Journal of Organometallic Chemistry, 233 (1982) C4—C6
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

SYNTHESIS OF BIS(η-PENTAMETHYLCYCLOPENTADIENYL)-DIMETHYLMOLYBDENUM USING MOLYBDENUM ATOMS

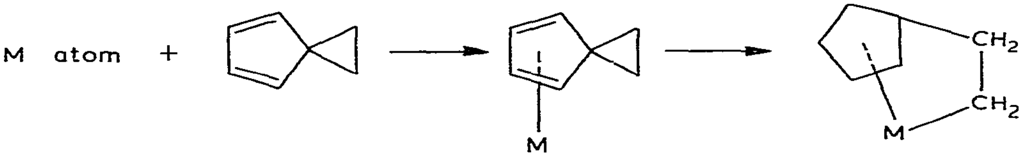
JENNIFER C. GREEN, MALCOLM L.H. GREEN and CHRISTOPHER P. MORLEY
Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR (Great Britain)
(Received April 5th, 1982)

Summary

Co-condensation of hexamethylcyclopentadiene with molybdenum atoms forms bis(η-pentamethylcyclopentadienyl)dimethylmolybdenum via a carbon—carbon bond addition reaction to the metal. The dimethyl compound is readily oxidised to the paramagnetic cation $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5Me_5})_2\mathrm{Me_2}]^+$.

η-Pentamethylcyclopentadienyl-transition metal compounds are currently of considerable interest since the electron releasing property of the C_5Me_5 ligand causes the metal centre to be electron-rich and hence reactive, for example, towards dinitrogen [1]; also the steric bulk of the ligand helps to stabilise the derivatives, for example, by inhibiting bimolecular decomposition pathways. For these reasons many interesting derivatives of pentamethylcyclopentadienyl-transition metal compounds have been prepared and studied [2].

Recently we showed that co-condensation of spiro-hepta-2,2-diene with molybdenum atoms forms the bis-alkyl derivative $[\overline{\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_4CH_2C}}\mathrm{H_2})_2]$ [3] and it is to be presumed that the reaction involves oxidative addition to the metal of a C—C bond of an initially coordinated spiro-hepta-2,2-diene ligand [4]. This is illustrated in the partial reaction scheme:



In order to explore the generality of this carbon—carbon bond addition reaction and in part to find useful routes to derivatives of the little studied bis(η-pentamethylcyclopentadienyl)molybdenum system $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5Me_5})_2]$ we have

0022-328X/82/0000—0000/$02.75

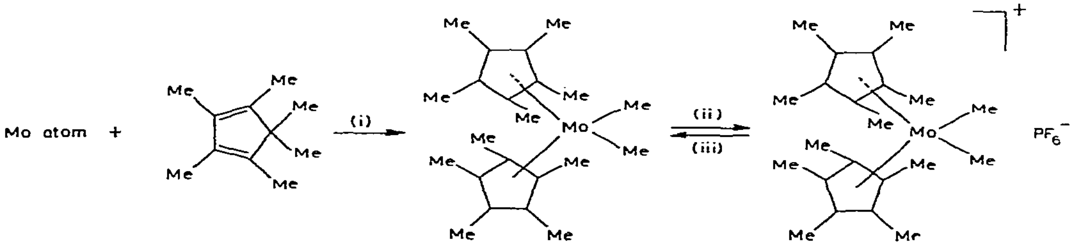
investigated the reaction between hexamethylcyclopentadiene and molybdenum atoms. The compounds $[Mo(\eta\text{-}C_5Me_5)_2X_2]$ (X = H, Cl) and $[Mo(\eta\text{-}C_5Me_5)_2CO]$ have been described previously [5].

Co-condensation of molybdenum atoms with hexamethylcyclopentadiene followed by chromatography of the less volatile products gave yellow-brown crystals of $[Mo(\eta\text{-}C_5Me_5)_2Me_2]$ (I). The yield based on the molybdenum arriving at the co-condensate wall was ca. 10%. The excess of hexamethylcyclopentadiene was largely recovered (80%) by distillation from the reaction mixture so that the yield of I based on consumed Me_6C_5 was 6—7%. In a typical experiment 8.0 g of molybdenum atoms, generated from a water-cooled hearth operating at a positive potential, were co-condensed with excess (110 cm^3) of hexamethylcyclopentadiene giving 3.25 g of I. The apparatus used for the synthesis has been described in detail elsewhere [6].

