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Synthesis and X-ray crystal structure of *trans*-$[MoF(\equiv CCH_2{}^tBu)(Ph_2PCH_2CH_2PPh_2)_2][BF_4]$, a paramagnetic alkylidynefluorocomplex

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Abstract

Treatment of the alkynylhydridocomplex $[MoH_3(C\equiv C{}^tBu)(dppe)_2]$(dppe = $Ph_2PCH_2CH_2PPh_2$) with $[Et_2OH][BF_4]$ gives *trans*-$[MoF(\equiv CCH_2{}^tBu)(dppe)_2]$, the first example of a stable paramagnetic alkylidyne complex, the X-ray structure of which is reported.

During the course of our studies on the activation of 1-alkynes (alternative substrates of nitrogenase) by electron-rich transition metal centres which can bind dinitrogen [1], we have observed C–H oxidative addition reactions at the electron-rich $\{M(dppe)_2\}$ (M = Mo or W, dppe = $Ph_2PCH_2CH_2PPh_2$) centres [2] to give a variety of alkynyl complexes. In particular, the compounds $[MH_2(C\equiv CR)_2(dppe)_2]$ (R = Ph, CO_2Me, or CO_2Et) have been obtained [2] from the reactions of $RC\equiv CH$ with *trans*-$[M(N_2)_2(dppe)_2]$.

However, when the bulky alkyne $^tBuC\equiv CH$ was used, the trihydridomonoalkynyl species $[MoH_3(C\equiv C{}^tBu)(dppe)_2]$ (A) resulted [3].

The tungsten complexes $[WH_2(C\equiv CR)_2(dppe)_2]$ (R = Ph or CO_2Me) were shown to undergo protonation to give the alkylidyne $[WF(\equiv CCH_2R)(dppe)_2]$ (R = CO_2Me) or the alkylidene $[WF(=CHCH_2R)(dppe)_2][BF_4]$ (R = Ph) compounds [2]. In the present work, we report an extension of these protonation studies to the trihydridomolybdenum species (A).

Treatment of a CH_2Cl_2 solution of **A** with a two-fold molar excess of $[Et_2OH][BF_4]$ in ether leads to the formation of a number of products. By

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concentration of the solution followed by addition of diethyl ether we have been able to isolate one of them, **B**, in about 15% yield as red-orange crystals. The molecular structure of **B**, *trans*-[MoF(≡CCH$_2$^{t}Bu)(dppe)$_2$][BF$_4$] has been authenticated by X-ray analysis * and is depicted in Fig. 1, together with relevant bond distances and angles. **B** is paramagnetic and in the solid at 77*K* shows a broad EPR resonance with g_{av} circa 2.03. As might be expected, its NMR spectrum is very broad and uninformative; it has a broad [BF$_4$] absorption at 1020–1100 cm^{-1} in its IR spectrum.

To our knowledge, **B** provides the first example of a stable *paramagnetic* alkylidyne species [4]. It also extends to molybdenum the rather limited number of known alkylidyne fluoro-complexes [5,6].

In this approximately octahedrally coordinated complex, the alkylidyne ligand is *trans* to the fluoride atom and is disordered with two possible orientations. The major arrangement (*ca.* 80% occupancy) is indicated in Fig. 1 by the filled bonds. The two alternative methylene groups at C(51) and C(51)x are quite distinct. The alkylidyne and tertiary C atoms, C(5) and C(52), presumably also have different pairs of positions corresponding to the two orientations; in each case, the two sites are not far apart and have been accommodated in this analysis by single, whole atoms with anisotropic thermal parameters. The bond dimensions in this ligand must therefore be considered with some caution, *e.g.*, the Mo≡C–C angle in each orientation is probably much closer to 180° than the values quoted in the legend of Fig. 1, with corresponding slight reductions in the Mo≡C and C–C bond lengths.

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* *Crystal structure analysis of* trans-*[MoF(≡CCH$_2$^{t}Bu)(dppe)$_2$][BF$_4$]·Et$_2$O*. Crystal data: C$_{58}$H$_{59}$FMoP$_4$·BF$_4$·C$_4$H$_{10}$O, $M = 1155.9$. Monoclinic, space group $P2_1/n$ (equivalent to no. 14), $a = 13.886(1)$, $b = 17.638(2)$, $c = 23.951(4)$ Å, $\beta = 97.03(1)°$, $V = 5821.9$ Å^3. $Z = 4$, $D_c = 1.319$ g cm^3. $F(000) = 2404$, μ(Mo-K_α) = 3.8 cm^{-1}, λ(Mo-$K_{\bar{\alpha}}$) = 0.71069 Å.

Crystals of the carbyne product were normally very fine, deep red needles bound in rosette formations. Eventually, more suitable larger orange plates were grown and one, *ca.* 0.07×0.30×0.40 mm was mounted on a glass fibre and coated in silicon grease. After photographic examination, this crystal was transferred to our Enraf–Nonius CAD4 diffractometer (with monochromated radiation) for determination of accurate cell dimensions (from the goniometer settings of 25 reflections with θ *ca.* 10.5°, each centred in four orientations) and measurement of diffraction intensities (7567 independent reflections to $\theta_{max} = 22.5°$). During processing, the intensities were corrected for Lorentz-polarisation effects and to eliminate negative net values (by Bayesian statistical methods). No corrections for crystal deterioration or absorption were necessary.

