β-C–H Interaction *vs.* Dihaptoacyl Co-ordination in a Molybdenum Acetyl Complex. *X*-Ray Crystal Structure of $[Mo(Ac)(S_2CNMe_2)(CO)(PMe_3)_2]$

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N.m.r. and *X*-ray studies of the title compound, obtained from $[MoCl(\eta^2\text{-}COCH_2SiMe_3)(CO)(PMe_3)_3]$ and NaS_2CNMe_2 in aqueous acetone, indicate that the molybdenum atom attains an 18-electron configuration by interacting with a β-C–H bond [Mo–C 2.60(1), Mo–H 2.06(9) Å] rather than by dihapto co-ordination to the acetyl group.

We have recently prepared[1] a series of dihaptoacyl complexes of Mo^{II} of composition $[MoX(\eta^2\text{-}COR)(CO)(PMe_3)_3]$, (X = Cl, Br, I, NCO, NCS; R = CH_2SiMe_3, CH_2Me_3, CH_2CMe_2Ph), in which the electronic requirements of the Mo atom are satisfied by dihapto co-ordination to the acyl group (Scheme 1)

$$\begin{tikzcd}[MoX_2(PMe_3)_4] \arrow[r, "\text{CO, 60 °C}", "\text{THF}"'] & {[MoX_2(CO)_2(PMe_3)_3]} \arrow[d, "\text{RMgCl-Et}_2\text{O}"] \\ & {[MoX(\eta^2\text{-COR})(CO)(PMe_3)_3]}\end{tikzcd}$$

Scheme 1. THF = tetrahydrofuran.

In investigating the reactivity of these complexes, we wondered whether the dihaptoacyl linkage would remain intact upon substitution of the X group by the strongly electron-releasing and powerful chelating ligand dimethyl dithiocarbamate.

$[MoCl(\eta^2\text{-}COCH_2SiMe_3)(CO)(PMe_3)_3]$
(1)

$[Mo(S_2CNMe_2)(Ac)(CO)(PMe_3)_2]$
(2)

$[Mo(COCH_2SiMe_3)(S_2CNMe_2)(CO)(PMe_3)_2]$
(3)

$[Mo(\eta^2\text{-}COCH_2SiMe_3)(S_2CNMe_2)(CO)_2(PMe_3)]$
(4)

The interaction of $[MoCl(\eta^2\text{-}COCH_2SiMe_3)(CO)(PMe_3)_3]$**(1)** with $NaS_2CNMe_2.2H_2O$ in aqueous acetone yields red crystals (from diethyl ether) of a complex analysing as $[Mo(S_2CNMe_2)(Ac)(CO)(PMe_3)_2]$**(2)**.† The i.r. spectrum of **(2)** shows no evidence for the presence of a dihaptoacyl group [ν(C–O) at 1790 and 1610 cm^{-1} for Mo–CO and Mo–$COCH_3$, respectively] and the ^1H n.m.r. spectrum has resonances at δ 2.68 (s, 6H, S_2CNMe_2), 1.87(t, 3H, $COCH_3$, J_{HP} 1.3 Hz), 1.38 (d, 18H, PMe_3, observed J_{HP} 9.9 Hz). Conversely, the $^{13}C\{^1H\}$ n.m.r. spectrum (22.50 MHz) displays bands at δ 38.6 and 7.9 p.p.m. (br.t, J_{CP} 3.4 Hz), that become quartets in the gated

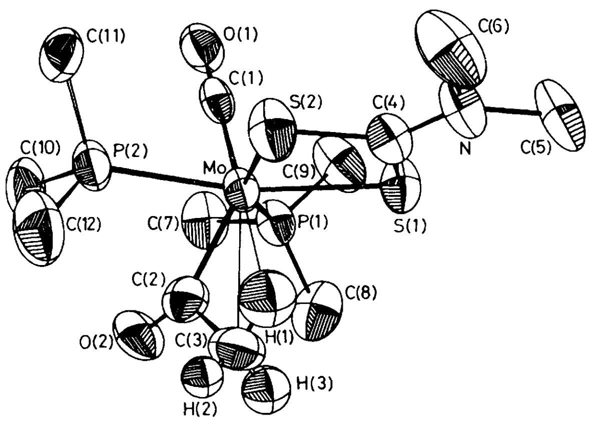

Figure 1. *X*-Ray crystal structure of $[Mo(Ac)(S_2CNMe_2)(CO)(PMe_3)_2]$, **(2)**. Important bond distances include: Mo–P(1) 2.435(2), Mo–P(2) 2.430(3), Mo–S(1) 2.547(2), Mo–S(2) 2.529(2), Mo–C(1) 1.83(1), C(2)–O(2) 1.21(1), C(2)–C(3) 1.57(2) Å.

