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Preliminary communication

Synthesis and crystal structure of $[MoH_3(C{\equiv}CBu^t)(Ph_2PCH_2CH_2PPh_2)_2]$, a trihydrido-alkynyl complex

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Abstract

Reaction of $Bu^tC{\equiv}CH$ with *trans*-$[Mo(N_2)_2(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) gives $[MoH_3(C{\equiv}CBu^t)(dppe)_2]$, whose X-ray structure is reported.

In pursuing our interest in the activation of nitrogenase substrates by dinitrogen-binding transition metal sites [1], we have investigated the reactions of alkynes with $[CoH(N_2)(PPh_3)_3]$ [2], *trans*-$[ReCl(N_2)(dppe)_2]$ [3,4] and *trans*-$[M(N_2)_2(dppe)_2]$ (M = Mo or W) [5,6], and observed that they undergo catalytic oligomerization and cyclization reactions at the labile cobalt-centre [2], but no intermediate complexes have been isolated. However, for the more robust metal sites $\{ReCl(dppe)_2\}$ and $\{M(dppe)_2\}$ (M = Mo or W), with chelating diphosphine ligands, a variety of complexes with ligating alkyne-derived species has been isolated. For the $\{ReCl(dppe)_2\}$ site, the dominant reactions involve hydrogen migration along the alkyne carbon framework to give the vinylidene complexes *trans*-$[ReCl(C{=}CHR)(dppe)_2]$ (from 1-alkynes, $RC{\equiv}CH$) [3] or the η^2-allene compound *trans*-$[ReCl(\eta^2\text{-}H_2C{-}C{=}CHPh)(dppe)_2]$ (from $CH_3C{\equiv}CPh$) [4], but at the more electron-rich $\{M(dppe)_2\}$ sites C–H oxidative addition reactions occur to form the hydridoalkynyl, dihydridodialkynyl and dialkynyl complexes $[MH(C{\equiv}CR)(dppe)_2]$ [5], $[MH_2(C{\equiv}CR)_2(dppe)_2]$ [5,6] and $[M(C{\equiv}CR)_2(dppe)_2]$ [5] from $RC{\equiv}CH$.

We now report that on treatment of a tetrahydrofuran solution of *trans*-$[Mo(N_2)_2(dppe)_2]$ with a circa eightfold molar excess of $Bu^tC{\equiv}CH$, the complex $[MoH_3(C{\equiv}CBu^t)(dppe)_2]$ is obtained, providing, to our knowledge, the first example of a trihydridoalkynyl species. It has been isolated as a yellow crystalline solid [ν(MoH) broad, medium intensity bands circa 1805 and 1740 cm^{-1}; δ(MoH) symmetrical complex pattern centred at -4.57 ppm rel. $SiMe_4$ in $C_2D_2Cl_2$]. Its

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molecular structure, as determined by an X-ray diffraction study *, is depicted in Fig. 1, together with important bond lengths and angles.

The displacements and dimensions of the phosphine and alkynyl ligands about the Mo atom were seen to conform to the normal dodecahedral pattern, with the four P atoms in the pseudo-equatorial (B) sites and the alkynyl ligand in an (A) site; the identification of the three hydride groups, in difference maps, and their well-behaved refinement to positions close to the remaining (A) sites in this scheme, establish the product as a trihydrido-Mo complex.

For the virtually linear alkynyl ligand, the Mo–C and the C≡C distances, 2.175(10) and 1.209(14) Å, are somewhat longer and shorter, respectively, than the corresponding ones, 2.093(8) and 1.237(12) Å [5], for the ligating alkynyls at *trans*-$[Mo(C{\equiv}CPh)_2(dppe)_2]$ where a metal–carbon bond order higher than one has been recognized. This lengthening of the Mo–C bond, and the concomitant shortening of the C≡C bonds in the trihydride complex, reflect the expected relatively weaker π-acceptance of the $-C{\equiv}CBu^t$ ligand at the trihydride-Mo^{IV} centre. The C≡C distance in the trihydride complex, 1.209(14) Å, is close to that of free acetylene, 1.205 Å [7], and approaches the lower limit of the range observed in other alkynyl complexes (1.19–1.25 Å) [8].

The complex $[MoH_3(C{\equiv}CBu^t)(dppe)_2]$ is particularly interesting in view of the suggested [9] involvement of a trihydride-molybdenum site in the enzymatic process. Its reactivity, towards hydrogen migration and protonation, is being investigated on

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* *Crystal structure analysis of* $[MoH_3(C{\equiv}CBu^t)(dppe)_2]\cdot THF$.

Crystal data: $C_{58}H_{60}MoP_4\cdot C_4H_8O$, $M = 1049.1$. Monoclinic, $a = 21.057(6)$, $b = 21.435(7)$, $c = 25.056(9)$ Å, $\beta = 103.19(3)°$, $V = 11011.2$ Å^3. Space group $I2/c$ (equivalent to no. 15), $Z = 8$, $D_c = 1.265$ g cm^{-3}, $F(000) = 4400$, μ(Mo-K_α) = 3.8 cm^{-1}, λ(Mo-K_α) = 0.71069 Å.