Compound I is air-sensitive, soluble in the common organic solvents and it can be sublimed at 80°C and ca. 10^{-2} torr. (Microanalysis. Found: C, 66.5; H, 8.9%. $C_{22}H_{36}Mo$ calcd.: C, 66.7; H, 9.1%. Mass spectrum: Parent ion peak at 396 for ^{96}Mo isotope. ^{1}H NMR data (C_6D_6) 8.48,s,*30*,C_5Me_5;10.63,s,*6*,$MoMe_2$.) The photoelectron spectrum of I shows a first ionisation band at 5.41 eV. assignable to ionisation from the essentially d^2 metal electrons. This low ionisation potential classifies the metal centre as being unusually electron rich.

As would be expected for such an electron rich compound it is readily oxidised. Treatment of I with iodine followed by addition of aqueous ammonium hexafluorophosphate gives the 17-electron cation $[Mo(\eta\text{-}C_5Me_5)_2Me_2]PF_6$ (II) isolated as purple-pink crystals of the hexafluorophosphate salt. (Found: C, 48.6; H, 6.51%. $C_{22}H_{36}F_6MoP$ calcd.: C, 48.8; H, 6.7%. ESR spectrum (acetone) band centres at 2.0135, no hyperfine structure observed.) Air oxidation of solutions of I also gives the cation II. Treatment of I with aqueous tetrafluoroboric acid forms II in high yield and does not cause cleavage of the molybdenum-methyl groups from the metal. Also, treatment of I with hydrogen chloride gas gives the cation II together with an unidentified insoluble yellow solid. When II was treated with deuterium chloride gas the volatile products were shown to contain some CH_3D indicating that some cleavage of the metal—carbon bond of I had occurred.

Reduction of II with sodium amalgam reforms I. Similarly, II reacts with aqueous potassium hydroxide giving I. The latter reaction presumably proceeds via disproportionation in a manner analogous to the reaction between $[Mo(\eta\text{-}C_6H_6)_2]^+$ and aqueous potassium hydroxide which gives the neutral $[Mo(\eta\text{-}C_6H_6)_2]$ [7].



SCHEME 1. (i) Co-condense at −195°C. (ii) I_2 or O_2 or aqueous H^+: then NH_4PF_6 aq. (iii) Na/Hg in tetrahydrofuran or KOH in acetone.

The reactions and proposed structures for I and II are shown in Scheme 1. The synthesis of I is a relatively rare example of carbon—carbon bond addition to a transition metal centre and emphasises that such reactions are not restricted to spiro-diene systems.

The reaction of I with aqueous acid giving II rather than forming the hydride cation $[Mo(\eta\text{-}C_5Me_5)_2Me_2H]BF_4$, or cleaving methane from the metal, is unexpected. Presumably, the available d^2 lone-pair of I is protonated and the intermediate hydride cation then undergoes a rapid homolytic cleavage of the Mo—hydrogen bond. The reaction is analogous to the oxidation of $[Mo(\eta\text{-}C_6H_6)_2]$ to $[Mo(\eta\text{-}C_6H_6)_2]^+$ by proton acids [7].

Acknowledgements. We thank the Petroleum Research Fund administered by the American Chemical Society for partial support and the Climax Molybdenum Company for a generous gift of chemicals.

References

1 J.M. Manriques and J.E. Bercaw, J. Am. Chem. Soc., 96 (1974) 6229.
2 P.J. Wolczanski and J.E. Bercaw, Acc. Chem. Res., 13 (1980) 121; P.M. Maitlis, Acc. Chem. Res., 11 (1978) 301.
3 A. Barretta, F.G.N. Cloke, A. Feigenbaum, and M.L.H. Green, J. Chem. Soc. Chem. Commun., (1981) 156.
4 P. Eilbracht and P. Dahler, Chem. Ber., 113 (1980) 542.
5 J.L. Thomas, J. Am. Chem. Soc., 95 (1973) 1838.
6 F.G.N. Cloke and M.L.H. Green, J. Chem. Soc. Dalton Trans., (1981) 1938.
7 E.O. Fischer, F. Scherer and H.O. Stahl, Chem. Ber., 93 (1960) 2065.