Paramagnetic Diene Complexes of Molybdenum(III) and a Transformation into a Diamagnetic, Fluxional Molybdenum–Thallium Complex, [MoTl($SC_6F_5)_4(\eta$-C_5H_5)]

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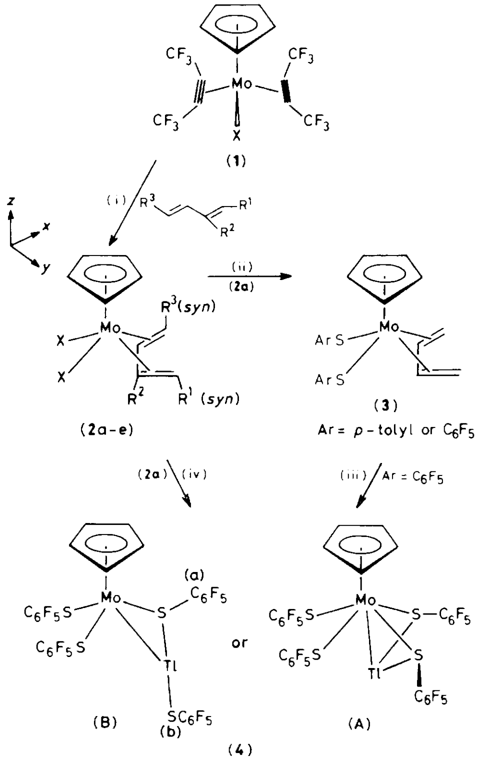
Paramagnetic diene complexes [MoX_2(diene)(η-C_5H_5)] (X = Cl, Br, I, SAr) give well resolved e.s.r. spectra in solution; reaction with $TlSC_6F_5$ produces the unusual fluxional, bimetallic complex [MoTl($SC_6F_5)_4(\eta$-C_5H_5)].

Diamagnetic bis-alkyne molybdenum(II) complexes of type [MoX(η-RC≡CR)$_2$(η-C_5H_5)] show a varied chemistry including ligand substitution reactions and attack at co-ordinated alkyne.[1,2] Although a complex [$MoCl_2$(butadiene)(η-C_5H_5)] has been briefly reported,[2] no proven examples of paramagnetic products from reactions of bis-alkyne molybdenum(II) complexes are known.

We have found that some dienes react with complexes (**1**) to give monomeric diene complexes (**2**)† in up to 40% yield [reaction (i), Scheme 1]. The mechanism of this oxidative, disproportionation reaction has not been established but, since no product is formed when $R^1 = R^3$ = Me or when diene = cyclohexa-1,3-diene, it appears to be influenced by steric effects.

Complexes (**2**) are unusual examples of $S = \frac{1}{2}$ diene complexes and metathetical exchange with TlSAr (Ar = *p*-tolyl or C_6F_5) forms related complexes (**3**; Ar = *p*-tolyl)† (72%) or (**3**; Ar = C_6F_5)† (15%) [reaction (ii), Scheme 1]. Complexes (**2**) and (**3**) give well resolved e.s.r. spectra in solution (*e.g*. see Figure 1) which exhibit coupling to $^{95/97}$Mo, $^{35/37}$Cl, $^{79/81}$Br, and some ^{1}H atoms of the diene ligands. By analysis of the spectra, especially comparisons between (**2a**), (**2d**), and (**2e**), it is apparent that only terminal ^{1}H atoms bonded to C(1) and C(4) of the diene ligands cause significant, resolvable superhyperfine splitting and that $A_{iso}(^1H_{syn}) \geqslant A_{iso}(^1H_{anti})$.†

Although not confirmed by *X*-ray analysis, the 'four-legged pianostool' structures for (**2**) and (**3**) are highly likely; structurally analogous diamagnetic species are [$NbCl_2$(diene)(η-C_5H_5)][3] and the ions [Mo(CO)$_2$(diene)(η-C_5H_5)]$^+$.[4] Calculations of electronic structures of molecules with such structures by Hoffmann *et al.*[5] show that the highest energy orbitals are chiefly metal d_{z^2} and d_{xy} (see Scheme 1 for the co-ordinate system). For d^3 complexes (**2**) and (**3**) the configuration will be $d^2_{z^2}$, d^1_{xy} and this is consistent with interaction of the unpaired electron with halogen ligands (p_π orbitals) and with terminal diene C–H bonds lying close to the square plane of the 3:4 structure. Also, the variation in the A_{iso} values for coupling to *syn* and *anti* ^{1}H atoms may be related to the extent of bending of these atoms out of the diene plane {*cf.* complexes [Co(diene)(η-C_5H_5)] for which *syn* atoms are bent towards and *anti* atoms away from the metal[6]}. It is particularly interesting that complexes (**3**; Ar = *p*-tolyl) and (**3**; Ar = C_6F_5) show markedly different A_{iso} (^{1}H) values.†



a; $R^1 = R^2 = R^3$ = H, X = Cl
b; $R^1 = R^2 = R^3$ = H, X = Br
c; $R^1 = R^2 = R^3$ = H, X = I
d; R^1 = Me, $R^2 = R^3$ = H, X = Cl
e; $R^1 = R^3$ = H, R^2 = Me, X = Cl

