

Hydride to Carbene Migration at Molybdenum; the Isomerisation of $\text{Mo(H)}\{\text{=C}[\text{CH}_2]_3\text{NMe}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ to $\text{Mo}(\text{CO})_2\{\eta^2\text{-CH}[\text{CH}_2]_3\text{NMe}\}(\eta\text{-C}_5\text{H}_5)$

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Treatment of the anion $[\text{Mo}\{\text{=C}[\text{CH}_2]_3\text{NMe}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]^-$ with acid leads to the hydrido molybdenum carbene $\text{Mo(H)}\{\text{=C}[\text{CH}_2]_3\text{NMe}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ which isomerises by a hydride to carbene migration process resulting in $\text{Mo}(\text{CO})_2\{\eta^2\text{-CH}[\text{CH}_2]_3\text{NMe}\}(\eta\text{-C}_5\text{H}_5)$.

Reactions which involve migration of hydride to carbene ligands are important in that they constitute C-H bond formations, represent fundamental processes for carbene ligands, are the reverse of α -elimination, and may be involved in some catalytic systems.¹ However, well defined direct observations of hydride to carbene migrations are apparently very rare, but known for at least zirconium² and iron.³ Recent calculations suggest that hydride to carbene migration in, for instance, the hypothetical $\text{Mn(H)}(\text{=CH}_2)(\text{CO})_4$ would be very facile.⁴ There are also some examples of inferred migrations.⁵ We report here an unambiguous example of a hydride to carbene migration at molybdenum.

Protonation of the carbene anion⁶ $[\text{Mo}\{\text{=C}[\text{CH}_2]_3\text{NMe}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]^-$ (**1**) with acetic acid leads to the hydrido molybdenum carbene $\text{Mo(H)}\{\text{=C}[\text{CH}_2]_3\text{NMe}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ (**2**)[†] isolated as an air sensitive pale yellow solid. The ¹H n.m.r. spectra are consistent with the existence of (**2**) as a rapidly interconverting mixture of *cis*-(**2c**) and *trans*-(**2t**) isomers in a fashion reminiscent of geometrically related $\text{Mo(H)}(\text{PR}_3)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ complexes.⁷ Thus, the

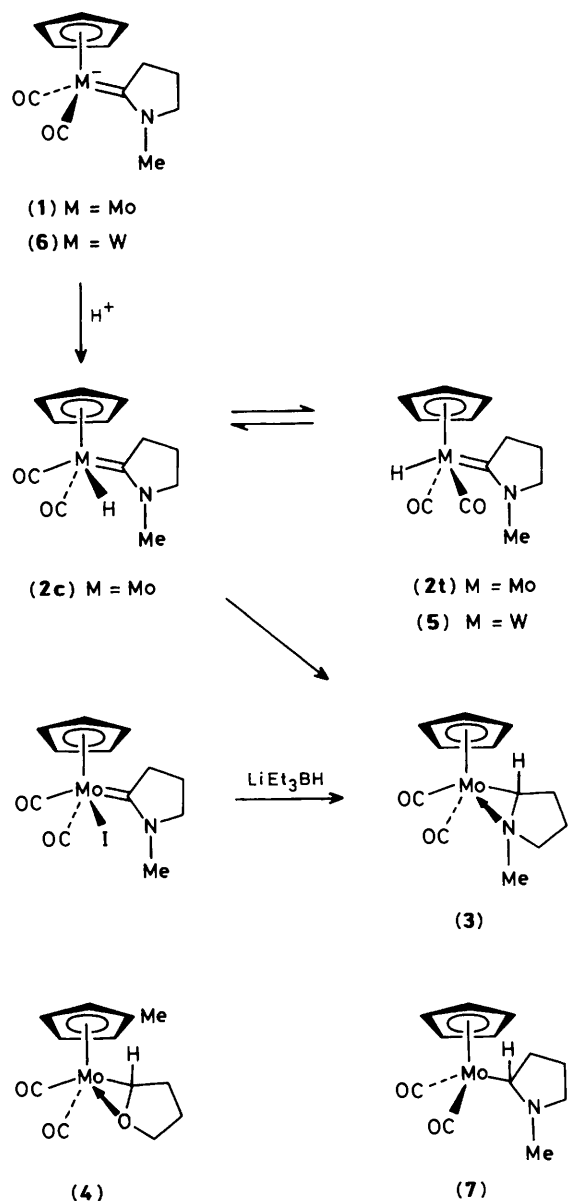
¹H n.m.r. spectrum of (**2**) in [²H₈]toluene at -50 °C shows biased pairs of singlets assigned to the cyclopentadienyl, methyl, and hydride groups for the *cis* and *trans* isomers. The *trans* isomer is predominant; integration of signals in the ¹H n.m.r. spectrum puts the proportion (**2t**):(**2c**) as 88:12 at -50 °C in toluene. The ¹H n.m.r. spectrum is temperature dependent and the coalescence temperature for the cyclopentadienyl signals is very close to ambient temperature. The temperature dependence is attributed to the interconversion of (**2c**) and (**2t**). The i.r. spectrum is also clearly consistent with a mixture of *cis* and *trans* dicarbonyls with the *trans* component predominant.

