

Preliminary communication

Hydride to carbene migration in the
 $\text{CpMH}\{\text{=C}(\text{NHEt})\text{Ph}\}(\text{CO})_2$ ($\text{M} = \text{Mo}, \text{W}$) system.
 X-Ray crystal structure of $\text{CpMo}\{\eta^2\text{-CH}(\text{Ph})\text{NHEt}\}(\text{CO})_2$

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Abstract

Addition of acetic acid to solutions of the anions $[\text{CpM}\{\text{=C}(\text{NHEt})\text{Ph}\}(\text{CO})_2]^-$ ($\text{M} = \text{Mo}$ or W) affords the hydrido metal carbene complexes $\text{CpMH}\{\text{=C}(\text{NHEt})\text{Ph}\}(\text{CO})_2$ as a mixture of *cis* and *trans* isomers. The molybdenum complex isomerizes rapidly to form fluxional $\text{CpMo}\{\eta^2\text{-CH}(\text{Ph})\text{NHEt}\}(\text{CO})_2$ which has been characterized by X-ray crystallography. The corresponding tungsten complex isomerizes more slowly. The simplest rationalization for these isomerizations involves a 1,2 hydride to carbene migration by the hydrides $\text{CpMH}\{\text{=C}(\text{NHEt})\text{Ph}\}(\text{CO})_2$ in forming $\text{CpM}\{\eta^2\text{-CH}(\text{Ph})\text{NHEt}\}(\text{CO})_2$.

Migrations of hydride to carbene or alkylidene [1,2] are important in the context of C–H bond forming reactions and in the sense that they represent the reverse of α -elimination [3]. They are also directly observed comparatively rarely. We recently reported a directly observable hydride to carbene migration involving the cyclic carbene complex $\text{CpMoH}\{\text{=C}(\text{CH}_2)_3\text{NMe}\}(\text{CO})_2$ (1) which gives $\text{CpMo}\{\text{CO}\}_2\{\eta^2\text{-CH}(\text{CH}_2)_3\text{NMe}\}$ (2) [2]. However, the analogous tungsten complex $\text{CpWH}\{\text{=C}(\text{CH}_2)_3\text{NMe}\}(\text{CO})_2$ [2] shows no sign of any such migration at ambient temperature. The synthetic strategy leading to the hydride $\text{CpMoH}\{\text{=C}(\text{CH}_2)_3\text{NMe}\}(\text{CO})_2$ (1) is based on the protonation of the anionic carbene complex $[\text{CpMo}\{\text{=C}(\text{CH}_2)_3\text{NMe}\}(\text{CO})_2]^-$, itself available by $\text{NaC}_{10}\text{H}_8$ reduction of $\text{CpMoI}\{\text{=C}(\text{CH}_2)_3\text{NMe}\}(\text{CO})_2$ [4]. We report here that related isomerizations involving the acyclic carbene ligands $\text{=C}(\text{NHEt})\text{Ph}$ proceed at *both* molybdenum and tungsten, and further report the X-ray crystal structure of the product arising in the molybdenum reaction.



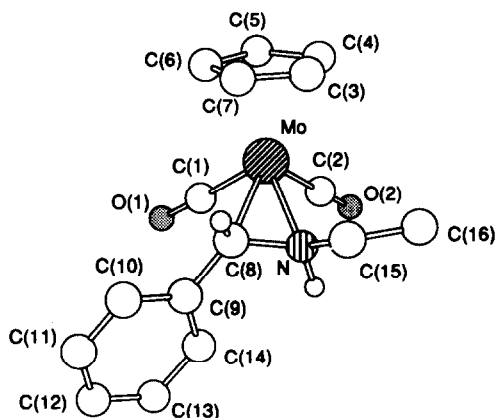
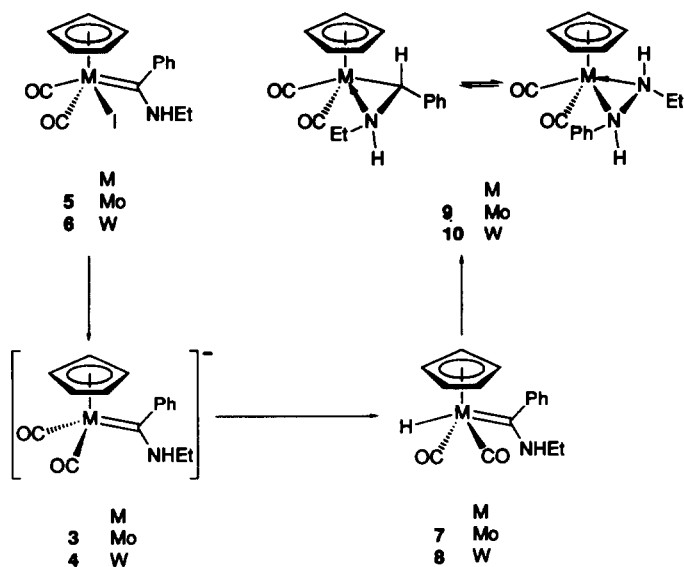


Fig. 1. Molecular structure of $\text{CpMo}(\eta^2\text{-CH(Ph)NHEt})(\text{CO})_2$ (**10**). Mo–C(1) 1.922(3), Mo–C(2) 1.953(3), Mo–N 2.189(3), Mo–C(8) 2.207(3), C(8)–N 1.427(4), C(8)–C(9) 1.479(5) Å. N–Mo–C(1) 104.5(1), C(2)–Mo–C(8) 115.0(1), C(1)–Mo–C(2) 76.5(1), N–Mo–C(2) 88.7(1), N–Mo–C(8) 37.9(1), C(1)–Mo–C(8) 84.3(1)°.

