

Preliminary communication

**Rapid binding and activation of small molecules by
[MoH₄(Ph₂PCH₂CH₂PPh₂)₂] in the presence of HBF₄ · OEt₂.
Crystal structure of the product obtained with phenylacetylene
trans-[MoF(η²-PhC≡CH)(Ph₂PCH₂CH₂PPh₂)₂]BF₄**

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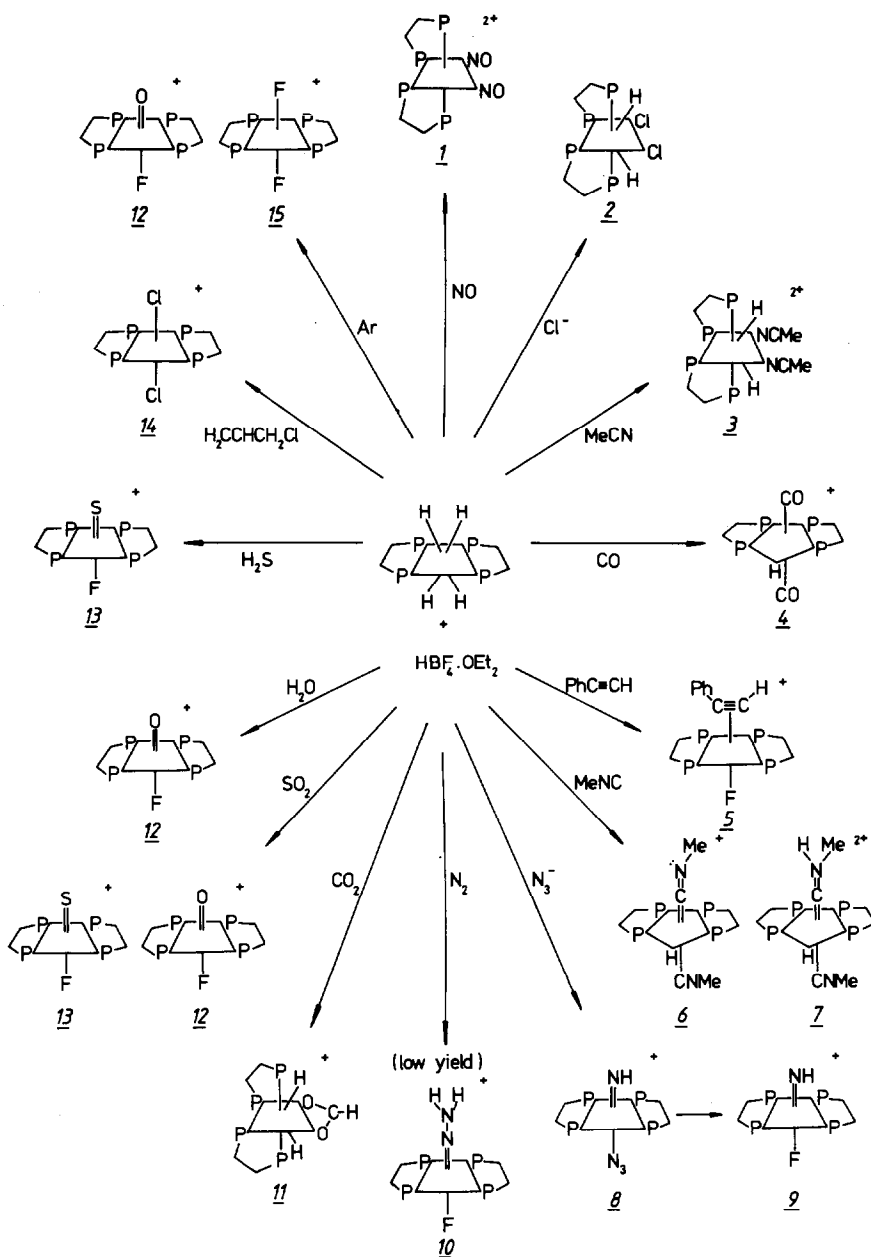
Abstract

In the presence of HBF₄ · OEt₂, [MoH₄(Ph₂PCH₂CH₂PPh₂)₂] exhibits a remarkably rapid and diverse range of reactions with a variety of small molecules. The crystal structure of the product obtained in the presence of phenylacetylene, *trans*-[MoF(η²-PhC≡CH)(Ph₂PCH₂CH₂PPh₂)₂]BF₄ is reported.

