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Synthesis, X-Ray Crystal Structure, and Chemistry of the Cation [(η-MePh)Mo-(μ-SMe)₄Mo(η-MePh)]²⁺; Easy D₂O–NaOD Catalysed H–D Exchange of the Methyl Hydrogens of a η-Bonded Toluene Ligand

By William E. Silverthorn*

(Department of Chemistry, Oregon State University, Corvallis, Oregon 97331)

and CLAIRE COULDWELL and KEITH PROUT* (Chemical Crystallography Laboratory, 9, Parks Road, Oxford, OX1 3PD)

PREVIOUS investigations have shown that a wide variety of 18-electron arene-molybdenum complexes can be prepared starting from bis- η -arenemolybdenum(0) complexes.¹ Some of these complexes were shown to promote unusual hydrocarbon ligand reactions.² Recently we have become interested in the possibility that related 17-electron arene molybdenum(I) complexes might also serve as precursors to new types of reactive molybdenum complexes.

We now find that the reaction between $[(arene)_2Mo]^+$ - $[PF_6^-]$ (arene = benzene or toluene), prepared by metathesis of the iodide salt³ in methanol solution, and pyridine at 50 °C affords the new 17-electron compounds $[(arene)Mo-(py)_3]^+[PF_6^-]$ (I) (py = pyridine) as air sensitive, darkmaroon crystalline solids in near-quantitative yield. The compounds are paramagnetic with $\mu_{eff} = 1.8$ B.M. The solids (I) react with an excess of methane thiol in aqueous methanol (see Scheme) to yield, after removal of solvent, a brown residue which, after extraction with acetone-HPF₆, $\begin{bmatrix} (\eta - PhR)_{2} Mo \end{bmatrix}^{+} \begin{bmatrix} PF_{6} \end{bmatrix}^{-} \frac{i}{R = H \text{ or } Me} \begin{bmatrix} (\eta - PhR) Mo (NC_{5}H_{5})_{3} \end{bmatrix}^{+} \begin{bmatrix} PF_{6} \end{bmatrix}^{-}$ R = H or Me ii, iii $\begin{bmatrix} (\eta - PhR) Mo (\mu - SMe)_{4} Mo (\eta - PhR) \end{bmatrix}^{2+} \begin{bmatrix} PF_{6} \end{bmatrix}_{2}$ $R = Me \\ \downarrow iii, iv, v$ $\begin{bmatrix} L \\ L \\ Mo \\ X \end{bmatrix}^{-} Mo \\ L \end{bmatrix}^{-} \begin{bmatrix} PF_{6} \end{bmatrix}_{3}^{+}$ L = N NMe , X = SMe

Scheme. i, py, 50 °C; ii, 20 % MeSH-10 % MeOH, - 50 °C; iii, excess of HPF₆-Me₂CO; iv, Zn-Hg, 20 % MeIm-MeCN; v, O₂.

affords an orange diamagnetic compound of composition $[(\operatorname{arene})\operatorname{Mo}(\operatorname{SMe})_2]_2(\operatorname{PF}_6)_2$ (II) in 10—20% yield. Addition of $\operatorname{H}_2\operatorname{SO}_4$ to an acetone solution of (II) yields a crystalline water soluble bisulphate salt from which the tetraphenylborate salt is obtained by metathesis reaction in aqueous solution. Single crystals of the tetraphenylborate salt (arene = toluene) suitable for X-ray investigation were grown by slow cooling of a warm saturated Me₂SO solution.

Crystal data: $C_{66}H_{68}B_2Mo_2S_4$, M 1203.0, triclinic, a = 11.362(1), b = 11.860(1), c = 13.246(2) Å, $\alpha = 68.38(1)^\circ$, $\beta = 64.70(1)^\circ$, $\gamma = 62.92(1)^\circ$, U = 1402.9 Å³, $D_m = 1.44$ g cm⁻³ (by flotation), Z = 1, $D_c = 1.42$ g cm⁻³, space group $\overline{P1}$. 4324 independent reflections were measured by fourcircle diffractometry using Mo- K_{α} radiation ($\lambda = 0.71069$ Å). The structure was solved by Patterson and Fourier methods and refined by large block least-squares. Hydrogen atoms were located from difference syntheses, but were positioned geometrically. The final *R*-value is 0.026 (R' 0.032).†

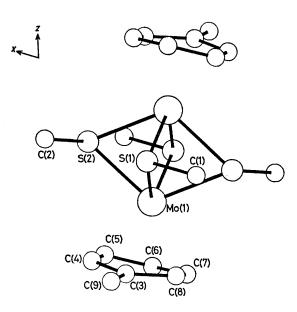


FIGURE. Structure of $[(\eta-MePh)Mo(\mu-SMe)_4Mo(\eta-MePh)]^{2+}$.

