

Preliminary communication

SYNTHESIS AND DEPROTONATION OF THE CYCLOHEPTATRIENYL-MOLYBDENUM VINYLIDENE COMPLEX



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Summary

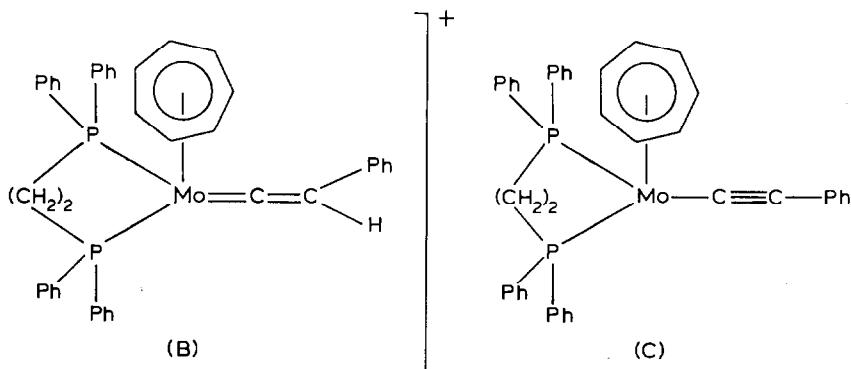
Reaction of the terminal alkyne $\text{PhC}\equiv\text{CH}$ with $[\text{Mo}(\text{NCMe})(\text{dppe})(\eta^7\text{-C}_7\text{H}_7)] [\text{PF}_6]$ ($\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) in refluxing acetone yields the cationic phenylvinylidene complex $[\text{Mo}(\text{C}=\text{CHPh})(\text{dppe})(\eta^7\text{-C}_7\text{H}_7)] [\text{PF}_6]$, which is readily deprotonated to give the η^1 -alkynyl complex $[\text{Mo}(\eta^1\text{-C}\equiv\text{CPh})(\text{dppe})(\eta^7\text{-C}_7\text{H}_7)]$.

Considerable recent interest has centred on the rearrangement of a 1-alkyne to a vinylidene at a metal d^6 centre. This process, which appears to be most prevalent in phosphine substituted complexes, is involved in the formation of *mer*- $[\text{W}(\text{C}=\text{CHPh})(\text{CO})_3(\text{dppe})]$ [1], *trans*- $[\text{ReCl}(\text{C}=\text{CHPh})(\text{dppe})_2]$ [2] and $[\text{Ru}(\text{C}=\text{CHPh})(\text{dppe})\text{Cp}] [\text{PF}_6]$ [3]. As part of our studies into the chemistry of cycloheptatrienyl complexes of the Group VIA metals we now show that such a rearrangement occurs in the reaction of phenylacetylene with the Mo^0 - d^6 -site in $[\text{Mo}(\text{NCMe})(\text{dppe})(\eta^7\text{-C}_7\text{H}_7)] [\text{PF}_6]$ (A) [4].

Prolonged reaction of complex A with $\text{PhC}\equiv\text{CH}$ in refluxing acetone leads to displacement of the acetonitrile ligand and formation of the orange-red, cationic phenylvinylidene complex $[\text{Mo}(\text{C}=\text{CHPh})(\text{dppe})(\eta^7\text{-C}_7\text{H}_7)] [\text{PF}_6]$ (B). Infrared and NMR data* for B ($\nu(\text{C}=\text{C})$ 1585(m), 1560(w) cm^{-1} ; ^1H NMR ($[\text{C}_6\text{H}_6]$ acetone), $\text{C}=\text{CHPh}$, δ 5.57 ppm, t; ^{13}C NMR (CD_3NO_2), $\text{C}\alpha$, 373.6 ppm, t, $J(\text{P}-\text{C})$ 32 Hz, $\text{C}\beta$, 120.1 ppm, t, C_7H_7 93.2 ppm, s) are fully consistent with its formulation as a mononuclear vinylidene complex. Deprotonation of B occurs on treatment with 1,8-bis(dimethylamino)naphthalene to give the

* ^{13}C NMR spectrum recorded at 75 MHz. Satisfactory microanalytical data were obtained for all new complexes.

neutral, purple-brown, η^1 -alkynyl complex $[\text{Mo}(\eta^1\text{-C}\equiv\text{CPh})(\text{dppe})(\eta^7\text{-C}_7\text{H}_7)]$ (C) which is identified by the observation of a molecular ion ($m/z = 688$) in the mass spectrum and a strong $\nu(\text{C}\equiv\text{C})$ at 2025 cm^{-1} in the infrared spectrum.



The isolation of complexes B and C represents a significant advance in the chemistry of the cycloheptatrienylmolybdenum system and an investigation into the structure and reactivity of these compounds is in progress. Such studies should permit interesting comparisons to be made with the extensive chemistry of the analogous complexes $[\text{Ru}(\text{C}=\text{CHPh})(\text{PPh}_3)_2\text{Cp}][\text{PF}_6]$ and $[\text{Ru}(\eta^1\text{-C}\equiv\text{CPh})(\text{PPh}_3)_2\text{Cp}]$ [3,5].

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