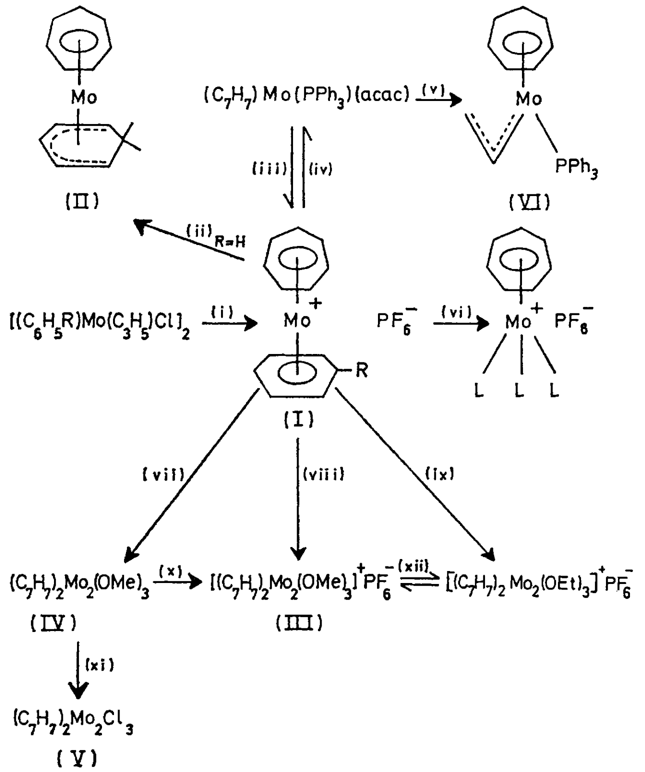
π-7e-Cycloheptatrienyl Molybdenum Chemistry: a Versatile Preparative Route

By EDWIN F. ASHWORTH, MALCOLM L. H. GREEN,* and JOHN KNIGHT
(*Inorganic Chemistry Laboratory, South Parks Road, Oxford* OX1 3QR)

Summary The preparation and reactions of a variety of π-cycloheptatrienyl derivatives of molybdenum are described.

SEVERAL π-cycloheptatrienyl transition-metal complexes have been known for a number of years.[1] However, relatively little is understood of the influence of this ligand



Scheme. (i) $EtAlCl_2$ + C_7H_8, 24 h, R=H or Me; then H_2O,PF_6^- 35%, green crystals. (ii) $NaBH_4$, THF, 30%, red crystals, *m/e* = 262 (^{92}Mo). (iii) $EtAlCl_2$ in arene; then H_2O,PF_6^- (arene = C_6H_6 or *sym*-$Me_3C_6H_3$), 50%. (iv) $Na^+(acac)^-$, PPh_3 in MeOH, 4 h, 40°, 60%, dark red crystals. (v) C_3H_5MgBr in Et_2O, 1 h, 20°, 30%, orange-red crystals. (vi) L=MeCN, 15 min, excess MeCN, 80°. L = PMe_2Ph, $PMePh_2$, in ethanol, 20 min, 80°, purple-pink crystals. (vii) NaOMe, MeOH, 5 h, 35°, 50%, dark green, sublimes 180° *in vacuo*, *m/e* = 459 ($^{92}Mo_2$). (viii) MeOH, 1 h, 65°, 75%, diamagnetic, green-brown crystals. (ix) EtOH, 1 h, 80°. (x) O_2, MeOH, NH_4PF_6. (xi) HCl in C_6H_6, dark green, sublimes 180° *in vacuo*, paramagnetic, *m/e* = 471 ($^{92}Mo_2$ $^{35}Cl_3$). (xii) Reflux in excess appropriate ROH, R=Me, Et. All the complexes are fully characterised except the binuclear derivatives for which possible isomers remain to be distinguished.

on metal properties. Here we describe the preparation of a variety of new π-cycloheptatrienyl molybdenum derivatives. The results show that the π-C_7H_7Mo system combines with ligands of widely different properties.

The Scheme shows the preparation of the mixed sandwich compounds $[(\pi\text{-}C_7H_7)Mo(\pi\text{-}C_6H_5R)]^+$ (I; R = H, Me). In contrast to the non-lability of the arene ligand in many arene molybdenum derivatives,[2] the cations (I) readily lose their arene groups under mild conditions. Thus the displacement of the arene ligand by acetonitrile giving the cation $[(\pi\text{-}C_7H_7)Mo(NCMe)_3]^+$ contrasts with replacement of acetonitrile by benzene in the system:[3]

$$(MeCN)_3Mo(CO)_3 + C_6H_6 \rightarrow (C_6H_6)Mo(CO)_3 + 3MeCN$$

It would be reasonable to predict that hydride attack on the cation (I; R = H) would yield zero-valent $(\pi\text{-}C_6H_6)$-$Mo(C_7H_8)$ analogous to dibenzenemolybdenum; however, the divalent cyclohexadienyl complex $(\pi\text{-}C_7H_7)Mo(C_6H_7)$ (II) is formed.

The arene ligand may also be removed from (I) by methanol and the diamagnetic complex $[(\pi\text{-}C_7H_7)_2$-$Mo_2(OMe)_3]^+$ PF_6^- (III) is isolated. A neutral complex $(\pi\text{-}C_7H_7)_2Mo_2(OMe)_3$ (IV) may be prepared from (I) using sodium methoxide in methanol and the corresponding paramagnetic chloride $(\pi\text{-}C_7H_7)_2Mo_2Cl_3$) (V) is made from it by reaction with hydrogen chloride.

The ^1H n.m.r. spectrum of the cation $[C_7H_7Mo(Ph_2MeP)_3]^+$ in acetone shows that one Ph_2MeP ligand dissociates and this may be contrasted with the inertness of the isoelectronic (arene)$Mo(R_3P)_3$.[2] Also, the π-allyl group in the complex $(\pi\text{-}C_7H_7)Mo(Ph_3P)(\pi\text{-}C_3H_5)$ (VI) is very sensitive to available protons, for example, it is displaced in methanol at 20° giving propene.

Although arenes are clearly less preferred than acetonitrile in the $[C_7H_7Mo]^+$ system, the re-addition of arenes may be achieved, starting from the acetoacetonate compound, as shown in the Scheme.

We thank Shell International Petroleum Co. Ltd., for a Research Fellowship (to J.K.) and The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(*Received, 7th September* 1973; *Com.* 1260.)

---

[1] M. L. H. Green, 'Organometallic Compounds, Vol. 2,' Methuen, London, 1967; T. W. Beall and L. W. Houk, *Inorg. Chem.*, 1973, **12**, 1979.

[2] See, for example, M. L. H. Green and W. E. Silverthorn, *J.C.S. Dalton*, 1973, 301; M. L. H. Green, L. C. Mitchard, and W. E. Silverthorn, *ibid.*, p. 1403.

[3] R. B. King and A. Fronzaglia, *Inorg. Chem.*, 1966, **5**, 1837.