

Arene Molybdenum Chemistry: Some π -Allyl, Hydrido, and Dinitrogen Derivatives

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Summary Treatment of the new compound $C_6H_6Mo(\pi-C_3H_5)(PPh_3)Cl$ with sodium borohydride forms the dihydride $C_6H_6Mo(PPh_3)_2H_2$ which reacts readily with nitrogen gas forming the binuclear dinitrogen complex $[C_6H_6Mo(PPh_3)_2]_2N_2$.

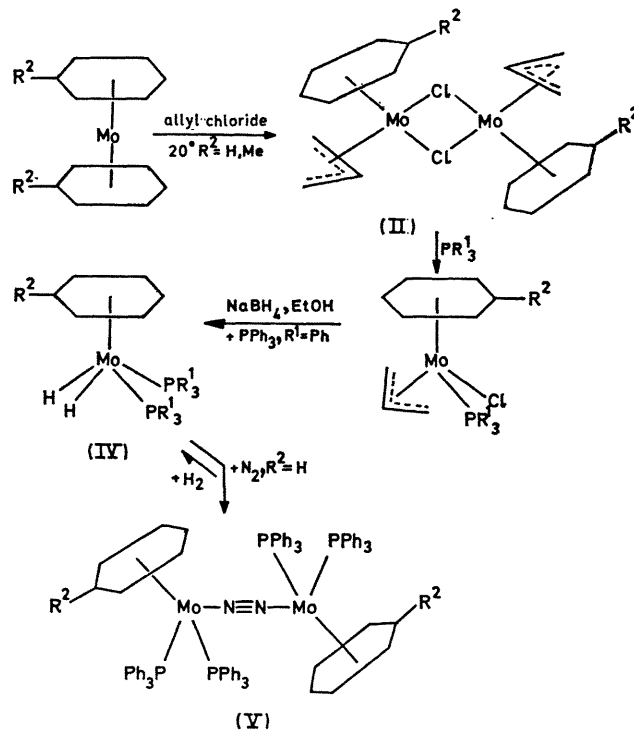
RECENTLY we found that bisbenzenemolybdenum reacts readily at *ca.* 120 °C with some tertiary phosphines forming the mono-benzene derivatives $C_6H_6Mo(PR_3)_3(I)$.¹ However, this reaction does not proceed when PR_3 is triphenylphosphine, possibly due to steric overcrowding. This observation may be contrasted with the report of the isolation of a dinitrogen complex of stoichiometry $PhMeMo(PPh_3)_2N_2$, from the reaction between molybdenum, acetylacetonone, triphenylphosphine, and tri-isobutylaluminum in toluene,² which presumably would have essentially the same structure as the complexes (I).

These observations suggested to us that formation of mono-arenemolybdenum complexes with triphenylphosphine as a ligand under mild conditions might lead to reaction with molecular nitrogen.

During a study of bis-arenemolybdenum chemistry we have found that treatment with allyl chloride causes smooth addition and the purple binuclear complexes $[PhR^2Mo(\pi-C_3H_5)Cl]_2$ (II; $R^2 = H$ or Me) have been isolated in high yields. The structure of the complex (II; $R^2 = H$) (see Scheme) has been established by X-ray diffraction studies.³

Treatment of the complexes (II) with tertiary phosphine ligands causes cleavage of the chloro-bridge and the purple mononuclear complexes $PhR^2Mo(\pi-C_3H_5)(PR_3)_2Cl$ (III; $R^2 = H$ or Me) are formed when $R_3^1 = Me_2Ph$, $MePh_2$, or Ph_3 . Reduction of ethanol solutions of the complexes (III; $R_3^1 = Me_2Ph$ or $MePh_2$) with sodium borohydride in the presence of excess of the phosphine causes formation of the corresponding triphosphine complexes (I). However, when $R^2 = H$ or Me and R_3^1P is triphenylphosphine, reduction

with sodium borohydride under hydrogen or argon produces the red dihydrides $PhR^2Mo(PPh_3)_2H_2$ (IV). {(IV; $R^2 = Me$) 1H n.m.r. (C_6D_6) τ 3.13 (m, 30H, 6Ph), 6.20 (m, 5H,



SCHEME

C_6H_5), 8.49 (s, 3H, CH_3), 14.35 [t, 2H, J (H_2 , ^{31}P) 50.2 Hz, MoH_2]; ν (Mo-H) (mull) 1740s, 1720sh cm^{-1} . (IV; $R^2 = H$) ν (Mo-H) (mull) 1730s, 1775w cm^{-1}). The 1H n.m.r.

spectrum of (IV; $R^2 = \text{Me}$) is consistent with either a *trans*-configuration, or, if it is a fluxional molecule, with a *cis*- or a *trans*-configuration.

The dihydride (IV; $R^2 = \text{H}$) in benzene reacts readily with nitrogen gas at room temperature and one atmosphere pressure forming a binuclear, maroon dinitrogen complex $[\text{C}_6\text{H}_6\text{Mo}(\text{PPh}_3)_2]_2\text{N}_2$ (V) in essentially quantitative yields. The reaction is reversible and treatment of (V) with hydrogen gas reforms (IV; $R^2 = \text{H}$). The complex

(V) does not show an absorption near 2000 cm^{-1} in the i.r. spectrum. However, the Raman spectrum of the solid shows a very intense band at $1910 \pm 5\text{ cm}^{-1}$ assignable to a symmetric $\text{N}\equiv\text{N}$ stretching frequency.

All the above complexes have been characterised by analysis, i.r. and, for the sufficiently soluble, ^1H n.m.r. spectra.

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¹ M. L. H. Green, L. C. Mitchard, and W. E. Silverthorn, to be published.

² M. Hidai, K. Tominari, Y. Uchida, and A. Misono, *Chem. Comm.*, 1969, 814 and 1392.

³ T. S. Cameron, C. K. Prout, and G. V. Rees, personal communication.