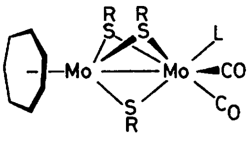
Sulphur Inversion in Dimolybdenum Complexes: *X*-Ray Crystal Structure of $[Mo_2(CO)_2\{P(OMe)_3\}(\mu_2\text{-}SBu^t)_3(\eta^7\text{-}C_7H_7)]$

By Ian B. Benson, Selby A. R. Knox,* Pamela J. Naish, and Alan J. Welch
(*Department of Inorganic Chemistry, The University, Bristol* BS8 1TS)

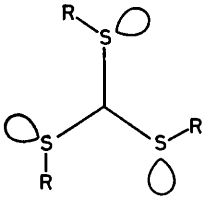
Summary Low energy barriers are observed for sulphur inversion in complexes $[Mo_2(CO)_2(L)(\mu_2\text{-}SR)_3(\eta^7\text{-}C_7H_7)]$ (R = Me, Et, Pr^i, or Bu^t); n.m.r. spectroscopy reveals complete averaging of R group environments when L = CO but only a limited averaging when L = PR'_3, a situation clarified by an *X*-ray diffraction study of $[Mo_2(CO)_2\{P(OMe)_3\}(\mu_2\text{-}SBu^t)_3(\eta^7\text{-}C_7H_7)]$.

THE barrier to sulphur inversion[1] in sulphoxides and sulphonium ions is high; free energies of activation are of the order 100—150 kJ mol^{-1}. In complexes where sulphur is bound to a single transition metal barriers are much lower (*ca.* 55—70 kJ mol^{-1}), perhaps owing to stabilisation of the transitional trigonal configuration of sulphur through sulphur–metal $(p\rightarrow d)\pi$ orbital overlap.[2] It might be expected, therefore, that inversion of sulphur bonded to two transition metals (*i.e.* 'bridging' sulphur) would experience even lower resistance, with the proviso that ring strain effects may be counteractive should the metals be linked to one another. We describe here an apparent justification of this argument; the observation of low energy sulphur inversion in complexes $[Mo_2(CO)_2(L)(\mu_2\text{-}SR)_3(\eta^7\text{-}C_7H_7)]$, with the first quantification of inversion barriers for 'bridging' sulphur.

The complexes $[Mo_2(CO)_3(\mu_2\text{-}SR)_3(\eta^7\text{-}C_7H_7)]$ (**1**; L = CO, R = Me, Et, Pr^i, or Bu^t), synthesised independently by Mohr *et al.*[3] and ourselves from $[MoX(CO)_2(\eta^7\text{-}C_7H_7)]$ (X = Br or I) and RSH and NEt_3, are capable of existence as the isomers (**2**) and (**3**) (viewed along the Mo ··· Mo axis). The i.r. spectrum of each complex (**1**; L = CO) shows six carbonyl bands at room temperature confirming that both isomers are in fact present. Moreover, these interconvert rapidly on the n.m.r. time scale at or above this temperature. Thus at −60 °C in $CDCl_3$ solution the ^1H n.m.r. spectrum of (**1**; L = CO, R = Me) exhibits resonances at τ 4·78 (7H; C_7H_7) and 7·84 (9H; SMe) due to isomer (**2**) and at τ 4·84 (7H; C_7H_7) and 7·26, 7·38, 8·68 (3H, 3H, 3H; SMe) due to isomer (**3**) [ratio (**2**) : (**3**) is 1 : 3]. On warming, broadening and then coalescence of signals occurs until at 120 °C (PhCl solution) the spectrum comprises sharp singlets at τ 5·30 (7H; C_7H_7) and 8·02 (9H; SMe). These changes, which are reversed on cooling, are attributed to rapid inversion at sulphur effecting a (**2**) $\rightleftharpoons$ (**3**) interconversion; similar behaviour is shown by (**1**; L = CO, R = Et or Pr^i), save that at low temperature the proportion of isomer (**3**) increases with increase in size of R. The extreme is reached for (**1**; L = CO, R = Bu^t) in that only isomer (**3**) is detectable at −45 °C [τ 4·60 (7H), 8·48 (9H), 8·51 (9H), and 9·01 (9H)]. Again, inversion is initiated on warming and the Bu^t group signals coalesce to a sharp singlet (τ 8·67) at 30 °C.



(1)



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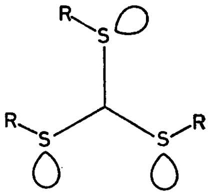

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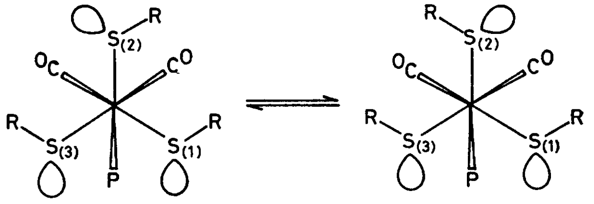

(4) (5)

Substitution of one carbonyl ligand in (**1**; L = CO, R = Bu^t) by a tertiary phosphine or phosphite has a marked effect. Where previously sulphur inversion effected complete averaging of Bu^t group environments, in (**1**; L = PR'_3, R = Bu^t) only a limited averaging occurs. This is exemplified by [**1**; L = $P(OMe)_3$, R = Bu^t], the ^1H n.m.r. spectrum of which varies between limits of −55 [τ 4·76 (7H), 6·44d (9H) $\{P(OMe)_3\}$, 8·56 (9H), 8·66 (9H), and 9·10 (9H)] and of +60 °C [τ 4·73 (7H), 6·37d (9H), 8·47 (9H), and 8·77 (18H)]. The coalescence of only the two high field Bu^t signals clearly indicates that a time-averaged mirror plane of molecular symmetry is generated, whose nature was revealed through an *X*-ray diffraction study of $[Mo_2(CO)_2\{P(OMe)_3\}(\mu_2\text{-}SBu^t)_3(\eta^7\text{-}C_7H_7)]$.