A plate-shaped yellow crystal (circa $0.57\times0.48\times0.29$ mm) was mounted, coated in silicone grease, and, after photographic examination, transferred to our Enraf-Nonius CAD4 diffractometer (with monochromated radiation) for determination of accurate cell dimensions (from 25 reflections with θ circa 10.5°, each centred in four orientations) and measurement of diffraction intensities (to $\theta_{max} = 23°$). During the data collection, the intensities of two monitored reflections decreased steadily to circa 60% of their starting values. Corrections for this deterioration, for Lorentz-polarisation effects and for absorption (from the crystal size and shape) were made. Data for 7181 unique reflections were input to the SHELX program system [12].

The structure was determined by the heavy atom method, and refined by block-diagonal least-squares methods [13], allowing anisotropic thermal parameters for the non-hydrogen atoms of the Mo-complex molecule. The three hydride ligands were identified in difference maps and were refined independently and satisfactorily using neutral H atom scattering factors; the isotropic thermal parameters are low for all three atoms, i.e. U_{iso} refined to $-0.017(13)$, $0.039(25)$ and $-0.001(16)$ Å^2 for H(6), H(7) and H(8). The other H atoms in this molecule were included with idealised parameters except in one methyl group, where refinement was unsatisfactory and the H atoms were omitted. Two solvent molecules (one of these disordered in two orientations) were found lying about 2-fold symmetry axes; the O atoms were not identified and, during refinement, the bond dimensions in these molecules were restrained.

Refinement was concluded with $R = 0.082$ and $R_w = 0.083$ [12] for 4717 reflections (i.e. those with $I > 3/2\sigma_I$) weighted $w = (\sigma_F^2 + 0.004F_o^2)^{-1}$. In the final difference map, the four major peaks, circa 0.8–0.9 e Å^{-3}, were each about 1.1 Å from the Mo atom; the next highest peaks (below 0.75 e Å^{-3}) were in the region of the solvent molecules.Scattering factors for neutral atoms were taken from reference [14]. Computer programs, as noted above and in Table 4 of reference [15], were run on the MicroVAX II computer in the Nitrogen Fixation Laboratory.

Tables of atomic coordinates and bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre.

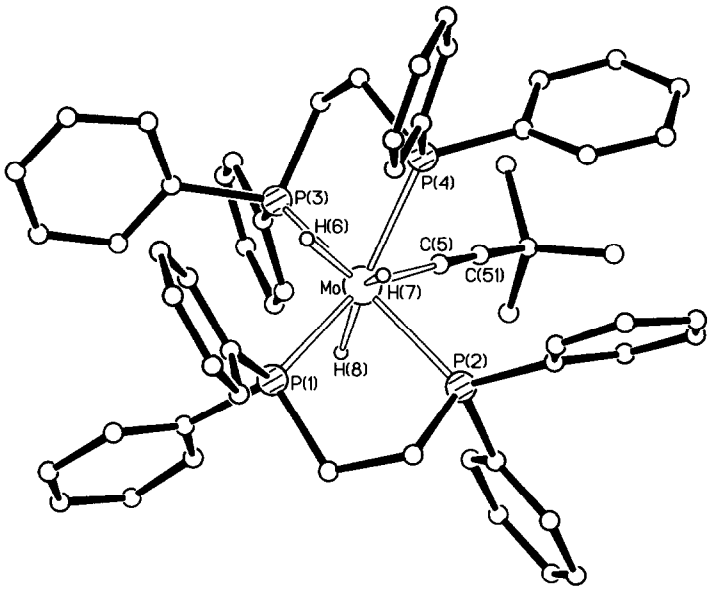

Fig. 1. The molecular structure of $[MoH_3(C{\equiv}CBu^t)(dppe)_2]$. Selected molecular dimensions (with e.s.d.s. in parentheses) are: Mo–P(1) 2.403(3), Mo–P(2) 2.436(3), Mo–P(3) 2.447(3), Mo–P(4) 2.465(3), Mo–C(5) 2.175(10), Mo–H(6) 1.44(5), Mo–H(7) 1.51(8), Mo–H(8) 1.69(6), C(5)–C(51) 1.209(14), C(51)–C(52) 1.458(15) Å; H(6)–Mo–H(7) 64(4), C(5)–Mo–H(8) 70(2), Mo–C(5)–C(51) 176.9(8), C(5)–C(51)–C(52) 177.1(11)°.

account of the known conversion of alkynes to alkenes by molybdenum nitrogenase [10] and to alkanes by the vanadium enzyme [11]. Moreover, the complex contains a number of hydrogens in the coordination sphere which, in principle, may be sufficient for the full conversion of the ligating alkyne-derived alkynyl group into the corresponding alkene.

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