Methyl and Benzyl C–H Activation through Carbene Insertion in $MR(CO)_2(carbene)(\eta\text{-}C_5H_5)$ (M = Mo or W; R = Me or $PhCH_2$)

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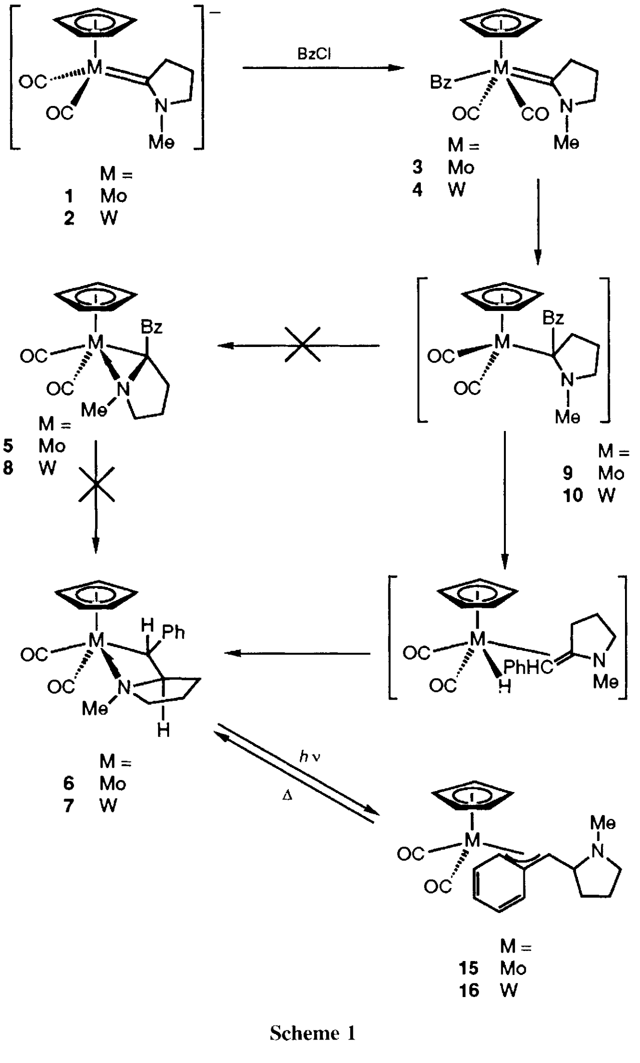
The anions $[M(CO)_2\{=C(CH_2)_3NMe\}(\eta\text{-}C_5H_5)]^-$ (M = Mo or W) react with BzCl (Bz = benzyl) to form the complexes $MBz(CO)_2\{=C(CH_2)_3NMe\}(\eta\text{-}C_5H_5)$, which isomerize into $M\{\eta^2\text{-}CHPhCH(CH_2)_3NMe\}(CO)_2(\eta\text{-}C_5H_5)$, while the corresponding reaction of MeI with $[Mo(CO)_2\{=C(NMe_2)Ph\}(\eta\text{-}C_5H_5)]^-$ produces $Mo(CO)_2\{\eta^2\text{-}CH_2CHPhNMe_2\}(\eta\text{-}C_5H_5)$; these reactions correspond to methyl and benzyl C–H activation through a net insertion of the carbene into the respective C–H bonds.

There is considerable interest in activation of alkyl C–H bonds,[1] and also in C–X bond formations that arise through migration of groups X (typically H or alkyl) from a metal to coordinated carbene.[2] Here, we report reaction sequences in which the migrations of alkyl groups to carbene enable C–H bond activations.

Previously, we reported hydride to carbene migration by the hydride $MoH(CO)_2\{=C(CH_2)_3NMe\}(\eta\text{-}C_5H_5)$ which gives $Mo\{\eta^2\text{-}CH(CH_2)_3NMe\}(CO)_2(\eta\text{-}C_5H_5)$.[3] The hydride is formed by protonation of the anion $[Mo(CO)_2\{=C(CH_2)_3NMe\}(\eta\text{-}C_5H_5)]^-$.[4] More recently, we reported migrations of benzoyl to carbene in which C–C bonds are formed as the complexes $M(COPh)(CO)_2\{=C(CH_2)_3NMe\}(\eta\text{-}C_5H_5)$ (M = Mo or W) rearrange into $M\{\eta^2\text{-}C(COPh)(CH_2)_3NMe\}(CO)_2(\eta\text{-}C_5H_5)$.[5]



Scheme 1

We, therefore, anticipated that reactions of the anion $[Mo(CO)_2\{=C(CH_2)_3NMe\}(\eta\text{-}C_5H_5)]^-$ and related anions with alkyl halides would result in related products arising through migration of alkyl to the coordinated carbene. These migrations certainly proceed but the overall sequence of reactions is more complex than we anticipated at the outset.