Currently there is a great deal of interest in the structure and reactivity of polyhydrido-transition metal complexes [1], but little is known about the influence of acid on the reactivity of simple hydrido complexes towards small molecules such as CO, N₂, CO₂, alkenes, alkynes etc. Indeed previous studies on the protonation of polyhydrido complexes have revealed only the coordination of either the solvent (MeCN) or the conjugate base derived from the acid [2–7]. We report here a study of the reaction between [MoH₄(dppe)₂] (dppe = Ph₂PCH₂CH₂PPh₂) and HBF₄ · OEt₂ in tetrahydrofuran (thf) in the presence of a variety of small molecules. The strategy of using the solvent, thf (which only weakly coordinates to the “Mo(dppe)₂” core), and an acid derived from the poorly coordinating BF₄⁻ allows other substrates a good opportunity to bind to the molybdenum atom.

The products isolated from the various reactions of [MoH₄(dppe)₂] with HBF₄ · OEt₂ are shown in Scheme 1*, from which it is immediately obvious that this

* All compounds shown in Scheme 1 have been fully characterised by elemental analysis, IR, ¹H and ³¹P{¹H} NMR spectroscopy, and where appropriate, ¹⁹F, ¹³C{¹H} and ¹³C NMR spectroscopy or bulk magnetic susceptibility measurements. Where applicable the spectroscopic and magnetic properties of the compounds were in agreement with those in the literature: 2[8], 4[9], 6 and 7[10], 9[11], 10[12] and 14[13].



Scheme 1.

system is capable of exhibiting a diverse range of reactivities. An important feature of the reactions is their rapidity: all are complete within one minute of mixing the component compounds in thf. This high reactivity of $[MoH_4(dppe)_2]$ in the presence of acid is in marked contrast to the rate of dihydrogen displacement from the tetrahydride alone, which has a half-life of several hours [14].

The reactivity exhibited by the $[\text{MoH}_4(\text{dppe})_2]/\text{HBF}_4 \cdot \text{OEt}_2$ mixture towards the various substrates falls broadly into three types: (a) binding without activation (products 1–5), (b) binding with activation (products 6–11), and (c) atom abstraction reactions (products 12–14).

In only one case (compound 5) did spectroscopic investigation of the reaction product fail to establish unambiguously the structure of the complex. In particular it seems that solutions of this complex are insufficiently stable over the prolonged accumulation times necessary to observe NMR coupling of the acetylenic hydrogen atom to the carbon nucleus in the ^{13}C NMR spectrum. However X-ray crystallographic analysis* of this product showed that it had the quasi-octahedral geometry shown in Fig. 1, containing a side-on coordinated phenylacetylene ligand.

It is rather surprising that, despite the high yield synthesis of 5, simple alkenes such as ethylene or styrene do not coordinate at this polyhydric site, at least not under the conditions we used.

There are two further reactions on which we should comment, namely the reactions with dinitrogen and sulphur dioxide. Under an atmosphere of dinitrogen, low concentrations of 10 can be detected in the product mixture (^{19}F NMR spectroscopy), in which the dinitrogen ligand has been protonated to the hydrazido(2–) species. However the major components of this mixture are complexes 12 and 15. This mixture is also obtained if the reaction is performed under argon or in the presence of alkenes (vide supra). We have been unable to separate 12 and 15.

The cleavage of sulphur dioxide to yield 12 and 13 was established unambiguously by the independent isolation of the two product complexes from the reactions with H_2O and H_2S , respectively. To the best of our knowledge, this is the first example of such a sulphur dioxide cleavage.

In conclusion we have shown that, in the presence of an excess of $\text{HBF}_4 \cdot \text{OEt}_2$, $[\text{MoH}_4(\text{dppe})_2]$ exhibits a remarkably diverse range of reactivities towards a variety

* Crystallographic analysis of 5, $[\text{MoF}(\text{PhC}\equiv\text{CH})(\text{dppe})_2][\text{BF}_4]$. Fine turquoise-blue plate crystals, mounted on glass fibres, were examined photographically. Accurate cell dimensions and diffraction intensities of a crystal ca. $0.60 \times 0.33 \times 0.10$ mm were measured on the Enraf–Nonius CAD4 diffractometer with monochromated radiation.

