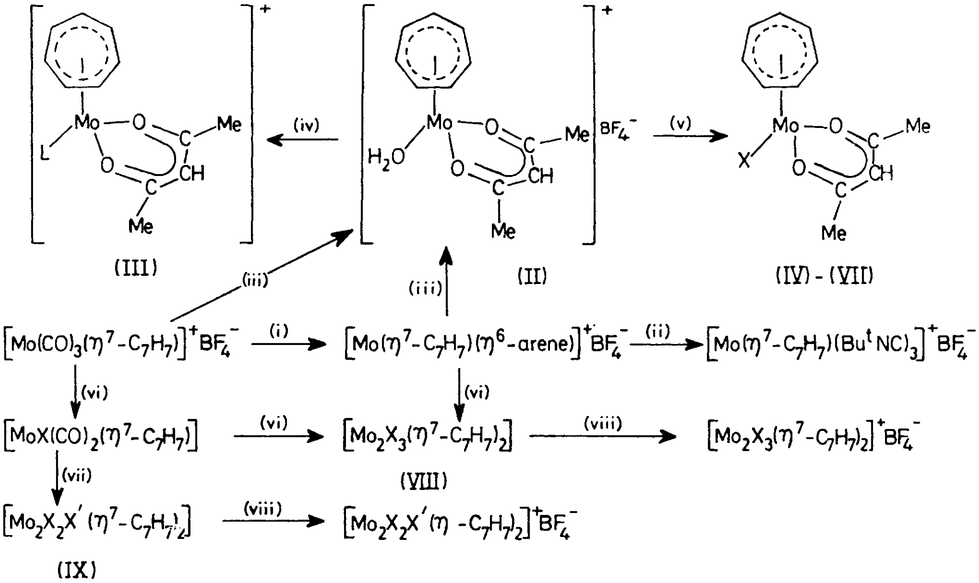
New Routes to η^7-Cycloheptatrienylmolybdenum Complexes: Crystal and Molecular Structures of $[Mo(acac)(H_2O)(\eta^7\text{-}C_7H_7)]^+BF_4^-$ and $[Mo(NCS)(acac)(\eta^7\text{-}C_7H_7)]$

By MANFRED BOCHMANN, MICHAEL COOKE, MICHAEL GREEN, HOWARD P. KIRSCH, F. GORDON A. STONE,*
and ALAN J. WELCH
(*Department of Inorganic Chemistry, The University, Bristol* BS8 1TS)

Summary Reaction of $[Mo(CO)_3(\eta^7\text{-}C_7H_7)]BF_4$ with arenes gives $[Mo(\eta^7\text{-}C_7H_7)(\eta^6\text{-arene})]BF_4$, whereas the halides Me_3SiX (X = Cl, Br, or I) form $[Mo_2X_3(\eta^7\text{-}C_7H_7)_2]$, the latter being reversibly oxidised to binuclear monocations; treatment of the mononuclear cations with acacH affords $[Mo(acac)(H_2O)(\eta^7\text{-}C_7H_7)]^+$, which with anions ($X^-$) yields the neutral species $[MoX(acac)(\eta^7\text{-}C_7H_7)]$, both these paramagnetic complexes being structurally characterised by *X*-ray crystallography.

TREATMENT of the violet solutions produced from $Al_2Et_2Cl_4$ and $[\{MoCl(\eta^3\text{-}C_3H_5)(\eta^6\text{-arene})\}_2]$ with cycloheptatriene affords[1] the cycloheptatrienyl sandwich compounds $[Mo(\eta^7\text{-}C_7H_7)(\eta^6\text{-arene})]PF_6$. As part of a study[2] of reactions of $[MoCl(CO)_3(\eta^5\text{-}C_5H_5)]$, we have investigated the potentially related chemistry of $[Mo(CO)_3(\eta^7\text{-}C_7H_7)]^+$ and have found (see Scheme) that this cation on refluxing with arenes affords the species $[Mo(\eta^7\text{-}C_7H_7)(\eta^6\text{-arene})]^+$ [arene = C_6H_5Me (90%, 19 h), C_6H_6 (70%, 260 h) and $C_6H_3Me_3$ (60%, 41 h)]. These observations are in interesting contrast with previous studies[3] of the reaction of $[M(CO)_3(\eta^7\text{-}C_7H_7)]^+$ (M = Cr, Mo, or W) with phosphorus ligands, and provide a particularly convenient entry into a relatively unexplored area of molybdenum chemistry.