Additions of BzCl to solutions of the anions $[M(CO)_2\{=C(CH_2)_3NMe\}(\eta\text{-}C_5H_5)]^-$ **1** or **2** in thf (thf = tetrahydrofuran) at −80 °C results in solutions containing the expected η^1-benzyls $MBz(CO)_2\{=C(CH_2)_3NMe\}(\eta\text{-}C_5H_5)$ **3** and **4**. The tungsten compound **4** is isolable, provided workup is prompt, and is fully characterized. However, the molybdenum complex **3** rearranges too rapidly for isolation (see below) and is, therefore, only characterized by its IR spectrum [ν_{CO}/cm^{-1} (thf); 1926m and 1851s], which is very similar to that of its tungsten analogue **4** [ν_{CO}/cm^{-1} (thf); 1926m and 1840s].

By the time reaction solutions containing the η^1-benzyl **3** reach ambient temperature, two new carbonyl stretching bands [ν_{CO}/cm^{-1} (thf); 1925s and 1828s] replace those of **3**. This new complex does not have the expected structure **5**. Rather, it is $Mo\{\eta^2\text{-}CHPhCH(CH_2)_3NMe\}(CO)_2(\eta\text{-}C_5H_5)$, **6**, whose X-ray crystal structure is illustrated in Fig. 1.† The tungsten complex **4** undergoes a similar rearrangement to give **7** over a period of 7 h at ambient temperature. Complex **8** was not identified in the reaction mixture. The ^1H and ^{13}C NMR spectra of complexes **6** and **7** show that they exist as major and minor isomers in solution at ambient temperature. We assume, but of course it is not necessarily the case, that the major isomer corresponds to that found in the crystal structure.

There are at least two possible mechanisms for the formation of **6**. We favour an initial benzyl to carbene migration from the η^1-benzyl **3** to form the 16-electron (but probably solvent stabilized) η^1-complex **9**. The conversion of **9** into the complex **6** then proceeds by a β-elimination process

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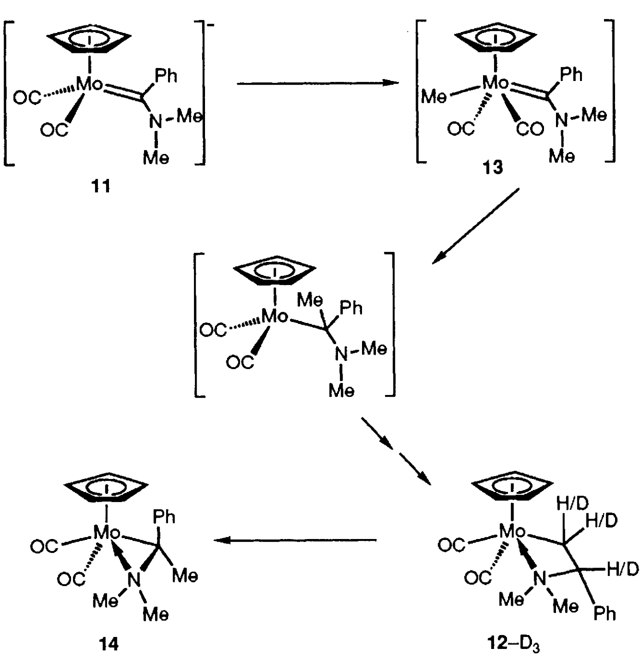
† *Crystal data* for **6**: M = 391.28, monoclinic, a = 10.963(26), b = 10.777(33), c = 14.117(23) Å; β = 93.58(16)°, U = 1665(7) Å^3, D_c = 1.561 g cm^{-3}, Z = 4, space group $P2_1/n$ (non-standard setting of $P2_1/c$ (C^5_{2h}, No. 14), Mo-Kα radiation (λ = 0.71069 Å), μ(Mo-Kα) = 7.77 cm^{-1}, F(000) = 799.73. Data were collected in the range $3.5 < 2\theta < 50°$ (ω-scan). 1333 independent reflections [$|F|/\sigma(|F|) > 4.0$]. R 0.0893, (Mo, O and N anisotropic).