Crystal data: $\text{C}_{60}\text{H}_{54}\text{BF}_3\text{MoP}_4$, $M = 1100.7$. Monoclinic, space group $P2_1/n$ (equiv. to no. 14), a 19.313(7), b 13.681(3), c 20.333(8) Å, β 99.97(4)°, V 5291.1 Å³. $Z = 4$, D_c 1.382 g cm⁻³. $F(000) = 2264$, $\mu(\text{Mo-K}\alpha)$ 4.2 cm⁻¹, $\lambda(\text{Mo-K}\alpha)$ 0.71069 Å.

Intensities of 4928 independent reflections ($\theta_{\text{max}} 20^\circ$) were corrected for Lorentz-polarisation effects, slight deterioration, absorption and to ensure no negative intensities. The Mo, P and F atoms were located in the automated Patterson routines of SHELXS [15], and all the other non-hydrogen atoms were found in electron density and difference Fourier syntheses [16]. The alkyne H-atom also appeared in a difference map and was refined independently; all other H atoms were included in idealised positions and were set to ride on their bonded C-atoms. The anion is disordered over two sites (having one common B–F bond), and was refined with some geometrical constraints applied. All non-hydrogen atoms (except the B atom) were refined anisotropically. Final cycles of block-diagonal least-squares refinement [17] gave $R = 0.075$, $R_w = 0.067$ for all data, weighted $w = (\sigma_F^2 + 0.001F^2)^{-1}$.

Scattering factor curves were from ref. 18, and computer programs, listed in Table 4 of ref. 19 were run on the VAX 11/750 machine at G.C.R.I., Littlehampton.

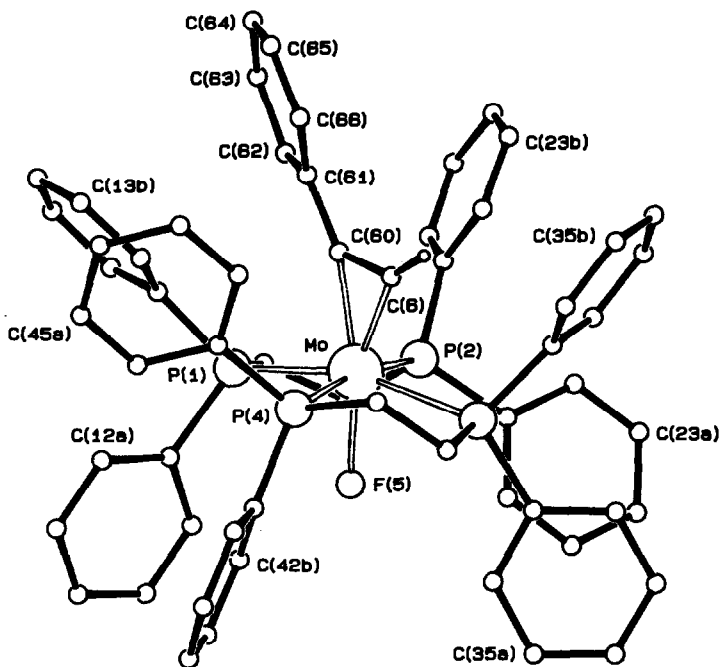


Fig. 1. View of the $[\text{MoF}(\text{PhC}\equiv\text{CH})(\text{ddpe})_2]^+$ cation in compound 5. Selected dimensions in this ion: Mo-P 2.535(2)–2.553(2), Mo-F(5) 1.981(4), Mo-C(6) 1.956(7), Mo-C(60) 2.047(7), C(6)–C(60) 1.26(1), C(6)–H(6) 0.91(8), C(60)–C(61) 1.46(1) Å; P(1)–Mo–P(3) 162.4(6), P(2)–Mo–P(4) 170.9(6), C(60)–C(6)–H(6) 138(5), C(6)–C(60)–C(61) 134.2(7)°.

of small molecules. Furthermore these transformations are accomplished extremely rapidly.

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