The anions $[\text{CpM}(\text{C}(\text{NHEt})\text{Ph})(\text{CO})_2]^-$ (**3** and **4**) are available through the reduction by $\text{NaC}_{10}\text{H}_8$ of the corresponding iodo metal carbene derivatives $\text{CpMI}(\text{C}(\text{NHEt})\text{Ph})(\text{CO})_2$ (**5** and **6**) [5]. Acidification of the anions **3** or **4** with MeCO_2H at -78°C in THF result in solutions containing the hydrides **7** or **8**. Addition of CHI_3 to solutions containing **7** or **8** cause the regeneration of the iodides **5** or **6**, typical behaviour of monometallic hydrides.

The tungsten complex is isolable as an air-sensitive oil $\text{CpWH}(\text{C}(\text{NHEt})\text{Ph})(\text{CO})_2$ (**8**).



Scheme 1.

Ph)(CO)₂ (**8**). The spectroscopic data for **8** * confirm that it exists as a mixture of one *cis* and two *trans* isomers. In particular, there are three hydride signals [¹H NMR δ (250 MHz, toluene-*d*₈, -50 °C): -5.14, -5.75, and -6.13] in the ratio 7 : 53 : 40. Prolonged stirring of a solution in THF of **8** affords the sensitive fluxional complex **9**. The ¹H NMR spectrum of **9** is temperature dependent within the range -80-+45 °C.

Complex **7** is not isolable since it isomerizes within a few minutes at ambient temperature to the fluxional dicarbonyl **10**. The spectroscopic properties of **10** ** are very closely related to those of **9**. The X-ray crystal structure of complex **10** ** is displayed in Fig. 1. The Ph and NHEt groups of the η²-EtNH-CHPh group are mutually *trans* with the Ph group *anti* with respect to the cyclopentadienyl ring.

* CpWH(=C(NHEt)Ph)(CO)₂ (**8**) exists as a mixture of one *cis* and two *trans* isomers, the two *trans* isomers evident at -50 °C are related by rotation about either the W=C or C-NHEt bonds: yield 51%; not obtained analytically pure. *Cis* component: IR ν(CO) (THF): 1917s, 1827s cm⁻¹; ¹H NMR δ (250 MHz, toluene-*d*₈, -50 °C, *J* in Hz): 7.16-6.68 (m, 6 H, Ph and NH), 4.72 (s, 5 H, Cp), 3.45-3.03 (m, 2 H, NHCH₂), 0.59 [t, 3 H, *J*(HH) 7, NHCH₂Me], -5.14 [s, 1 H, *J*(WH) 57, WH]. An inadequate signal-to-noise ratio prevents assignment of the ¹³C NMR spectrum of the *cis* component. *Trans* component: IR ν(CO) (THF): 1930m, 1849s cm⁻¹; ¹H NMR δ (250 MHz, toluene-*d*₈, -50 °C, *J* in Hz): 7.16-6.68 [m, 8 H, 2(Ph-*m* + *p*) with 2(NH)], 6.44 (m, 2 H, Ph-*o*), 6.35 (m, 2 H, Ph-*o*), 4.56 (s, 5 H, Cp), 4.54 (s, 5 H, Cp), 3.68 [quintet, 2 H, *J*(HH) 7, NHCH₂], 2.17 [quintet, 2 H, *J*(HH) 7, NHCH₂], 0.63 [t, 3 H, *J*(HH) 7, NHCH₂Me], 0.30 [t, 3 H, *J*(HH) 7, NHCH₂Me], -5.75 [s, 1 H, *J*(WH) 40, WH], -6.13 [s, 1 H, *J*(WH) 38, WH]; ¹³C NMR δ (62.9 MHz, toluene-*d*₈, -50 °C: 254.8 (W=C), 253.1 (W=C), 223.1 (CO), 222.2 (CO), 155.5 (Ph-*i*), 149.9 (Ph-*i*), 128.7-124.6 [m, 2(Ph-*m* + *p*) overlapped by solvent peaks], 123.3 (Ph-*o*), 122.2 (Ph-*o*), 90.3 (Cp), 90.1 (Cp), 46.1 (NHCH₂), 43.7 (NHCH₂), 15.7 (NHCH₂Me), 14.7 (NHCH₂Me).

