## Paramagnetic Diene Complexes of Molybdenum(III) and a Transformation into a Diamagnetic, Fluxional Molybdenum–Thallium Complex, [MoTI(SC<sub>6</sub>F<sub>5</sub>)<sub>4</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)]

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Paramagnetic diene complexes  $[MoX_2(diene)(\eta - C_5H_5)]$  (X = CI, Br, I, SAr) give well resolved e.s.r. spectra in solution; reaction with TISC<sub>6</sub>F<sub>5</sub> produces the unusual fluxional, bimetallic complex  $[MoTI(SC_6F_5)_4(\eta - C_5H_5)]$ .

Diamagnetic bis-alkyne molybdenum(II) complexes of type  $[MoX(\eta-RC=CR)_2(\eta-C_5H_5)]$  show a varied chemistry including ligand substitution reactions and attack at co-ordinated alkyne.<sup>1,2</sup> Although a complex  $[MoCl_2(butadiene)(\eta-C_5H_5)]$  has been briefly reported,<sup>2</sup> 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)<sup>†</sup> 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 TISAr (Ar = *p*-tolyl or C<sub>6</sub>F<sub>5</sub>) forms related complexes (3; Ar = *p*-tolyl)† (72%) or (3; Ar = C<sub>6</sub>F<sub>5</sub>)† (15%) [reaction (ii), Scheme 11. Complexes (2) and (3) give well resolved e.s.r. spectra in solution (*e*.<sub>5</sub>. see Figure 1) which exhibit coupling to  ${}^{95/97}$ Mo,  ${}^{35/37}$ Cl,  ${}^{79/81}$ Br, and some <sup>1</sup>H atoms of the diene ligands. By analysis of the spectra, especially comparisons between (2a), (2d), and (2e), it is apparent that only terminal <sup>1</sup>H atoms bonded to C(1) and C(4) of the diene ligands cause significant, resolvable superhyperfine splitting and that  $A_{iso}({}^{1}\text{H}_{ayn}) \ge A_{iso}({}^{1}\text{H}_{anti})$ .†

Although not confirmed by X-ray analysis, the 'four-legged pianostool' structures for (2) and (3) are highly likely; structurally analogous diamagnetic species are  $[NbCl_2(diene)(\eta-C_5H_5)]^3$ and the ions  $[Mo(CO)_2(diene)(\eta-C_5H_5)]^+$ .<sup>4</sup> 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<sup>3</sup> complexes (2) and (3) the configuration will be  $d_{z^2}^2$ ,  $d_{xy}^1$  and this is consistent with interaction of the unpaired electron with halogen ligands (p<sub>7</sub> 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 1H atoms may be related to the extent of bending of these atoms out of the diene plane {cf. complexes  $[Co(diene)(\eta - C_5H_5)]$  for which syn atoms are bent towards and anti atoms away from the metal6}. It is particularly interesting that complexes (3; Ar = p-tolyl) and (3;  $Ar = C_6F_5$ ) show markedly different  $A_{iso}$  (<sup>1</sup>H) values.<sup>†</sup>



Scheme 1. (i) Excess of diene, hexane or ether solvent, 60 °C; (ii) tetrahydrofuran (THF), room temp., TISAr [excess for Ar = p-tolyl and 2:1 TISAr:(2a) for Ar = C<sub>6</sub>F<sub>5</sub>; for Ar = C<sub>6</sub>F<sub>5</sub> (4) is also formed]; (iii) and (iv) THF, excess of TISC<sub>6</sub>F<sub>5</sub>.

The reaction of (2a) with TISC<sub>6</sub>F<sub>5</sub> unexpectedly produces, in addition to (3; Ar = C<sub>6</sub>F<sub>5</sub>), a diamagnetic, monomeric derivative [MoTl(SC<sub>6</sub>F<sub>5</sub>)<sub>4</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] (4)† ( $M_r$  = 1100 in toluene). This product can also be formed from (3; Ar = C<sub>6</sub>F<sub>5</sub>) and results from a redox reaction between Mo<sup>111</sup> and Tl<sup>1</sup>. The <sup>19</sup>F n.m.r. spectrum of (4) is both solvent and temperature dependent. Four inequivalent C<sub>6</sub>F<sub>5</sub> 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<sub>6</sub>F<sub>5</sub> environments while at 20 °C in acetone complete exchange of all four C<sub>6</sub>F<sub>5</sub> 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

