Multiple α-agostic interactions in a metal–methyl complex: the neutron structure of $[Mo(NC_6H_3Pr^i{}_2\text{-}2,6)_2Me_2]$

Jacqueline M. Cole*[a,b]† Vernon C. Gibson,[c] Judith A. K. Howard,[a] Garry J. McIntyre[b] and Gary L. P. Walker[c]

[a] *Department of Chemistry, University of Durham, South Road, Durham, UK DH1 3LE*
[b] *Institut Laue Langevin, B.P. 156, 38042 Grenoble Cedex 9, France*
[c] *Department of Chemistry, Imperial College, South Kensington, London, UK SW7 2AY*

The neutron structure of $[Mo(NC_6H_3Pr^i{}_2)\text{-}2,6)_2Me_2]$ reveals two highly distorted methyl ligands; this distortion is due to the presence of multiple C–H···M α-agostic interactions.

Since the formalisation of the three-centre C–H···M 'agostic' interaction by Brookhart and Green in the mid 1980s,[1] these interactions have been found to occur in many coordinatively unsaturated alkyl, aryl and polyhapto hydrocarbon metal complexes.[2] They are relatively readily observed and detected in alkyl derivatives possessing β-hydrogens, either in solution for rapidly averaging agostic hydrogens *via* the effect of isotopic perturbation on C–H coupling constants and chemical shift positions, or in the solid state by X-ray crystallography.‡ Agostic interactions in metal–methyl species have proved more difficult to detect because (1) any isotopic perturbation of the resonance effect is diluted over a greater number of hydrogen environments and (2) in X-ray structure determinations, there are no obvious ligand distortions of the type seen in longer chain alkyls and it is inherently difficult with X-rays to locate the methyl hydrogen atom positions with any accuracy. The only reliable method of establishing the presence of agostic interactions in metal–methyl complexes is *via* diffraction.

To date, the only metal methyl complex to have been characterised by neutron diffraction that shows clear evidence for an α-agostic methyl C–H···M interaction is $[TiMeCl_3(Me_2PCH_2CH_2PMe_2)]$.[3] Here, we describe the neutron structure of the coordinatively unsaturated molybdenum α-agostic dimethyl complex $[Mo(NC_6H_3Pr^i{}_2\text{-}2,6)_2Me_2]$ which was prepared from the reaction of $[Mo(NC_6H_3Pr^i{}_2\text{-}2,6)_2Cl_2(dme)]$ with 2 equiv. of methylmagnesium chloride. Full synthetic details will be reported elsewhere.[4] A crystal of dimensions 6.0 × 2.0 × 1.0 mm was grown from a saturated pentane solution at −35 °C. The molecular structure of $[Mo(NC_6H_3Pr^i{}_2\text{-}2,6)_2Me_2]$ is shown in Fig. 1, along with selected bond lengths and angles.

The geometry about the metal centre is best described as distorted tetrahedral with inter-ligand angles in the range 107–114°. The bond distances for the Mo–N and N–C(*ipso*) bonds [1.756(2) and 1.382(2) Å, respectively] in combination with Mo–N–C angles [159.6(1)°] are consistent with linear imido ligands.[5] The two methyl groups are crystallographically equivalent so the following discussion concentrates on only one methyl group. Each methyl group shows a partial positional disorder amongst the hydrogen atom sites, which can be described as resulting from a slight rocking motion about C(13), the pivot atom for a fluxional rotation which, averaged over all possible sites in all unit cells, gives the 'static average' picture shown. H(13A) can be resolved into two positions [(H13A) and (H13′)] with occupancies in the ratio 2:1 and these refine independently both isotropically and anisotropically. The latter tends to a distortion and an overlap in the two density distributions, but with derived molecular parameters very close to those reported herein, which result from an isotropic description of the disordered sites.

A large amount of librational motion therefore exists, thus disguising the precise position of the hydrogen atoms. However, despite the librational effects, the average geometry gives conclusive results. The coordination of each methyl group is markedly distorted from regular tetrahedral geometry and of special note are the particularly small angles Mo(1)–C(13)–H(13A) [103.7(4)°] and Mo(1)–C(13)–H(13B) [104.7(3)°] which are consistent with the hydrogen atoms being drawn towards the metal centre. Consequently, the angles, Mo(1)···H(13A)–C(13) (52.6°) and Mo(1)···H(13B)–C(13) (51.8°) are noticeably larger than those corresponding to the hydrogen atoms H(13C) and H(13′) (43.0 and 43.9° respectively).

The Mo(1)···H(13A) and Mo(1)···H(13B) distances [2.585(8) and 2.598(5) Å, respectively] are also significantly shorter than Mo(1)···H(13C) and Mo(1)···H(13′) [2.755(5) and 2.76(1) Å] and the Mo(1)–C(13) bond length of 2.112(2) Å is very short,

