η-Benzene(η-cyclopentadienyl)molybdenum Chemistry

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Summary An improved synthesis of the compound $[(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)Mo]$ is described and the new 'bent' sandwich compounds $[(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)MoX]$ (X = Me, H, Cl or I) and $[(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)MoL]^+PF_6^-$ ($L = C_2H_4$, C_2H_2, or PPh_3) are reported.

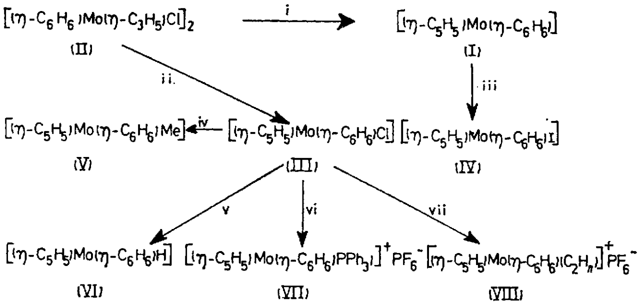
BIS-η-ARENEMOLYBDENUM and bis-η-cyclopentadienylmolybdenum compounds show extensive but very different chemistries.[1,2] We were, therefore, interested to explore the chemistry of the mixed η-benzene-η-cyclopentadienylmolybdenum system. The 17-electron compound $[(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)Mo]$ (I) has been previously described[3,4] but could be prepared only in inconveniently small yields so that it was not usefully available for further study.

The dimer $[(\eta\text{-}C_6H_6)Mo(\eta\text{-}C_3H_5)Cl]_2$ (II) is known to be capable of dehydrogenating straight-chain olefins in the presence of $EtAlCl_2$ dimer,[5] and we have now synthesized (I) in high yield by application of this method to a cyclic mono-olefin. Thus the reaction of (II) with cyclopentene during 2 h at 20 °C in the presence of $EtAlCl_2$ gave a brown oil which could be converted into (I) (*ca.* 65%) by hydrolytic reduction using alkaline sodium dithionite at −40 °C. Alternatively, the new 'bent', mixed-sandwich, 18-electron compound $[(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)MoCl]$ (III) may be prepared in *ca.* 85% yield by treatment of the brown oil with LiCl in MeOH. The corresponding iodo-complex $[(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)MoI]$ (IV) was obtained essentially quantitatively by reaction of (I) in light petroleum with iodine. Both (III) and (IV) form purple, air-sensitive crystals.

The new compounds $[(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)MoMe]$ (V) and $[(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)MoH]$ (VI) may be prepared in good yield by treatment of (III) with MeMgBr or $NaBH_4$ respectively. They are red, air-sensitive compounds which sublime with decomposition *in vacuo* at 80—90 °C [$\tau(C_6D_6)$; (V): 5·35 (5H, s, $\eta\text{-}C_5H_5$), 6·14 (6H, s, $\eta\text{-}C_6H_6$), and 9·64 (3H, s, Me); (VI): 5·35 (5H, s, $\eta\text{-}C_5H_5$), 5·85 (6H, s, $\eta\text{-}C_6H_6$), and 11·77 (1H, s, Mo-H)].

As would be expected by analogy with bis-η-cyclopentadienylmolybdenum compounds the red crystalline cationic derivatives $[(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)MoL]^+PF_6^-$ where L = Ph_3P (VII), ethylene or acetylene (VIII) are formed from (III) by treatment with the appropriate ligand L in the presence of $TlPF_6$ in Me_2CO. In contrast to the non-labile ethylene compound $[(\eta\text{-}C_5H_5)_2Mo(\eta\text{-}C_2H_4)]$[2,6] the ethylene ligand in (VIII) is readily replaced by a donor solvent such as Me_2CO in the absence of excess of ethylene.

Details of the above reactions are given in the Scheme; it is clear that this 'bent' mixed sandwich system has an extensive chemistry of obvious synthetic potential.



SCHEME. *Reagents:* i, $EtAlCl_2$ in C_6H_6 and excess of cyclopentene, 20 °C, 2 h; then $Na_2S_2O_4$ in 30% aq. KOH at −40 °C; ii, $EtAlCl_2$ in C_6H_6 and cyclopentene, 20 °C, 2 h; then LiCl in MeOH at −50 °C; iii, Stoicheiometric I_2 in pentane, 20 °C, 10 min, >90%; iv, MeMgBr in $Et_2O\text{–}C_6H_6$, 20 °C 30 min; v, $NaBH_4$ in tetrahydrofuran, 20 °C, 2·5 h; vi, excess of PPh_3 and stoicheiometric $TlPF_6$ in Me_2CO, 20 °C, 30 min; vii, Stoicheiometric $TlPF_6$ in acetone under C_2H_4 or C_2H_2, 20 °C, 30 min, $n = 2$ or 4.

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