The hydride (**2**) rearranges in tetrahydrofuran solution at ambient temperature to the fully spectroscopically characterised complex $\text{Mo}(\text{CO})_2\{\eta^2\text{-CH}[\text{CH}_2]_3\text{NMe}\}(\eta\text{-C}_5\text{H}_5)$ (**3**).⁸ The rearrangement is conveniently followed by Fourier transform i.r. spectroscopy. Initial results show that the isomerisation follows first order kinetics; the rearrangement of (**2**) to (**3**) at 31 °C proceeds with a half life of ca. 10 h, indicating a unimolecular process.

We have previously made complex (**3**)⁸ by the reaction of $\text{MoI}\{\text{=C}[\text{CH}_2]_3\text{NMe}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ with LiEt_3BH (Scheme 1). In that synthesis we have no reason to suppose that the reaction proceeds *via* the intermediacy of (**2**). The spectroscopic properties of (**3**) are closely related to those of the crystallographically characterised $\text{Mo}(\text{CO})_2\{\eta^2\text{-CH}[\text{CH}_2]_3\text{O}\}(\eta\text{-C}_5\text{H}_4\text{Me})$ (**4**)⁹ so there is little doubt concerning its structure.

Complex (**5**), the tungsten analogue of (**2**), is similarly formed by acidification of a solution of $[\text{W}\{\text{=C}[\text{CH}_2]_3\text{NMe}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]^-$, (**6**)⁶ but only the *trans* isomer is apparent in its i.r. and n.m.r. spectra and we have yet

[†] $\text{Mo(H)}\{\text{=C}[\text{CH}_2]_3\text{NMe}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ (**2**): mass (chemical ionisation, NH_3) m/z 302 [$(M + 1)^+$]; $\nu(\text{CO})$ 1944m, 1936m, 1868s cm^{-1} (hexane); ¹H n.m.r., δ ($\text{C}_6\text{D}_5\text{CD}_3$, -50 °C), (**2t**), 4.90 (s, 5H, C_5H_5), 3.07 (s, 3H, Me), 2.28 (m, 4H, 2CH₂), 0.73 (m, 2H, central CH₂), and -5.31 (s, 1 H, Mo-H); (**2c**), 5.05 (s, 5H, C_5H_5), 2.72 (s, 3H, Me), -5.09 (s, 1 H, Mo-H), ring signals not unambiguously identified owing to lack of symmetry, overlaps, and signal-to-noise problems; ¹³C n.m.r. δ ($\text{C}_6\text{D}_5\text{CD}_3$, -50 °C), (**2t**), 260.5 (Mo=C), 233.5 (2CO), 90.2 (C_5H_5), 59.2 (CH₂), 53.8 (CH₂), 40.4(Me), 20.7 (central CH₂); (**2c**), 266.0 (Mo=C), 92.1 (C_5H_5), 59.0 (CH₂), 53.9 (CH₂), 40.9(Me), and 21.2 (central CH₂), two expected Mo-CO signals not seen as a consequence of inadequate signal-to-noise ratio.



Scheme 1

to observe any hydride to carbene migration involving the tungsten system.

We regard the transformation of (2) to (3) as a hydride to carbene migration. It is highly likely that this proceeds from the *cis*-(2c) rather than the *trans*-(2t) isomer. We are not yet able to say whether the 16-electron species (7) (probably solvent stabilised) is intermediate, but during, or after, migration the nitrogen atom does bind to the molybdenum atom. This has the effect of producing an 18-electron count in the final product (3).

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