Interaction of an Aliphatic C–H Bond with a Metal Atom Can Compete Successfully with a Metal–Olefin Interaction

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Summary The structure of $[(C_2H_5)_2B(pyrazolyl)_2](C_7H_7)(CO)_2Mo$ shows that the molybdenum atom attains a formal 18-electron configuration by strong interaction with an α-hydrogen atom of an ethyl group (H–Mo = 1·93 Å) thus leaving four "unused" $p\pi$ electrons in the *trihapto*cycloheptatrienyl ring.

The structural characterization of a compound containing a very strong interaction between an aliphatic C–H group and a transition-metal atom has recently been reported.[1] The compound in question is $(Et_2Bpz_2)Mo(CO)_2(2\text{-}PhC_3H_4)$, (**1**), and the interatomic distances having to do with the interaction are those shown in Figure 1(a). In this compound, the electronic structure of the C–H–Mo group can be described as a 3-centre, 2-electron bond, the existence of which enables the molybdenum atom to achieve a formal 18-electron configuration by having a share in the pair of electrons which would otherwise be confined to the aliphatic C–H bond. In (**1**), there is no other source of the electron pair so provided since the olefinic ligand, $H_2CC(Ph)CH_2$, has only three π-electrons to offer and these are already fully used in binding it to the molybdenum atom.

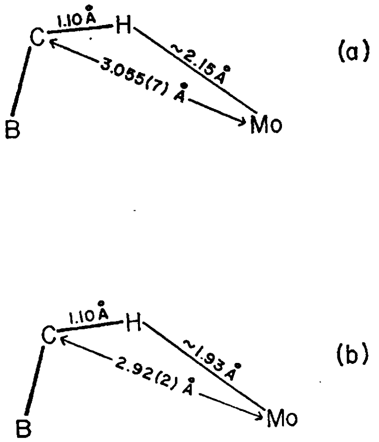

Figure 1. Interatomic distances pertaining to the C–H–Mo 3-centre 2-electron bonds in (a) compound (**1**), and (b) compound (**3**). In each case the C–H distance, 1·10 Å, is assumed.

A formally similar situation had earlier been found[2] in $[H_2B(3,5\text{-dimethylpz})_2]Mo(CO)_2(\eta^3\text{-}C_7H_7)$, (**2**), where a B–H–Mo 3-centre, 2-electron bond supplied the electrons necessary for the completion of a formal 18-electron configuration at molybdenum. It is to be noted that in the case of (**2**) this could, in principle, have been accomplished in an alternative way, namely, by omitting the B–H–Mo interaction and having instead a *pentahapto*-C_7H_7 ring (which would supply 5 rather than only 3 electrons to Mo). The preference in (**2**) for the B–H–Mo-η^3-C_7H_7 combination is not particularly surprising since B–H bonds in BH_4^- and $B_3H_8^-$ are well known to enter into this sort of interaction with metal atoms,[3] whereas η^5-C_7H_7 rings are rare, though known to occur.[4]

In view of the results for (**1**) and (**2**), the following question appeared to be of considerable interest and capable of being answered:

In a situation where a molybdenum atom could obtain the pair of electrons necessary to complete an 18-electron configuration either by formation of a C–H–Mo 3-centre, 2-electron bond together with a η^3-C_7H_7 ring, or by omitting the C–H–Mo interaction and having a η^5-C_7H_7 ring, which would happen? In other words, can a CH-to-metal interaction, of the type found in (**1**), but until recently an unknown entity, be strong enough to compete with the far better established process of more extended interaction of a metal atom with a cyclic polyolefinic ligand?

The compound with which to determine the answer was already known to exist,[5] namely, $(Et_2Bpz_2)Mo(CO)_2(C_7H_7)$ (**3**). A sample was prepared by Dr. F. Carré and has been subjected to crystallographic study. Only poor quality crystals appear to be obtainable and so the structure is not a highly precise one. However, the question posed above is answered unequivocally.

The structure is shown in Figure 2. It is clear that the C_7H_7 ring is a three-electron donor and that there is a C–H–Mo interaction very similar to, but even stronger than, that previously observed in (**1**), as indicated by the representation in Figure 1(b). We believe that this result is of exceptional significance since it adds to the previously reported discovery of such a C–H–Mo interaction the additional information that such an interaction is structurally and thermodynamically competitive with olefin–metal bonding. It is notable that the i.r. spectrum of (**3**) in hexane solution shows two pairs of CO stretching bands, one pair being about six times as intense as the other. A possible interpretation of this is that the two sets of bands correspond to two structures, one being that in the crystal (the C-H-Mo-η^3-C_7H_7 structure) and the other having no C–H–Mo interaction but a η^5-C_7H_7 ring. We hope to be able to report more fully on this when n.m.r. studies now in progress are completed.

Crystal data: space group, $P2_1/n$; $Z = 4$; $a = 16{\cdot}242(7)$ Å, $b = 9{\cdot}602(5)$, $c = 12{\cdot}777(7)$ Å, $\beta = 94{\cdot}45(4)°$. As reported here, the structure is based on 2023 reflections for which $I > \sigma(I)$ and $2\theta(\text{Mo}K_\alpha) < 43°$; R_1 (unit weights) = 0·095 for 27 anisotropic atoms. Additional data are being collected and refinement will be continued.

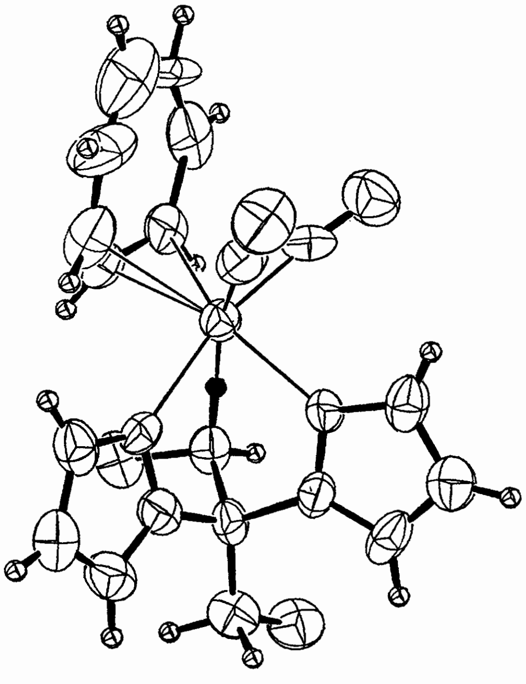

FIGURE 2. An overall view of the molecular structure of compound (**3**), drawn by ORTEP with atoms represented by their thermal vibration ellipsoids drawn to encompass 50% of the electron density. The hydrogen atom (filled circle) involved in the C–H–Mo bond has been introduced at its calculated position (C–H = 1·10 Å). Other hydrogen atoms are also shown at calculated positions (C–H = 0·97 Å).

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