A Versatile Synthesis of Cyclic Molybdenum- and Tungsten-Carbon σ-Bonded Complexes

By K. P. Wainwright and S. B. Wild*

(*Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, Western Australia*)

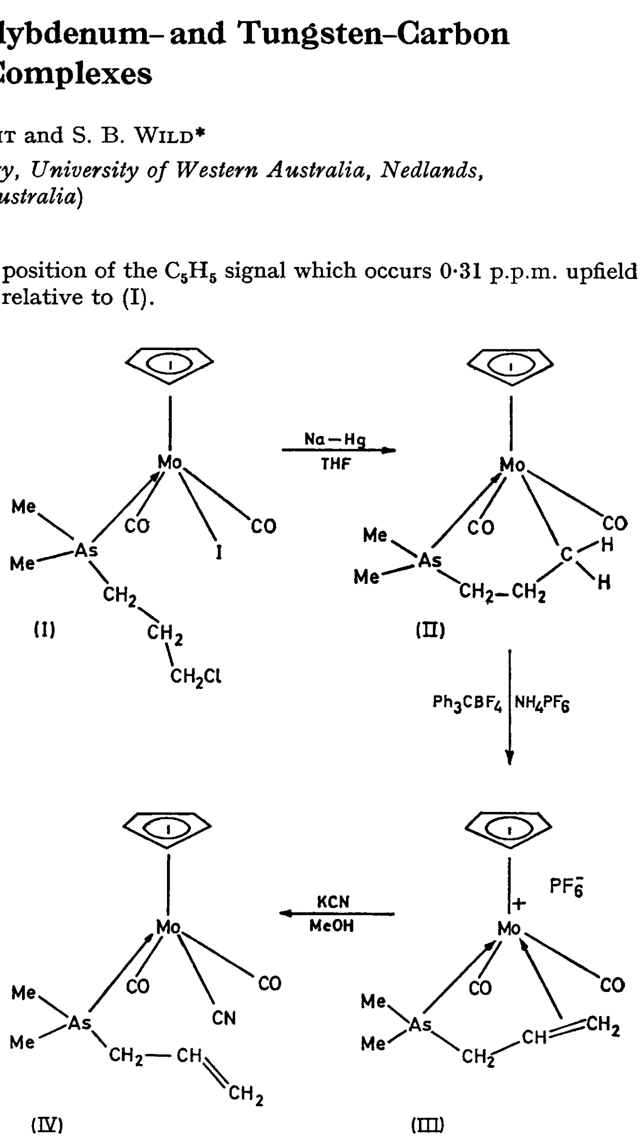
Summary A simple dehalogenation takes place when dicarbonyl-(3-chloropropyldimethylarsine)-η-cyclopentadienyliodomolybdenum(II) is treated in tetrahydrofuran with sodium amalgam; the cyclic Mo–C compound so formed undergoes an hydride elimination reaction to give a cationic derivative of chelated allyldimethylarsine.

Cyclic compounds containing a metal–carbon σ-bond provide a means of stabilising alkyl intermediates considered important in the reduction of olefins by transition metal complexes. An insertion reaction occurs when tertiary phosphines bearing an unsaturated moiety react with metal hydrides[1] giving cyclic metal–carbon compounds derived from either Markownikoff or anti-Markownikoff addition depending on the metal employed.[2]

We have found a convenient method for the preparation of chelate metal–carbon σ-bonded complexes, which involves the reduction of a suitably substituted metal carbonyl halide with sodium amalgam.

Thus, treatment of $(\eta\text{-}C_5H_5)Mo(CO)_3I$ with $Me_2As[CH_2]_3Cl$[3] for 12 h in benzene at reflux gave (I) as purple prisms m.p. 85—86° (94%) after chromatography on alumina. A *cis* structure is clearly indicated for (I) by its ^1H n.m.r. spectrum (60 MHz) which shows the two signals expected for diastereotopic magnetic non-equivalence of the two methyl groups. Additional support for the *cis* formulation of (I) is found in the i.r. spectrum where ν_{CO} is at 1960s and 1860m cm^{-1} (benzene) show the intensity variation accepted for *cis*-compounds of this type.[4]

Cyclisation was achieved in a few minutes by reduction of (I) with a three-fold excess of sodium amalgam in tetrahydrofuran as solvent giving (II) as air-stable yellow needles (96%) m.p. 107—108° after sublimation (80°/0·1 mm) and recrystallisation from benzene. Compound (II) shows ν_{CO} at 1940s and 1860m cm^{-1} (n-heptane). Evidence of cyclisation is observed in its n.m.r. spectrum by the loss of the resonance due to the $-CH_2Cl$ protons and by the position of the C_5H_5 signal which occurs 0·31 p.p.m. upfield relative to (I).



Trityl fluoroborate abstracts a hydride ion from (II) to give the cationic species (III). The hexafluorophosphate salt of (III) shows a weak band at 1525 cm^{-1} attributed to a co-ordinated olefinic bond.[5] In addition, a cationic molybdenum species is indicated by the i.r. spectrum in the ν_{CO} region where bands occur at 2015m and 1930s (Nujol), approximately 80 cm^{-1} to higher frequencies than those found in the neutral starting material. The allyl resonances in the ^{1}H n.m.r. spectrum of (III) are similar to those found in (IV) but shifted downfield due to formation of the salt.

Reaction of (III) with a methanol solution of potassium cyanide did not lead to addition to the co-ordinated double bond, but resulted in displacement of the unsaturated residue giving (IV) in small yield together with extensive decomposition. The presence of an unco-ordinated double bond in (IV) was confirmed by comparison with the iodo-analogue prepared by direct substitution of $(\eta\text{-}C_5H_5)Mo(CO)_3I$ with allyldimethylarsine. Both (IV) and its iodo-analogue show clearly $\nu_{C=C}$ at *ca.* 1625 cm^{-1} characteristic of an unco-ordinated double bond. The downfield shift of the resonance of the C_5H_5 protons in the n.m.r. spectrum of (IV) relative to the same resonance in (II) indicates decreased shielding of the cyclopentadienyl protons due to direct attachment of the cyanide group in the metal atom. The *cis* geometry of (IV) is indicated by the i.r. spectrum in the ν_{CO} region [($CHCl_3$) 1975s, 1890m cm^{-1}]. The n.m.r. spectrum which shows a sharp singlet methyl resonance at δ 1·51 p.p.m. is consistent with this formulation owing to the reduced chirality of the molecule, resulting from the structural similarity of the adjacent carbonyl and cyano groups. Accordingly, the chemical shift difference between the diastereotopic methyl groups in (IV) is expected to be small or negligible, as found in this case.

Tungsten forms analogues of (I) and (II) under similar reaction conditions and the extent to which this cyclisation reaction applies to other metals is also under investigation.

All neutral compounds show molecular ion peaks in their mass spectra. Satisfactory elemental analyses have been obtained in all cases.

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