The unit cell contains one cation with the structure shown in the Figure, together with two tetraphenylborate anions. The cation exists as a discrete dimeric species of crystallographic point-group symmetry C_i , the centre of symmetry being situated midway between the Mo atoms. The two (η -MeP)Mo species are linked to each other by four symmetrically positioned bridging methanethiolato ligands [Mo-S distances range from $2\cdot451(1)-2\cdot462(1)$ Å] and the molecular structure is very similar to those of the [(η -C₅H₅)Mo(SMe)₂]₂ⁿ complexes (n = 0 or +1).⁴

It is suggested that there is a direct metal-metal bond between the Mo atoms, and this is in accord with the short Mo-Mo distance of 2.614(1) Å, the acute Mo-S-Mo bridging angles of 64.39(2) and $64.27(2)^{\circ,5}$ and the observed diamagnetism of the cation.

While the Mo–C distances $[2\cdot287(3)-2\cdot416(3) \text{ Å}]$ and the ring C–C distances $[1\cdot381(7)-1\cdot451(6) \text{ Å}]$ are normal⁶ it is

interesting to note that the η -MePh ligand is significantly non-planar and is folded with 9.6° about the C(3) · · · C(6) vector.

The compounds (II) are redox active. Cyclic voltametry studies at a Pt wire electrode in acetonitrile solution show a reversible 1-electron oxidation wave at +1.4 V vs. S.C.E. for the toluene derivative $(\operatorname{Bu}_4{}^n\operatorname{N+PF}_6{}^-$ was used as supporting electrolyte). An irreversible reduction wave is observed at ca. -1.0 V vs. S.C.E. in acetonitrile solution. Zinc amalgam reduction of compound (II) in 1-methylimidazoleacetonitrile solution yields, after air oxidation, a green, weakly paramagnetic compound of stoicheiometry [Mo2- $({\rm SMe})_3(C_3H_3{\rm N}_2{\rm Me})_6][{\rm PF}_6]_3\,(\mu_{eff}=1\cdot45~{\rm B.M.})~\text{in}~30\%~\text{yield.}$ Conductivity measurements and the observation of singlet resonances for each of the three aromatic protons as well as for both methyl groups in the n.m.r. spectrum indicate the centrosymmetric, dimeric structure shown in the Scheme.[‡] The ready expulsion of a thiolate group in the above reaction is unusual and the reaction is under further investigation.

The compounds (II) are very stable and can be recovered unchanged from concentrated H_2SO_4 or $5 \text{ M} \text{HNO}_3$ after 24 h. A 10% solution of the toluene derivative (bisulphate salt) in saturated Na₃PO₄-D₂O buffer (pD = 11) undergoes complete H-D exchange at the toluene methyl position within 12 h at 25 °C. The exchange was followed by observing the disappearance of the singlet methyl resonance at τ 7·3 in the n.m.r. spectrum. The SMe and aromatic protons resonances remained unchanged. The exchange rate is dependent on the base concentration. At a pD of 9 complete H-D exchange of a 5% solution of (II) in saturated Na₂B₄O₇-D₂O buffer requires *ca.* 3 days at 60 °C. The i.r. spectrum of the deuteriated derivative (hexafluorophosphate salt) shows a weak C-D stretch at 2120 cm⁻¹.



Transition metal catalysed H–D exchange of hydrocarbons has often been observed with 'electron rich' complexes.⁷ The mechanism is believed to involve an oxidative addition of a C–H bond to the metal atom. However, the chemistry and stereochemistry of compound (II) makes it unlikely that such a mechanism is involved here. The easy H–D exchange observed above (comparable H–D exchange rates for free toluene require very strong bases such as lithium cyclohexylamide in cyclohexylamine solution)⁸ is presumably due to strong electron withdrawal from the aromatic rings by the Mo atoms

[‡] It is likely that the well defined resonances observed for this paramagnetic complex are due to a rapid spin relaxation mechanism (see, for example, A. Abragam and B. Bleaney, 'Electron Paramagnetic Resonance of Transition Ions,' Clarendon Press, Oxford, 1970).

[†] The atomic co-ordinates for this work 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.

causing enhanced stabilization of the carbanion (A) thereby rendering the methyl groups kinetically acidic.

All of the above compounds have been characterized by elemental analyses, conductivity measurements, and i.r. and ¹H n.m.r. spectra.

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¹ W. E. Silverthorn, in 'Advances in Organometallic Chemistry,' Vol. 13, Academic Press, 1975, p. 47.

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