SCHEME. (i) arene; (ii) MeCN, then Bu^{t}NC; (iii) acacH; (iv) L = $P(OMe)_3$, THF reflux; (v) $X^- = Cl^-, Br^-, I^-, SCN^-$; (vi) Me_3SiX (X = Cl, Br, I), THF reflux; (vii) X = Cl, Br; Me_3SiX' (X′ = Br or Cl); (viii) $PhN_2^+BF_4^-$, THF, room temperature.

Toluene is readily displaced (room temp., 66 h) from (I) with acetonitrile to form $[Mo(\eta^7\text{-}C_7H_7)(MeCN)_2]^+$, whereas in refluxing MeCN the known[1] cation $[Mo(\eta^7\text{-}C_7H_7)(MeCN)_3]^+$ is produced. Both the bis- and the tris-acetonitrile complexes react with Bu^{t}NC giving the pink complex $[Mo(\eta^7\text{-}C_7H_7)(Bu^tNC)_3]BF_4$ (83%, ν_{NC}(max) (Nujol), 2165vs 2138vs, 2125vs, sh, and 2062m cm^{-1}). Treatment of (I) (arene = C_6H_5Me) with acetylacetone (acacH) [23 h reflux, tetrahydrofuran (THF)] leads to an unusual reaction and the formation (80%) of the paramagnetic aquo-cation (II),† whose molecular structure (Figure) was established by a single crystal *X*-ray diffraction study.

Crystal data: $[C_{12}H_{16}MoO]BF_4$, *M* = 391·00, monoclinic, $P2_1/n$, *a* = 8·664(9), *b* = 18·997(14), *c* = 9·623(13) Å, β = 112·39(8)°, *U* = 1465(2) Å^3, D_c = 1·772, *Z* = 4, μ(Mo-K_α) = 9·9 cm^{-1}; *R* is currently 0·06 for 3662 reflections [I ≥ 1·0σ (*I*)] recorded at *ca.* 215 °K (Syntex $P2_1$ four-circle diffractometer).

The Mo atom is essentially octahedrally co-ordinated, the metal lying *ca.* 1·58 Å from the centre of the 7-membered ring (3 facial sites), the acetylacetonate ligand occupying two sites at an average Mo–O distance of 2·085 Å, the remaining site being occupied by a water molecule with Mo–O = 2·201(5) Å.

The co-ordinated water in (II) exchanges with D_2O, and is displaced by trimethylphosphite to give (III).‡ The reaction (reflux, acetone, 1—2 h) of (II) with $Et_4N^+Cl^-$, $Me_4N^+Br^-$, KI, or KSCN afforded, respectively, the neutral paramagnetic complexes (IV), (V), (VI), and (VII). A crystal structure determination with (VII) showed that the neutral species is isostructural with (II), with the water molecule replaced by an N-bonded thiocyanate (Figure).

Crystal data: $C_{13}H_{14}MoNO_2S$, *M* = 344·26, monoclinic, $P2_1/a$, *a* = 12·762(2), *b* = 12·634(4), *c* = 8·813(3) Å, β = 100·70(2)°, *U* = 1396·1(6) Å^3, D_c = 1·637, *Z* = 4, μ(Mo-K_α) = 9·93 cm^{-1}; *R* is currently 0·07 for 2788 reflections recorded at 295 K. For the thiocyanate ligand angles of 157° and 179° are subtended at N and C, respectively, with Mo–N = 2·125(9), (N=C) = 1·169(14), and (C=S) = 1·596(10) Å.

