = 1.268$ g cm^{-3}, $F(000) = 6348$. $\mu(Mo-K_\alpha) = 3.4$ cm^{-1}. $\lambda(Mo-K_{\bar\alpha}) = 0.71069$ Å.

Crystals were deep red plates of irregular shape. The sample selected for single-crystal analysis was ca. 0.31×0.29×0.10 mm, and diffracted only weakly. After photographic examination, this crystal was mounted on an Enraf–Nonius CAD4 diffractometer (with graphite monochromator) for measurement of accurate cell parameters (from settings of 24 centred reflections with $\theta = 10–11°$) and diffraction intensities (5700 unique reflections with $\theta_{max} = 25°$). In processing, the data were corrected for Lorentz-polarisation and absorption effects, and statistically for negative net intensities.

The molecular structure was determined by the heavy atom method, and refined by full-matrix least-squares methods in the program SHELX [9]. Hydrogen atoms were included, in idealised positions, on the ligands of the Mo complex. The atoms of the solvent THF molecule are disordered in at least two orientations, in which four atom peaks are approximately common to the two arrangements; the oxygen atom has not been identified. At completion $R = 0.103$, $R_w = 0.098$ for 4250 reflections (with $I > \sigma(I)$ and a refined weighting scheme: $w = (\sigma_F^2 + 0.00433\ F^2)^{-1}$.

Scattering curves were from ref. 10. The programmes, adapted for use on a VAX 11/750 computer, used in the data processing, analysis of results and for the drawing of the diagram are listed in ref. 11. Tables of atomic parameters and molecular dimensions are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1 EW (Great Britian). Any request should be accompanied by the full literature citation for this communication.

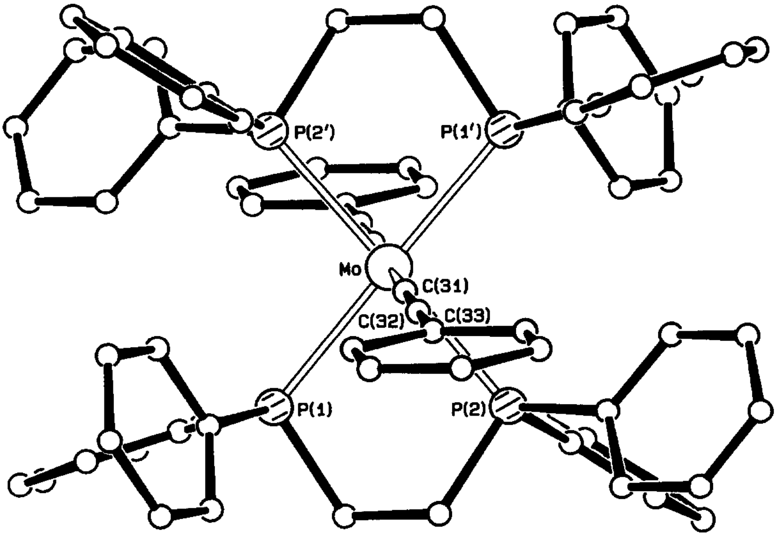

Fig. 1. The molecular structure of *trans*-$[Mo(C{\equiv}CPh)_2(Ph_2PCH_2CH_2PPh_2)_2]$. Selected molecular dimensions are: Mo–P(1) 2.501(2), Mo–P(2) 2.514(2), Mo–C(31) 2.093(8), C(31)–C(32) 1.237(12), C(32)–C(33) 1.422(12) Å; P(1)–Mo–P(2) 79.8(12), P(1)–Mo–C(31) 86.7(3), P(2)–Mo–C(31) 79.1(2), Mo–C(31)–C(32) 175.6(7), C(31)–C(32)–C(33) 177.8(9)°.

group. The phenyl group of the alkynyl ligand extends far beyond the phosphine ligands.

We believe this to be the first structurally characterised alkynylmolybdenum complex, and that only one similar (mono-nuclear) tungsten complex, viz. $[W(CO)_2(PMe_3)(C_5H_5)(C{\equiv}C{-}C_3H_5)]$, has been structurally characterized [5]. Our C≡C distance, (1.24(1) Å) is longer than that of free acetylene, 1.205 Å [6] and is at the longer end of the range observed in other alkynyl complexes (1.19–1.25 Å) [7]; in the W complex it is 1.205(15) Å [5]. The lengthening in the Mo complex is balanced by a slight shortening in the M–C bond; Mo–C is 2.093(8) Å compared with 2.134(11) Å in the W complex. Both these M–C bonds seem to have a bond order of rather more than one; in a remarkable alkylalkylidenealkylidyne-tungsten (VI) complex [8], formula $[W(dmpe)(CH_2CMe_3)({=}CHCMe_3)({\equiv}CCMe_3)]$ (dmpe = $Me_2PCH_2CH_2PMe_2$), the W–C(alkyl) single-bond length is 2.258(9) Å and the W=C(alkylidene) double-bond length is 1.942(9) Å.