Scheme 1. (i) Excess of diene, hexane or ether solvent, 60 °C; (ii) tetrahydrofuran (THF), room temp., TlSAr [excess for Ar = *p*-tolyl and 2:1 TlSAr:(**2a**) for Ar = C_6F_5; for Ar = C_6F_5 (**4**) is also formed]; (iii) and (iv) THF, excess of $TlSC_6F_5$.

The reaction of (**2a**) with $TlSC_6F_5$ unexpectedly produces, in addition to (**3**; Ar = C_6F_5), a diamagnetic, monomeric derivative [MoTl($SC_6F_5)_4(\eta$-C_5H_5)] (**4**)† (M_r = 1100 in toluene). This product can also be formed from (**3**; Ar = C_6F_5) and results from a redox reaction between Mo^{III} and Tl^I. The ^{19}F n.m.r. spectrum of (**4**) is both solvent and temperature dependent. Four inequivalent C_6F_5 environments in a single isomer are indicated at −79 °C in toluene, since two well separated and two partially overlapping sets of *ortho*-fluorine resonances are observed. At higher temperatures (> −20 °C, toluene) exchange leads to a collapse to two equally occupied, distinct C_6F_5 environments while at 20 °C in acetone complete exchange of all four C_6F_5 groups is observed. These and related experimental data are consistent with structure (A) although we cannot exclude the less likely related structure (B), for complex (**4**) (see Scheme 1); structure

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† All complexes give satisfactory elemental microanalyses, mass spectra with parent ions, and consistent i.r. spectra. E.s.r. spectra in α-methyltetrahydrofuran solutions: (**2a**) (−60 °C): g_{iso} = 1.994, A_{iso} = 3.78($^{95/97}$Mo), 0.664 ($^1H_{syn}$), 0.394 ($^1H_{anti}$), 0.132 ($^{35/37}$Cl) mT; (**2b**) (−55 °C): g_{iso} = 2.029; A_{iso} = 3.68 ($^{95/97}$Mo), 0.53 ($^1H_{syn}$, $^1H_{anti}$), 0.54 ($^{79/81}$Br) mT; (**2c**) (−55 °C): g_{iso} = 2.085, A_{iso} = 3.3 ($^{95/97}$Mo) mT; (**2d**) (−60 °C): g_{iso} = 1.994, A_{iso} = 3.86 ($^{95/97}$Mo), 0.625 ($^1H_{syn}$), 0.43 and 0.34 ($^1H_{anti}$), 0.145 ($^{35/37}$Cl) mT; (**2e**) (0 °C): g_{iso} = 1.995, A_{iso} = 3.86 ($^{95/97}$Mo), 0.66 ($^1H_{syn}$) 0.39 ($^1H_{anti}$) 0.13 ($^{35/37}$Cl); (**3**; Ar = *p*-tolyl) (room temp.): g_{iso} = 2.002, A_{iso} = 3.13 ($^{95/97}$Mo), 0.40 ($^1H_{syn}$), 0.225 ($^1H_{anti}$) mT; (**3**; Ar = C_6F_5) (room temp.): g_{iso} = 2.004, A_{iso} = 3.35 ($^{95/97}$Mo), 0.66 ($^1H_{syn}$, $^1H_{anti}$) mT.