The structure was determined by the heavy atom method in the SHELX program system [8], and refined by large-block-matrix least-squares methods, with SHELXN [9], to $R = 0.058$, $R_g = 0.077$ [8] for 5579 reflections (those having $I > 3/2\sigma_I$) weighted $w = (\sigma_F^2 + 0.00243\ F^2)^{-1}$. Hydrogen atoms were included in idealised positions in the diphosphine ligands but not in the carbyne ligand which was disordered in two orientations, with occupancy ratio *ca.* 0.80/0.20. The anion was also disordered, with one fixed B–F bond common to three distinct arrangements for the remaining F atoms. A solvent molecule, presumed to be ether, is disordered and not fully resolved.

All the ordered non-hydrogen atoms were refined anisotropically; those with part occupancy were refined isotropically. In the carbyne ligand, the ligating and tertiary C atoms, C(5) and C(52), are assumed common to both orientations of the ligand and were refined as single, whole atoms with anisotropic thermal parameters. In the final difference map, the highest peaks (to *ca.* 0.6 e Å^{-3}) were in regions of disorder in all the three moieties.

Atomic scattering curves for neutral atoms were taken from reference 10. Computer programs used in this analysis have been noted above and in Table 4 of reference 11, and were run on the MicroVAX II system in the Nitrogen Fixation Laboratory.

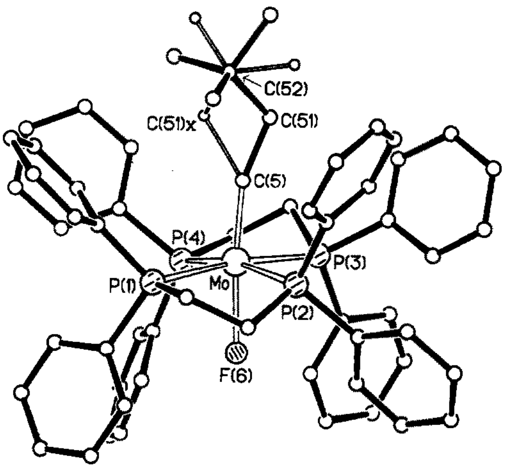

Fig. 1. The molecular structure of the cation of *trans*-[MoF(≡CCH$_2{}^t$Bu)(dppe)$_2$][BF$_4$]·Et$_2$O. Selected molecular dimensions are: Mo–C(5), 1.821(7), Mo–F(6) 2.016(3), C(5)–C(51) 1.542(13), C(5)–C(51)x 1.70(4) Å; C(5)–Mo–F(6) 173.0(3), Mo–C(5)–C(51) 161.9(6), Mo–C(5)–C(51)x 142.7(14)°.

Nevertheless, the bond distances obtained are sufficiently reliable for some comparisons to be made with diamagnetic analogues of **B**.

The Mo≡C(alkylidyne) bond length, 1.821(7) Å, of our Mo^V d^1 species appears to be very close to that of the complex *trans*-[MoBr(≡CSiMe$_3$)(dppe)$_2$] (**C**) [1.819(12) Å] [7] in which the metal is in the IV oxidation state. Therefore the fluoride ligand appears to have a significant *trans* influence which compensates for the expected shortening of the metal–carbon distance on passing from **C** to **B** as a result of the higher metal oxidation state in **B**. Moreover, conceivably in relation to this, the Mo–F distance in **B**, 2.016(3), Å, is shorter than that quoted [6] [2.134(4) Å] for the crystallographically isostructural, diamagnetic d^2 complex *trans*-[ReF(≡CCH$_2{}^t$Bu)-(dppe)$_2$][BF$_4$].

Complex **B** undergoes two single-electron reversible reductions at $E_{1/2}^{red} = -1.17$ and -1.52 V (*vs* SCE, by cyclic voltammetry, at a Pt electrode in 0.2 *M* [Bu$_4$N][BF$_4$]/thf), corresponding to the molybdenum(V/IV) and molybdenum (IV/III) redox processes. Therefore, at least on the common cyclic voltammetric time scale, the derived Mo^{IV} and Mo^{III} alkylidynefluorospecies are stable (they do not appear to undergo further reactions). Compound **B** also does not appear to react with stoichiometric amounts of base such as [Bu$_4$N]OH.

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References

1 A.J.L. Pombeiro and R.L. Richards, Coord. Chem. Rev., 104 (1990) 13; A.J.L. Pombeiro, Polyhedron, 8 (1989) 1595; A.J.L. Pombeiro, in U. Schubert (Ed.), NATO ASI Series, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1989, p. 79.

2 A. Hills, D.L. Hughes, N. Kashef, M.A.N.D.A. Lemos, A.J.L. Pombeiro and R.L. Richards, J. Organomet. Chem., 350 (1988) C4.
3 A.J.L. Pombeiro, A. Hills, D.L. Hughes and R.L. Richards, J. Organomet. Chem., 398 (1990) C15.
4 H.P. Kim and R.J. Angelici, Adv. Organomet. Chem., 27 (1987) 51.
5 K.R. Birdwhistell, T.L. Tonker and J.L. Templeton, J. Am. Chem. Soc., 107 (1985) 4474.
6 A.J.L. Pombeiro, A. Hills, D.L. Hughes and R.L. Richards, J. Organomet. Chem. 352 (1988) C5.
7 K.J. Ahmed, M.H. Chisholm and J.C. Huffman, Organometallics, 4 (1985) 1168.
8 G.M. Sheldrick, SHELX-76, Program for crystal structure determination, University of Cambridge, 1976.
9 G.M. Sheldrick, SHELXN, extended version of SHELX-76, University of Cambridge, 1977.
10 International Tables for X-ray Crystallography, Vol. 4, Kynoch Press, Birmingham, 1974, pp. 99 and 149.
11 S.N. Anderson, R.L. Richards and D.L. Hughes, J. Chem. Soc., Dalton Trans., (1986) 245.