An Organoimido Molybdenum(VI) Complex: Preparation and Structure of (*p*-TolylN)-$MoCl_4$(thf)†

C. Y. Chou,[a] John C. Huffman,[b] and Eric A. Maatta*[a]

[a] *Department of Chemistry, Kansas State University, Manhattan, Kansas 66506, U.S.A.*
[b] *Molecular Structure Center, Indiana University, Bloomington, Indiana 47405, U.S.A.*

The product of the reaction between *p*-tolyl azide and $MoCl_4(thf)_2$ (thf = tetrahydrofuran) is shown to be the organoimido Mo^{VI} complex $Mo(Ntolyl)Cl_4(thf)$, and its molecular structure is described; in the presence of bipyridine or tertiary phosphine ligands, the title complex is readily reduced to yield organoimido Mo^{V} complexes $Mo(Ntolyl)Cl_3L_2$ ($L = PPh_3, PPh_2Et$; L_2 = bipy, $Ph_2PC_2H_4PPh_2$).

The reactions of covalent azides ($R\text{–}N_3$) with molybdenum(IV) halide complexes result in a diverse array of products. However, these reactions have not led to imido–molybdenum [Mo(NR)] species; rather, the isolated products arise *via* the rupture of the R–N bond of the azide. Thus, the reaction of Me_3SiN_3 with $MoCl_4(thf)_2$ (thf = tetrahydrofuran) affords solutions of the Mo^{VI} nitrido complex $MoNCl_3(thf)_2$,[1] while excess of Me_3SiN_3 reacts with $MoCl_4$(bipy) to yield $MoN(N_3)_3$(bipy) (bipy = bipyridine).[2] The reaction of IN_3 with $MoBr_4$ yields $MoNBr_3$ *via* the intermediacy of $Mo(N_3)Br_3$.[3] In a complex process, the interaction of toluene-*p*-sulphonyl azide with $MoCl_4(PPh_2Pr)_2$ yields the Mo^{V} phosphine imine derivative $MoCl_4(NPPh_2Pr)(OPPh_2Pr)$.[4] We report here that the reaction of *p*-tolyl azide with $MoCl_4(thf)_2$ follows a different course and forms an organoimido Mo^{VI} complex, $Mo(Ntolyl)Cl_4(thf)$ (**1**), as shown in equation (1).

$$MoCl_4(thf)_2 + \text{tolyl-}N_3 \xrightarrow[C_2H_4Cl_2]{30\ °C} \underset{(\mathbf{1})}{Mo(Ntolyl)Cl_4(thf)} + N_2 \qquad (1)$$

This procedure gives excellent yields of (**1**) as a dark red, diamagnetic, air- and moisture-sensitive solid. The i.r. spectrum of (**1**) displays bands associated with the *p*-tolylimido group at 1580, 1165, 811, and 444 cm^{-1}, while absorptions at 1008 and 845 cm^{-1} are attributed to the co-ordinated thf. Elemental analyses and ^1H n.m.r. results are in accord with the proposed formulation of (**1**). Since transition metal organoimido complexes are of considerable current interest in inorganic and organometallic chemistry,[5] a single-crystal *X*-ray diffraction study of (**1**) was performed.

Crystal data for (**1**): $C_{11}H_{15}Cl_4MoNO$, $M = 415.00$, monoclinic, space group $P2_1/a$, $a = 13.687(4)$, $b = 17.494(7)$, $c = 7.072(2)$ Å, $\beta = 113.36(1)°$, $Z = 4$, $D_c = 1.773\ g\ cm^{-3}$, $T = -160$ °C, Mo-K_α ($\lambda = 0.71069$ Å), $\mu = 15.063\ cm^{-1}$, 1800 unique intensities with $F > 3.0\sigma(F)$, $R = 0.0242$.‡

The molecular structure of (**1**) is shown in Figure 1 and reveals a pseudo-octahedral geometry, with virtual C_{4v} local symmetry about the Mo atom. The four chlorine atoms are distorted away from the organoimido ligand; the average N–Mo–Cl angle is 95.3°. The short Mo–N bond length [1.717(3) Å] and near-linear Mo–N–C bond angle [174.6(3)°] imply considerable triple bond character in the Mo–N bond and indicate that the *p*-tolylimido ligand acts as a formal four-electron donor. In this 16-electron complex, the *p*-tolylimido ligand exerts a profound *trans*-influence on the thf molecule: the Mo–O bond distance of 2.234(3) Å exceeds the expected Mo–O single bond length[6] by *ca.* 0.2—0.3 Å. Significantly, the phenylimido ligand in the 17-electron complex $W(NPh)Cl_3(PPh_3)_2$ exerts a much smaller *trans*-influence (*ca.* 0.06 Å), while in the 18-electron species $W(NPh)Cl_2(PMe_3)_3$ the phenylimido ligand does not display a *trans*-influence.[5b]