<sup>†</sup> All complexes give satisfactory elemental microanalyses, mass spectra with parent ions, and consistent i.r. spectra. E.s.r. spectra in  $\alpha$ -methyltetrahydrofuran solutions: (2a) (-60 °C):  $g_{iso} = 1.994$ ,  $A_{iso} = 3.78(^{95/97}M_{\rm O})$ , 0.664 (<sup>1</sup>H<sub>syn</sub>), 0.394 (<sup>1</sup>H<sub>arti</sub>), 0.132 (<sup>35/37</sup>Cl) mT; (2b) (-55 °C):  $g_{iso} = 2.029$ ;  $A_{iso} = 3.68(^{85/97}M_{\rm O})$ , 0.53 (<sup>1</sup>H<sub>syn</sub>, <sup>1</sup>H<sub>anti</sub>), 0.54 (<sup>79/81</sup>Br) mT; (2c) (-55 °C):  $g_{iso} = 2.085$ ,  $A_{iso} = 3.3$  (<sup>95/97</sup>M\_{O}) mT; (2d) (-60 °C):  $g_{ism} = 1.994$ ,  $A_{iso} = 3.86(^{95/97}M_{\rm O})$ , 0.625 (<sup>1</sup>H<sub>syn</sub>), 0.43 and 0.34 (<sup>1</sup>H<sub>anti</sub>), 0.145 (<sup>35/37</sup>Cl) mT; (2e) (0 °C):  $g_{isn} = 1.995$ ,  $A_{iso} = 3.86(^{95/97}M_{\rm O})$ , 0.625 (<sup>1</sup>H<sub>syn</sub>), 0.43 and 0.34 (<sup>1</sup>H<sub>anti</sub>), 0.145 (<sup>35/97</sup>M\_{O}), 0.66 (<sup>1</sup>H<sub>syn</sub>), 0.39 (<sup>1</sup>H<sub>anti</sub>) 0.13 (<sup>35/97</sup>Cl); (3; Ar = *p*-tolyl) (room temp.):  $g_{iso} = 2.002$ ,  $A_{iso} = 3.13(^{95/97}M_{\rm O})$ , 0.40 (<sup>1</sup>H<sub>syn</sub>), 0.225 (<sup>1</sup>H<sub>anti</sub>) mT; (3; Ar = C<sub>6</sub>F<sub>5</sub>) (room temp.):  $g_{iso} = 2.004$ ,  $A_{iso} = 3.35(^{95/97}M_{\rm O})$ , 0.66 (<sup>1</sup>H<sub>syn</sub>, <sup>1</sup>H<sub>anti</sub>) mT; (3; Ar = C<sub>6</sub>F<sub>5</sub>) (room temp.):  $g_{iso} = 2.004$ ,  $A_{iso} = 3.35(^{95/97}M_{\rm O})$ , 0.66 (<sup>1</sup>H<sub>syn</sub>, <sup>1</sup>H<sub>anti</sub>) mT;



**Figure 1.** 9.4 GHz E.s.r. spectra: (A) (3; Ar =  $C_8F_5$ ) in  $\alpha$ -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  $\alpha$ -MeTHF (i) experimental, (ii) simulated,  $\Delta w = 0.2$  mT.

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

The more likely structure (A), contains two  $(\mu$ -SC<sub>5</sub>F<sub>5</sub>) ligands and must be the anti-isomer with respect to orientation of C<sub>6</sub>F<sub>5</sub> substituents of the 4-membered Mo-S-TI-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  $\mu$ -SC<sub>6</sub>F<sub>5</sub> 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  $SC_{e}F_{5}$  ligand scrambling. In spite of the uncertainty in structure for (4), both interpretations of the <sup>19</sup>F n.m.r. data invoke novel, ready bridge-terminal pentafluorophenylthioligand exchanges in a heterobimetallic complex. Since exchange involves both bridging and terminal SC<sub>6</sub>F<sub>5</sub> 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 coordinate to the metal and thus promote cleavage.

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