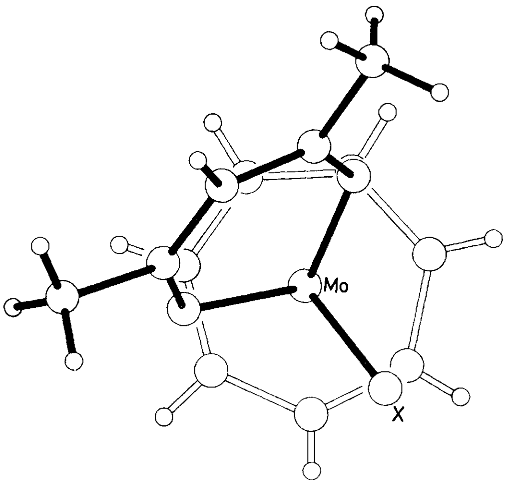


FIGURE. Molecular geometry of (a) the cation $[Mo(acac)(X)(\eta^7\text{-}C_7H_7)]^+$ (X = H_2O) and (b) the complex $[Mo(acac)(X)(\eta^7\text{-}C_7H_7)]$ (X = NCS).

E.s.r. solution spectra of (II) and (III), and the neutral species (IV)—(VII), show very similar *g* values and hyper-

---

† (II) can also be obtained (65%) by the reaction of $[Mo(CO)_3(\eta^7\text{-}C_7H_7)]BF_4$ with acetylacetone (reflux, THF, 16 h).

‡ Similar cations are obtained in the corresponding reactions with phosphines and arsines, and it is interesting that a diamagnetic neutral species $[Mo(acac)(\eta^7\text{-}C_7H_7)(PPh_3)]$ has been reported.[1]

fine couplings [(II), $g = 1{\cdot}954$, A_{iso} *ca.* 44 G; (VII), $g = 1{\cdot}958$, A_{iso} *ca.* 43 G], thus providing added confirmation that (II) contains co-ordinated water.

The reaction (45 °C, THF, 1 h) of $[\mathrm{Mo(CO)_3}(\eta^7\text{-}\mathrm{C_7H_7})]\mathrm{BF_4}$ with $\mathrm{Me_3SiCl}$ or $\mathrm{Me_3SiBr}$ affords $[\mathrm{MoX(CO)_2}(\eta^7\text{-}\mathrm{C_7H_7})]$ (X = Cl or Br), which react further with silyl halides in refluxing THF to give, in high yield, the neutral dinuclear complexes (VIII, X = Cl or Br). Complex (VIII) (X = I) can also be obtained by treating (I) with $\mathrm{Me_3SiI}$. The dinuclear trichloro-species has been obtained previously[1] from (I) and NaOMe–MeOH, followed by reaction of the resultant $[\mathrm{Mo_2(OMe)_3}(\eta^7\text{-}\mathrm{C_7H_7})_2]$ with HCl. The use of silyl halides as halogen transfer reagents was extended to the synthesis of the mixed halogen bridged systems (IX) (see Scheme).

Cyclic voltammetry at a stationary Pt wire electrode in $\mathrm{CH_2Cl_2}$ solution [0·5M in $\mathrm{Et_4NClO_4}$ as base electrolyte] showed that (VIII) undergoes reversible one-electron oxidation reactions. The trend in oxidation potentials for $[\mathrm{Mo_2X_3}(\eta^7\text{-}\mathrm{C_7H_7})_2]$ [E_{p} −0·11 V (X = I), −0·13 (X = Br), and −0·15 (X = Cl)] can be explained if the electron is removed from an antibonding metal orbital. This could be confirmed by comparison of Mo–Mo bond lengths in the cationic and neutral species. Phenyldiazonium salts can be used conveniently to form the cations (see Scheme).

We thank the Evangelisches Studienwerk Villigst e.V. (B.R.D.) for a scholarship (M.B.).

(*Received*, 24*th March*, 1976; *Com.* 308.)

---

[1] E. F. Ashworth, M. L. H. Green, and J. Knight, *J.C.S. Chem. Comm.*, 1974, 5; M. L. H. Green and J. Knight, *J.C.S. Dalton*, 1976, 213.

[2] J. L. Davidson, M. Green, D. W. A. Sharp, F. G. A. Stone, and A. J. Welch, *J.C.S. Chem. Comm.*, 1974, 756; *J.C.S. Dalton*, 1976, 738; J. L. Davidson and D. W. A. Sharp, *ibid.*, 1975, 2531.

[3] A. Salzer, *Inorg. Chim. Acta*, 1976, **17**, 221; and references therein; D. A. Sweigart, M. Gower, and L. A. P. Kane-Maguire, *J. Organometallic Chem.*, 1976, **108**, C15.