Crystal data for **16**: M = 479.18, monoclinic, a = 16.431(43), b = 8.409(20), c = 13.181(29) Å, β = 110.64(19)°, U = 1704(8) Å^3, D_c = 1.868 g cm^{-3}, Z = 4, space group $P2_1/c$ (C^5_{2h}, No. 14), Mo-Kα radiation (λ = 0.71069 Å), μ(Mo-Kα) = 69.32 cm^{-1}, F(000) = 927.72. Data were collected in the range $3.5 < 2\theta < 50°$ (ω-scan). 2176 independent reflections [$|F|/\sigma(|F|) > 3.0$] R 0.0579, (all non-hydrogen atoms anisotropic).

Data for both **6** and **16** were corrected for Lorentz, polarisation, and absorption effects. Structures were solved by Patterson and Fourier techniques and refined by blocked-cascade least-squares methods. Atomic coordinates, bond lengths, bond angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 2

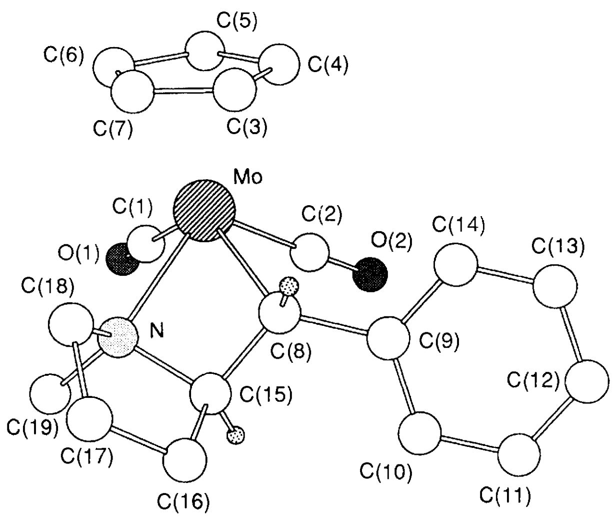


Fig. 1 Molecular structure of $Mo\{\eta^2\text{-}CHPhCH(CH_2)_3NMe\}(CO)_2(\eta\text{-}C_5H_5)$ **6**. Selected bond lengths (Å) and angles (°), Mo–C(1) 1.924(26), Mo–C(2) 1.912(20), Mo–N 2.306(19), Mo–C(8) 2.263(20), C(8)–C(15) 1.493(28), N–C(15) 1.512(25), N–Mo–C(1) 87.0(9), N–Mo–C(2) 113.1(7), C(1)–Mo–C(2) 75.2(10), N–Mo–C(8) 60.9(6), C(1)–Mo–C(8) 126.7(9), C(2)–Mo–C(8) 80.1(8), Mo–N–C(15) 90.8(12).

(Scheme 1), involving H migration to the empty coordination site, migration of the hydride back to the adjacent carbon, and nitrogen coordination. Complex **5** is not an intermediate in this process. This compound is available from the reaction of LiBz with $MoI(CO)_2\{=C(CH_2)_3NMe\}(\eta\text{-}C_5H_5)$ and shows no sign of being converted into **6** under the same reaction conditions. Given the existence of **5**, and the fact that it does not convert into **6**, it would seem that the β-elimination path from **9** leading to **6** is far quicker than intramolecular nitrogen coordination within **9**, which would give **5**.

We find related results in the reaction of MeI with the anionic carbene complex $[Mo(CO)_2\{=C(NMe_2)Ph\}(\eta\text{-}C_5H_5)]^-$ **11**. In this case the reaction is altogether quicker and production of the complex **12** is complete within ≈1 min at −70 °C (Scheme 2). There is no sign in the IR spectrum at this temperature of signals attributable to **13** and, at this stage, we, therefore, assume rearrangement to **12** is very fast. An isotopic tracking experiment is consistent with the proposed mechanism. Treatment of **11** with CD_3I results in **12**-D_3. The ^1H and ^2H NMR spectra of this material shows no loss of label, or scrambling of label, within experimental limits of detection and confirm the deuteriated sites are those shown.