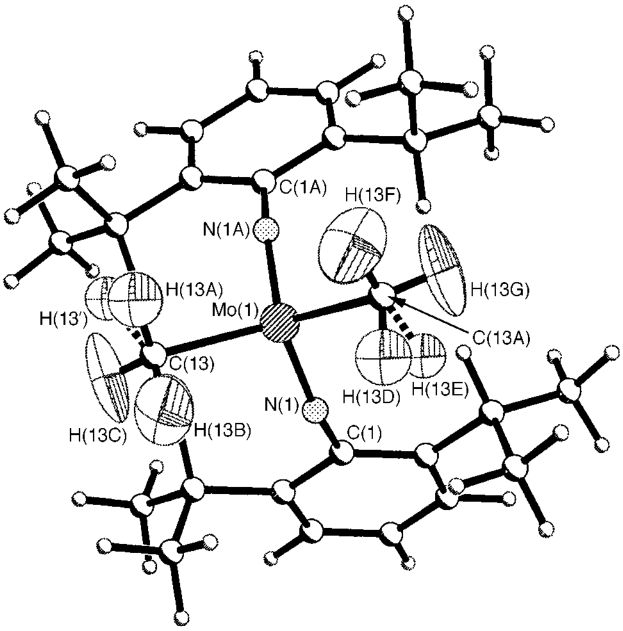

Fig. 1 The molecular structure of $[Mo(NC_6H_3Pr^i{}_2\text{-}2,6)_2Me_2]$ with 50% probability thermal ellipsoids shown on the methyl hydrogen atoms, thus indicating the extent of libration. Selected bond dimensions (Å and °): Mo(1)–N(1) 1.756(2), Mo(1)–C(13) 2.112(2), Mo(1)···H(13A) 2.585(8), Mo(1)···H(13′) 2.76(1), Mo(1)–H(13B) 2.598(5), Mo(1)···H(13C) 2.755(5), N(1)–C(1) 1.382(2), C(13)–H(13A) 1.07(1), C(13)–H(13′) 1.09(1), C(13)–H(13B) 1.068(7), C(13)–H(13C) 1.049(8); N(1)–Mo(1)–N(1A) 112.5(1), N(1)–Mo(1)–C(13) 107.86(7), C(13)–Mo(1)–C(13A) 114.1(2), C(13)–Mo(1)···H(13A) 23.7(2), C(13)–Mo(1)···H(13′) 21.0(3), C(13)–Mo(1)···H(13B) 23.4(2), C(13)–Mo(1)···H(13C) 19.8(2), Mo(1)–N(1)–C(1) 159.6(1), Mo(1)–C(13)–H(13A) 103.7(4), Mo(1)–C(13)–C(13′) 115.1(6), Mo(1)–C(13)–H(13B) 104.7(3), Mo(1)–C(13)–H013C) 117.2(3).

comparing with literature values of 2.554 Å (mean) and 2.189 Å (lower quartile).[6] This short Mo–C distance is also likely to be a consequence of the agostic interactions. All C–H distances are identical within experimental error. Of the two α-agostic hydrogen atoms per methyl group (therefore, four agostic interactions per molecule) both appear strong and of the same strength, judging by their relative geometries.

More than one agostic interaction in [$Mo(NC_6H_3Pr^i_2$-2,6)$_2Me_2$] is not unreasonable since this molecule is quite severely coordinatively unsaturated. It is not possible to place a precise electron count on the complex since, for symmetry reasons, the two *cis* imido ligands are in direct competition for one of the metal d_π orbitals. This means that the electron count must be below 16 electrons (the count derived from assuming that both imido ligands can form two π bonds) and formally could be as low as 14 electrons (*i.e.* the count arising from three π-bonds between the molybdenum and the two imido groups). In general, the results described here underscore the notion that agostic interactions will occur whenever a metal centre possesses a suitably oriented and energetically accessible vacant orbital, and that multiple interactions of this kind may occur at a single metal centre. The neutron diffraction study described here shows clear evidence for four α-agostic methyl C–H···M interactions within [$Mo(NC_6H_3Pr^i_2$-2,6)$_2Me_2$]. It represents the second metal–methyl complex showing α-agostic interactions and the first one to show multiple agostic interactions.

The authors wish to thank the Institut Laue Langevin, Grenoble, France (J. M. C.) and the EPSRC (J. M. C. and G. L. P. W.) for financial support.

Notes and References

† Present address: School of Physical Sciences, University of Kent at Canterbury, Canterbury, Kent, UK CT2 7NR. E-mail: J.M.Cole@ukc.ac.uk

‡ It should be noted that the evidence for β-agostic interactions is often derived from other structural parameters such as a low M–C–C bond angle rather than direct location of the agostic hydrogen atom position.

§ *Crystal data* for [$Mo(NC_6H_3Pr^i_2$-2,6)$_2Me_2$] : $C_{26}H_{40}MoN_2$, M_r = 475.94, deep orange–red rectangular crystal (6.0 × 1.8 × 1.0 nm), monoclinic, space group $C2/c$, a = 20.240(4), b = 6.550(1), c = 19.910(4) Å, β = 103.99(3)°, V = 2561.2(8) Å^3, Z = 4, T = 150.0(2) K, D_c = 1.234 g cm^{-3}, $F(000)$ = 348, μ = 0.233 mm^{-1}, 2110 unique reflections ($6.56 \leq 2\theta \leq 60.02°$) were measured on the D9 four circle diffractometer at the Institut Laue Langevin (ILL), Grenoble, France in a beam of wavelength 0.8405(2) Å obtained by reflection from a Cu(220) monochromator. Half-wavelength contamination was removed with an erbium filter. The sample was mounted on the cold head of an Air Products closed-cycle refridgerator. Background corrections following Lehmann and Larsen[7] and Lorentz corrections were applied. Cryostat shield and absorption corrections were made using the local program ABSCAN and the DATAP program[8] respectively (transmission range: 0.6477–0.8045). The structure was refined by full-matrix least-squares refinement using SHELXL-93[9] against 2100 reflections. Refinement of 312 positional and anisotropic displacement parameters for all atoms [except for isotropic H(13A) and H(13′)] converged to $R1$ [$I > 2\sigma(I)$] = 0.0467 and wR_2 [$I > 2\sigma(I)$] = 0.0462 [$w = 1/\sigma^2(F_o)^2$] with S = 1.431.

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Received in Cambridge, UK, 29th April 1998; 8/03221A