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† Satisfactory analytical data for all new compounds have been obtained.

decoupled spectrum. The first can be assigned to the $S_2CN\mathit{Me}_2$ groups, while the second, due to the acetyl methyl carbon (J_{CH} 130 Hz) is at markedly higher field than is found in other acetyl derivatives {*cf.* δ 52 p.p.m. in $[(cp)Fe(CO)(PBu_3)(Ac)]$ (cp = η^5-C_5H_5),[2a] and 27 p.p.m. in $[RuX(Ac)(CO)(PMe_2Ph)_3]$ (X = Cl, I)[2b] complexes}. The observation of coupling between the acetyl protons and the phosphorus nuclei together with the high chemical shift found for the acetyl methyl carbon suggest a strong interaction of the methyl group with the molybdenum atom. This was confirmed by a complete *X*-ray structure determination.

Crystal Data: $C_{12}H_{27}MoNO_2P_2S_2$, M = 425.4, monoclinic, space group $P2_1/c$, a = 11.633(5), b = 9.962(4), c = 17.266(6) Å, β = 95.80(3)°, U = 1990.6 Å^3, Z = 4, D_c = 1.42 g cm^{-3}, μ(Mo-K_α) = 10.04 cm^{-1}. Intensity data were recorded on an Enraf-Nonius CAD-4 diffractometer using the ω–2θ scan technique. All reflections in one independent quadrant out to 2θ = 36° were measured; 1116 reflections were considered observed $[I > 3\sigma(I)]$. The structure was solved by Patterson and difference Fourier techniques, and refined to a conventional R value of 0.029.‡

The C(3)–H(1)····Mo interaction can be seen in the ORTEP illustration of (2) (Figure 1). The Mo–C(O) distance in (2) [2.05(1) Å] is similar to that found in $[MoCl(\eta^2$-$COCH_2SiMe_3)(CO)(PMe_3)_3]$[1] [2.024(6) Å], however, the Mo–C(O)–C angle differs considerably [90.9(8) *vs.* 149.0(4)°], clearly indicating the displacement of the methyl group towards the molybdenum centre. The Mo–C(3) distance at 2.60(1) Å is only *ca.* 0.3 Å longer than the average Mo–CH_3 bond length in the arenes $[(\eta^6$-$C_6H_5R)Mo(Me)_2(PMe_2Ph)_2]$[3] (R = H, Me) and similarly, the Mo–H(1) distance, at 2.06(9) Å, is only 0.24 Å longer than in $[Mo_2H_4(PMe_3)_6]$.[4] Both distances are sufficiently short to indicate substantial Mo–C(3) and Mo–H(1) bonding interactions. The C(3)–H(1) bond could therefore be considered as a non-classical donor ligand, allowing the Mo atom formally to attain an 18-electron configuration. Other systems showing similar C–H····M interactions have been reported recently.[5] It is interesting that the C–H····Mo interaction in (2) appears to be structurally and thermodynamically competitive with the dihaptoacyl co-ordination, a situation that clearly parallels Cotton's observation[6] of analogous competition between C–H····Mo interaction and alkene metal bonding.

With the hope of further clarifying the formation of (2) and of finding a system in which both the β-C–H···Mo and the dihapto interactions could be observed, we carried out the reaction of (1) with anhydrous NaS_2CNMe_2, under strictly anhydrous conditions. Crystals of $[Mo(COCH_2SiMe_3)(S_2CNMe_2)(CO)(PMe_3)_2]$ (3), were obtained in this way from petroleum–Et_2O mixtures. Addition of small amounts of water to solutions of (3) produces carbon–silicon heterolysis[7] and quantitative formation of (2). Complex (3) seems to exist in two isomeric forms; the red (**3a**) [i.r. bands at 1750 and 1490 cm^{-1}, ν(C–O) for M–CO and M–COR groups respectively] and the orange (**3b**) (1760 and 1615 cm^{-1}). Both forms have identical ^{1}H n.m.r. spectra, consistent with the existence in solution of (**3a**) and small amounts (*ca.* 15%) of the other isomer. Although it seems likely that (**3a**) contains a dihaptoacyl group, no definite conclusions can as yet be obtained with regard to the constitution of (**3b**). Future n.m.r. and *X*-ray studies on both compounds may clarify these points. The reaction of (3) with CO, at 5 °C, gives yellow crystals of $[Mo(\eta^2$-$COCH_2SiMe_3)(S_2CNMe_2)(CO)_2(PMe_3)]$ (4), for which only the isomeric form having a dihaptoacyl group has been observed so far.

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.