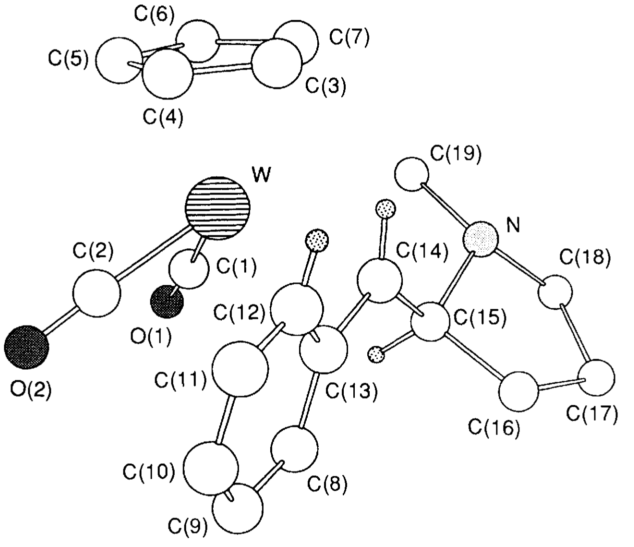


Fig. 2 Molecular structure of $W(CO)_2\{\eta^3\text{-}C_6H_5\text{-}CHCH(CH_2)_3NMe\}(\eta\text{-}C_5H_5)$ **16**. Selected bond lengths (Å) and angles (°), W–C(1) 1.929(17), W–C(2) 1.935(16), W–C(12) 2.448(10), W–C(13) 2.355(9), W–C(14) 2.317(12), C(1)–W–C(2) 75.7(7).

Gentle warming (+50 °C in toluene) of complex **12** results in its isomerization into complex **14**. At this temperature, the sequence leading to **12** is sufficiently reversible to allow leakage through to the thermodynamically preferred species **14**.

We suggest that the β-elimination pathway in these reactions is enabled through the creation of a vacant coordination site resulting from the methyl and benzyl to carbene migrations. We note intriguing analogies between the formation of **6** by this route and the mechanistic proposal for the β-elimination initiated exchange of labelled sites in $IrBr(^{13}CH_3)(CH_2OMe)(PMe_3)_3$,[6] insertion of isonitrile into a methyl C–H bond within $MoMe(CO)_2(CNBu^t)(\eta\text{-}C_5H_5)$, which results in η^3-azaallyl complexes,[7] and in the formation of C–C coupled species during the reaction of isonitriles with butadiene hafnium complexes.[8]

Finally, we note the unusual behaviour of complexes **6** and **7** under photolysis. Irradiation of complexes **6** or **7** with visible light (2 × 20 W fluorescent strip lights, water cooled Schlenk tube) over 5 h causes rearrangement to the η^3-benzyls $M(CO)_2\{\eta^3\text{-}C_6H_5CHCH(CH_2)_3NMe\}(\eta\text{-}C_5H_5)$ **15** and **16**. The X-ray crystal structure of the tungsten complex **16** is illustrated in Fig. 2 and shows the $CH(CH_2)_3NMe$ substituent of the benzyl is located in the *anti* position. The ^1H and ^{13}C NMR spectra indicate that both complexes **15** and **16** exist as single isomers in solution. These photolysis reactions are thermally reversed over a period of days at ambient temperature to reform complexes **6** or **7**.

We currently envisage the photolysis step as proceeding through cleavage of the N → M bond in a manner reminiscent of the visible light reactions of $Mo\{\eta^2\text{-}CH(CH_2)_3NMe\}(CO)_2(\eta\text{-}C_5H_5)$[9] and $Mo(CO)_4(P\text{-}N)$ (P-N = bidentate P, N donor).[10] The coordination site thus released is then bound by the phenyl ring to form the η^3-benzyl structure. The thermal conversion back into **6** or **7** involves an η^3 to η^1 benzyl rearrangement with the nitrogen donor as intramolecular, incoming nucleophile.

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