Crystal data: $C_{24}H_{43}Mo_2O_5PS_3$, *M* = 730·6, monoclinic, *a* = 10·186(7), *b* = 15·677(7), *c* = 19·821(15) Å, β = 96·31(3)°, *U* = 3145·8(17) $Å^3$, *Z* = 4, D_c = 1·542 g cm^{-3}, *F*(000) = 1496, Mo-K_α radiation ($\bar{\lambda}$ = 0·71069 Å), μ(Mo-K_α) = 10·5 cm^{-1}, space group $P2_1/n$ (alternative setting of $P2_1/c$, C^5_{2h}, No. 14).

The structure was solved by standard Patterson and difference-Fourier techniques and refined by least squares to *R* 0·046† for 5151 reflections ($I \geqslant 1{\cdot}0\sigma$) measured to

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

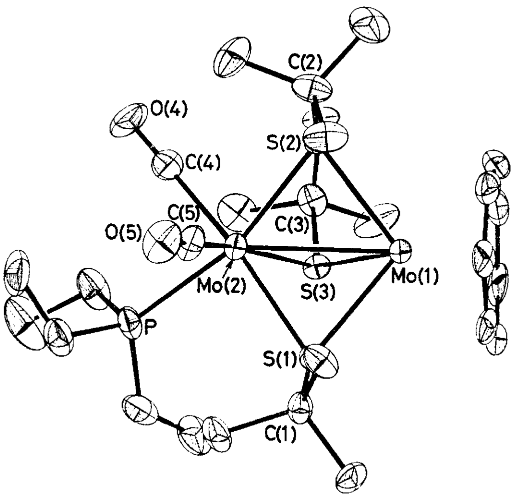

FIGURE. Molecular structure of $[Mo_2(CO)_2\{P(OMe)_3\}(\mu_2\text{-}SBu^t)_3(\eta^7\text{-}C_7H_7)]$. Thermal ellipsoids are drawn at the 30% probability level. Pertinent internuclear distances are Mo(1)–Mo(2) 2·9460(15), Mo(1)–S(1) 2·523(2), Mo(1)–S(2) 2·483(2), Mo(1)–S(3) 2·549(2), Mo(2)–S(1) 2·444(2), Mo(2)–S(2) 2·411(2), Mo(2)–S(3) 2·534(2), Mo(2)–P 2·445(2), Mo(2)–C(4) 2·009(7), Mo(2)–C(5) 1·931(8), C(4)–O(4) 1·149(9), and C(5)–O(5) 1·175(10) Å.

$2\theta = 50°$ on a Nonius CAD4 diffractometer. The molecular geometry is shown in the Figure. Each molybdenum atom is seven co-ordinate with an approximately capped octahedral geometry such that each metal is the cap of the other's co-ordination sphere, with the two octahedra thus being fused about a common S_3 face. The Bu^tS groups are disposed as in (**4**), in accord with the low temperature n.m.r. spectrum, with the variation in non-bonded S ··· S distances [S(1) ··· S(3) 2·939(3), S(2) ··· S(3) 3·256(3), S(1) ··· S(2) 3·890(3) Å] being traceable to intramolecular $Bu^t \cdots Bu^t$ steric effects. All three sulphur atoms favour Mo(2) in asymmetrically bridging the single metal–metal bond. Furthermore, the Mo(1)–C(ring) distances [2·282(8)—2·336(7) Å] are rather long for this type of system and Mo(1)–S–C angles are consistently wider (by *ca.* 5°) than Mo(2)–S–C angles. All three features are compatible with the recognition of several $Bu^t \cdots$ C (ring) distances within the van der Waals sum for a methyl group and an aromatic ring.

On the basis of the *X*-ray diffraction study, the time-averaged mirror plane evident in the limiting high temperature n.m.r. spectra of complexes (**1**; $L = PR'_3$, $R = Bu^t$) arises from a process (**4**) $\rightleftharpoons$ (**5**). Environmental averaging of the Bu^t groups attached to S(1) and S(3) can be effected only by rapid inversion of S(2), independent of whether inversion occurs rapidly at S(1) and S(3) or not. In fact, the i.r. spectra of (**1**; $L = PR'_3$, $R = Bu^t$) at room temperature show four carbonyl bands, providing evidence for the existence of two isomers and thus of inversion at S(1) and S(3). Inversion at S(2) is the rate-controlling factor in the averaging process and is, not unexpectedly, sensitive to the nature of the *trans* phosphorus ligand. Free energies of activation derived from coalescence temperatures show a value of 58·8 ± 1·0 kJ mol^{-1} for [**1**; $L = P(OMe)_3$, $R = Bu^t$] reducing to 46·9, 47·7, and 46·7 (±1·0) kJ mol^{-1} for (**1**; $L = PPh_2Me$, $R = Bu^t$), (**1**; $L = PPhMe_2$, $R = Bu^t$), and (**1**; $L = PMe_3$, $R = Bu^t$), respectively. These latter, very low barriers for sulphur inversion may be in part correlated with the more basic phosphines increasing electron density in the *trans* Mo–S bond and thus causing the Mo–S–C angle to expand and more nearly approach the transitional trigonal angle.

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