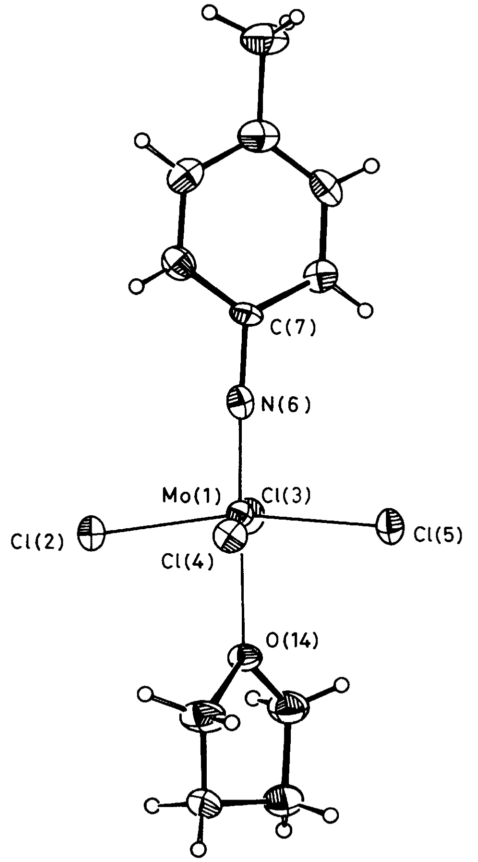

Figure 1. The molecular structure of $Mo(Ntolyl)Cl_4(thf)$. Important dimensions: Mo–N(6) 1.717(3), Mo–O(14) 2.2343(27), Mo–Cl(2) 2.3413(12), Mo–Cl(3) 2.3371(12), Mo–Cl(4) 2.3582(12), Mo–Cl(5) 2.3327(12) Å; Mo–N(6)–C(7) 174.6(3), O(14)–Mo–N(6) 177.80(13)°.

Preliminary studies have revealed that addition of tertiary phosphines or bipyridine to solutions of (**1**) result in the formation of tolylimido Mo^{V} complexes of the type $Mo(Ntolyl)Cl_3L_2$ ($L = PPh_3$, $PEtPh_2$; $L_2 = Ph_2PC_2H_4PPh_2$, bipy). These paramagnetic air-stable species display solid state magnetic moments ($\mu_{eff} = 1.74 \pm 0.03\ \mu_B$) close to the expected spin-only value. We have also found that the chloride ligands in (**1**) and its Mo^{V} derivatives are prone to anionic substitution reactions.

---

† Tetrachloro(*p*-tolylimido)(tetrahydrofuran)molybdenum(VI).

‡ 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.

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Bureau of General Research at Kansas State University for support of this research. We also thank the Marshall H. Wrubel Computer Center for a generous allocation of computer time.

Received, 8th May 1984; Com. 627

References

1 J. Chatt and J. R. Dilworth, *J. Chem. Soc., Chem. Commun.*, 1974, 517; M. W. Bishop, J. Chatt, J. Dilworth, M. B. Hursthouse, and M. Motevalle, *J. Less-Common Met.*, 1977, **54**, 487.

2 E. Schweda and J. Strahle, *Z. Naturforsch., Teil B*, 1980, **35**, 1146.

3 K. Dehnicke and N. Kruger, *Z. Naturforsch., Teil B*, 1978, **33**, 1242.

4 D. Scott and A. G. Wedd, *J. Chem. Soc., Chem. Commun.*, 1974, 527.

5 (a) W. A. Nugent and B. L. Haymore, *Coord. Chem. Rev.*, 1980, **31**, 123; K. Dehnicke and J. Strahle, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 413; S. M. Rocklage and R. R. Schrock, *J. Am. Chem. Soc.*, 1982, **104**, 3077; S. F. Pederson and R. R. Schrock, *ibid.*, 1982, **104**, 7483; (b) D. C. Bradley, M. B. Hursthouse, K. M. A. Malik, A. J. Nielson, and R. L. Short, *J. Chem. Soc., Dalton Trans.*, 1983, 2651; (c) W. A. Nugent, *Inorg. Chem.*, 1983, **22**, 965.

6 F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 1965, **6**, 867; F. A. Schroder, *Acta Crystallogr., Sect. B*, 1975, **31**, 2294.