The contrast between the reactions promoted by **C** as opposed to **A** and **B** is interesting. The dominant feature of the rhenium-centred reactions is the formation of Re–C multiple bonds with apparent H migration within the carbon chain of the alkyne. In contrast, the dominant feature of the reactions of **A** is cleavage of the C–H bond with formation of metal-hydride species and no internal H-migration. Presumably the precursors to *trans*-$[M(C{\equiv}CR)_2(dppe)_2]$ are hydrides and reactions of **A**, **B** and **C** involve alkyne-complex intermediates although they appear to be very labile under the conditions used for experiments with **C**.

The presence of the π-donor chloride ligand in **C** which would help stabilisation of Re–C multiple bonds (and destabilise the rhenium–alkyne $\pi\perp$ bond component) [3] may explain why vinylidene and η^2-allene complexes are favoured by this centre. The ease of loss of N_2 to give an open centre, ease of oxidation and lack of a π-donor ligand are factors which would favour C–H oxidative addition with **A**.

Although hydride-alkynyl intermediates have been suggested to be involved in the formation of some vinylidene complexes [12], this does not appear to be the case in the reactions described here. Indeed, a theoretical study of these reactions at d^6-ML_5 metal centres suggests that hydrogen transfer occurs via an η^2- to η^1-alkyne rearrangement followed by proton migration [13].

Further studies on the mechanism of these reactions and the reactions of the hydride-alkynyl complexes are under investigation to help clarify these points.

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References

1 A.J.L. Pombeiro, D.L. Hughes, R.L. Richards, J. Silvestre and R. Hoffmann, J. Chem. Soc. Chem. Commun., (1986) 1125 and ref. therein.

2 J.R. Postgate, The Fundamentals of Nitrogen Fixation, Cambridge Univ. Press, London, 1982, p. 41.

3 A.J.L. Pombeiro, J.C. Jeffery, C.J. Pickett and R.L. Richards, J. Organomet. Chem., 277 (1984) C7.

4 D.L. Hughes, A.J.L. Pombeiro, C.J. Pickett and R.L. Richards, J. Chem. Soc. Chem. Commun., (1984) 992.

5 W. Sieber, M. Wolfgruber, D. Neugebauer, O. Orama, and F.R. Kreissl, Z. Naturforsch. B, 38 (1983) 67.

6 M.T. Christensen, D.R. Eaton, B.A. Green and H.W. Thompson, Proc. Roy. Soc. A, 238 (1956) 15.

7 e.g. R. Goddard, J. Howard and P. Woodward, J. Chem. Soc. Dalton Trans., (1974) 2025; M.I. Bruce, T.W. Hambley, M.R. Snow and A.G. Swincer, J. Organomet. Chem., 235 (1982) 105; A. Furlani, S. Licoccia, M.V. Russo, A.C. Villa and C. Guastini, J. Chem. Soc. Dalton Trans., (1982) 2449; A. Blagg, A.T. Hutton, P.G. Pringle and B.L. Shaw, Inorg. Chim. Acta, 76 (1983) L265; J. Geisenberger, U. Nagel, A. Sebalt and W. Beck, Chem. Ber., 116 (1983) 911.

8 M.R. Churchill and W.J. Youngs, Inorg. Chem., 18 (1979) 2454.

9 G.M. Sheldrick, SHELX-76, Program for Crystal Structure Determination, University of Cambridge, 1976.

10 International Tables for X-ray Crystallography, Kynoch Press, Birmingham, 1974, vol. 4, 99 and 149.

11 S.N. Anderson, R.L. Richards and D.L. Hughes, J. Chem. Soc. Dalton Trans. (1986) 245.

12 F.J.G. Alonso, A. Hölm, J. Wolf, H. Otto and H. Werner, Angew. Chem. Int. Ed. Eng., 24 (1985) 407.

13 J. Silvestre and R. Hoffmann, Helv. Chim. Acta, 68 (1985) 1461 and ref. therein.