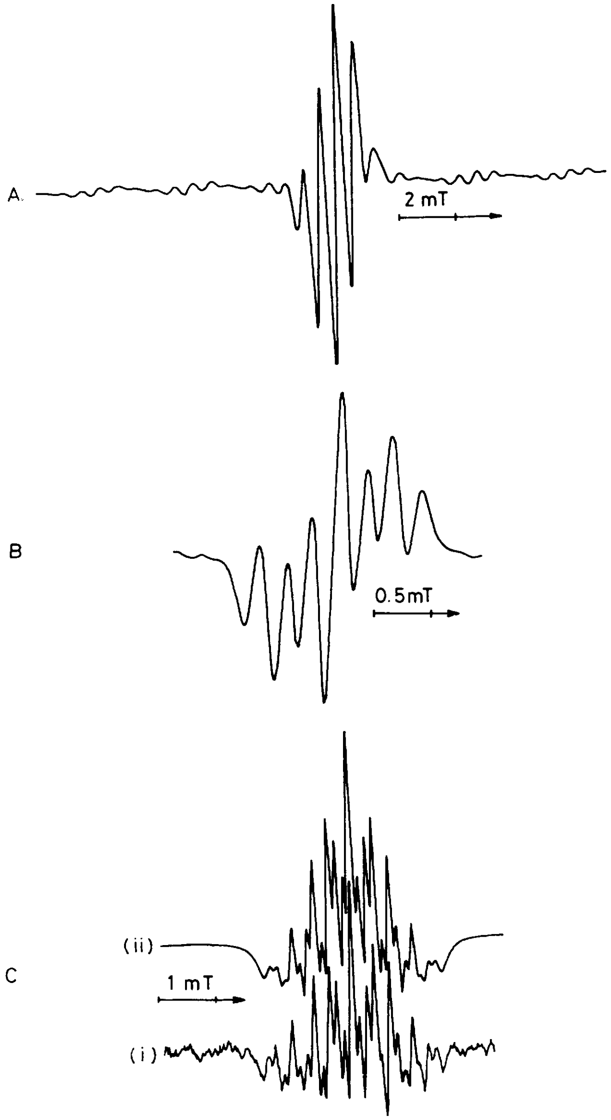

Figure 1. 9.4 GHz E.s.r. spectra: (A) (**3**; Ar = C_6F_5) in α-MeTHF; (B) (**3**; Ar = *p*-tolyl), central band (Mo, *I* = 0 isotopes), in THF; (C) (**2a**), central band (Mo, *I* = 0 isotopes) 2nd derivative in α-MeTHF (i) experimental, (ii) simulated, Δw = 0.2 mT.

(A) is analogous to $[W\overline{\{C(CF_3)=C(CF_3)C(CF_3)=C}(CF_3)\}(CO)_2(\eta\text{-}C_5H_5)Co(CO)_2]$[1a] and (B) bears some resemblance to $[Mo(\eta^2\text{-}CH_2SMe)(CO)_2(\eta\text{-}C_5H_5)]$.[7]

The more likely structure (A), contains two (μ-SC_5F_5) ligands and must be the *anti*-isomer with respect to orientation of C_6F_5 substituents of the 4-membered $\overline{Mo\text{-}S\text{-}Tl\text{-}S}$ ring; the lower-energy dynamic process will involve interchange of these axial and equatorial C_6F_5 substituents, without forming a stable *syn*-isomer, and the higher-temperature process involves interchange of all SC_6F_5 ligands. The alternative structure (B), possesses only one μ-SC_6F_5 group: a lower energy exchange process would involve exchange of groups (a) and (b), whereas the higher energy process is analogous to that of (A), involving complete SC_6F_5 ligand scrambling. In spite of the uncertainty in structure for (**4**), both interpretations of the ^{19}F n.m.r. data invoke novel, ready bridge–terminal pentafluorophenylthio-ligand exchanges in a heterobimetallic complex. Since exchange involves both bridging and terminal SC_6F_5 ligands, bond cleavage must be involved at some stage in the process. Consequently the higher exchange rates observed in acetone solutions can be attributed to the ability of this solvent to co-ordinate to the metal and thus promote cleavage.

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References

1 (a) J. L. Davidson, Lj. Manojlović-Muir, K. W. Muir, and A. N. Keith, *J. Chem. Soc., Chem. Commun.*, 1980, 749; (b) J. L. Davidson, G. Vasapollo, Lj. Manojlović-Muir, and K. W. Muir, *ibid.*, 1982, 1025.
2 J. L. Davidson, M. Green, F. G. A. Stone, and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1977, 287.
3 M. J. Bunker, M. L. H. Green, C. Couldwell, and K. Prout, *J. Organomet. Chem.*, 1980, **192**, C6; M. J. Bunker and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1981, 85.
4 J. W. Faller and A. M. Rosan, *J. Am. Chem. Soc.*, 1977, **99**, 4858.
5 P. Kubáček, R. Hoffmann, and Z. Havlas, *Organometallics*, 1982, **1**, 180.
6 Y. Wakatsuki, K. Aoki, and H. Yamazaki, *J. Chem. Soc., Dalton Trans.*, 1982, 89.
7 E. R. de Gil and L. F. Dahl, *J. Am. Chem. Soc.*, 1969, **91**, 3751.