** CpMo(η²-CH(Ph)-NHEt)(CO)₂ (**10**): Found: [*M*⁺], 353 (⁸⁶Mo); C, 54.71; H, 4.88; N, 3.99. C₁₆H₁₇MoNO₂ calc.: [*M*⁺], 353 (⁹⁸Mo); C, 54.56; H, 4.99; N, 3.77%. IR ν(CO) (Et₂O): 1927s, 1836s cm⁻¹. ¹H NMR δ (250 MHz, acetone-*d*₆, -80 °C, *J* in Hz): 7.28-6.85 [m, 10 H, 2(Ph)], 5.79 (s, br, 1 H, NH), 5.50 (s, 5 H, Cp), 5.23 (s, br, 1 H, NH), 4.99 (s, 5 H, Cp), 3.96 [d, 1 H, *J*(HH) 8.5, CH], 3.59 [d, 1 H, *J*(HH) 8.5, CH], 3.08 (m, 1 H, NHCH₂), 2.92-2.60 [m, 2 H, 2(NHCH₂)], 2.18 (m, 1 H, NHCH₂), 1.24 [t, 3 H, *J*(HH) 7, NHCH₂Me], 1.23 [t, 3 H, *J*(HH) 7, NHCH₂Me]. ¹³C NMR δ(62.9 MHz, acetone-*d*₆, -50 °C): 254.3 (CO), 252.5 (CO), 249.4 (CO), 246.4 (CO), 149.0 (Ph-*i*), 148.5 (Ph-*i*), 129.0 [(Ph-*o*) or (Ph-*m*)], 128.5 [(Ph-*o*) or (Ph-*m*)], 124.2 (Ph-*p*), 123.9 (Ph-*p*), 123.7 [(Ph-*o*) or (Ph-*m*)], 122.7 [(Ph-*o*) or (Ph-*m*)], 94.3 (Cp), 92.7 (Cp), 57.1 (NHCH₂), 55.7 (NHCH₂), 49.2 (CH), 44.5 (CH), 17.1 (NHCH₂Me), 16.5 (NHCH₂Me); two isomers seen at low temperature due to fluxionality of the metallaziride group [6].

Crystal data: *M* = 351.26. Crystallizes from Et₂O/pentane as orange plates; crystal dimensions 0.16 × 0.37 × 0.54 mm. Monoclinic, *a* = 10.172(4), *b* = 14.462(6), *c* = 10.283(4) Å, β = 94.24(3)°, *U* = 1508.7(10) Å³; *D*_c = 1.546 g cm⁻³, *Z* = 4. Space group *P*2₁/*n* (a non-standard setting of *P*2₁/*c* (*C*_{2h}, No. 14), *Mo-K*_α radiation (λ = 0.71069 Å), μ(*Mo-K*_α) = 8.48 cm⁻¹, *F*(000) = 711.74. Three-dimensional, room temperature X-ray data were collected in the range 3.5 < 2θ < 50° on a Nicolet R3 diffractometer by the ω-scan method. The 2206 independent reflections (of 2955 measured) for which |*F*|/σ(|*F*|) > 3.0 were corrected for Lorentz and polarisation effects, and for absorption by analysis of 10 azimuthal scans (minimum and maximum transmission coefficients 0.446 and 0.492). The structure was solved by conventional Patterson and Fourier techniques and refined by blocked cascade least squares methods. Hydrogen atoms were placed in calculated positions with isotropic thermal parameters related to those of the supporting atoms and refined in riding mode. Refinement converged at a final *R* 0.0242 (187 parameters; final minimum and maximum δ/σ 0.001 and 0.004) with allowance for the thermal anisotropy of all ordered non-hydrogen atoms. A final difference electron density map showed minima and maxima of -0.25 and +0.22 e Å⁻³. Tables of atom coordinates, bond lengths, and bond angles are available from the Cambridge Crystallographic Data Centre, Lensfield Road, Cambridge CB2 1EW, UK. Tables of thermal parameters and structure factors are available from the authors.

Given the solid state structure of **10**, and the published fluxional properties of related complexes such as $\text{CpMo}\{\eta^2\text{-C}(\text{C}_5\text{H}_4\text{N-}o\text{)-NHR}\}(\text{CO})_2$ {R = (*R*)-1-phenylethyl}, the fluxional behaviour of complexes **9** and **10** is probably that shown in Scheme 1.

The simplest rationalization for the formations of **9** and **10** from **7** and **8** in this fashion involve 1,2 hydride to carbene migrations within the hydrides **7** and **8**, respectively. These particular hydride migrations are much quicker than those involving the cyclic systems $\text{CpMoH}\{\text{=}\overline{\text{C}}(\text{CH}_2)_3\text{NMe}\}(\text{CO})_2$ (**1**) (several hours to complete) and $\text{CpWH}\{\text{=}\overline{\text{C}}(\text{CH}_2)_3\text{NMe}\}(\text{CO})_2$ (which we have yet to observe [2]).

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