Methyl to alkylidene migration within *trans*-[WMe(=CHPh)(CO)$_2$(η-C$_5$H$_5$)]

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Treatment of the anionic carbene complex [W(=CHPh)(CO)$_2$(η-C$_5$H$_5$)]$^-$ with MeI affords a complex *trans*-[WMe(= CHPh)(CO)$_2$(η-C$_5$H$_5$)] which isomerises by means of an intramolecular methyl to carbene migration to afford the η^3-benzyl complex [W{η^3-CH(Me)C$_6$H$_5$}(CO)$_2$(η-C$_5$H$_5$)].

The migration of an alkyl ligand to a coordinated carbene is of interest as a method for creating a new C–C bond within the coordination sphere of a metal. Such reactions are postulated frequently as mechanistic steps in multistep organometallic reactions.[1–6] The process is not particularly well characterized because of the comparative scarcity of isolable or spectroscopically identifiable precursors [MR(carbene)L$_n$] (R = alkyl). One particular concern is the difference in reactivity between alkyl migrations to heteroatom-stabilized (Fischer type) carbenes and nonheteroatom-stabilized (Schrock type) carbenes. We report here the *direct* observation of an alkyl migration in the nonheteroatom-stabilized system [MR(CO)$_2$(=CR^{1}R^2)-(η-C$_5$H$_5$)] (M = group 6 metal; R = alkyl; =CR^{1}R^2 = nonheteroatom-stabilized carbene).

The reaction of MeI with the anion [W(=CHPh)(CO)$_2$(η-C$_5$H$_5$)]$^-$ **1** in thf at −80 °C results in a solution containing *trans*-[WMe(=CHPh)(CO)$_2$(η-C$_5$H$_5$)], *trans*-**2**. This complex is isolable (34%) provided work up is prompt and it has been fully characterised.† In particular, there is a high frequency resonance in the ^{1}H NMR spectrum at δ 12.17 with ^{183}W satellites for the =C*H*Ph proton. The methyl protons resonate at δ 0.50 and also possess satellites due to ^{183}W.

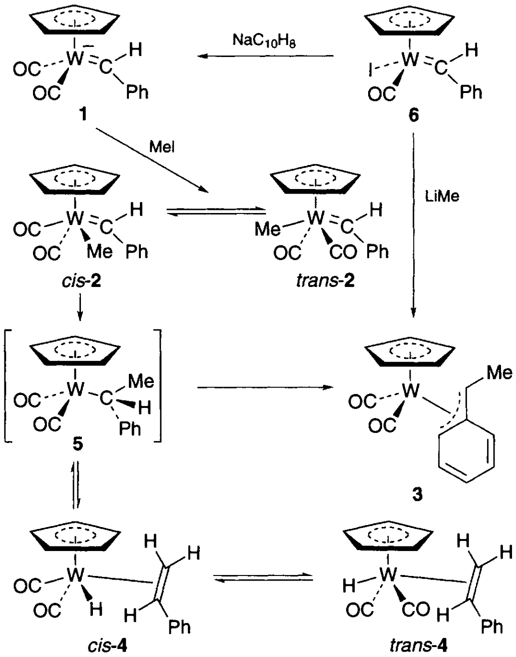
Complex *trans*-**2** undergoes a rearrangement in thf, toluene, or hexane to give the known benzyl complex [W(CO)$_2${η^3-CH(Me)Ph}(η-C$_5$H$_5$)] **3**.[7] The rearrangement occurs in high yield (73%) and is complete after 2 h at ambient temperature in thf. A small amount of another complex is observed during the rearrangement, spectroscopically identified (IR, ^{1}H NMR)‡ as *trans*-[WH(CH$_2$=CHPh)(CO)$_2$(η-C$_5$H$_5$)] *trans*-**4**.[8] We favour the mechanism shown in Scheme 1 for the formation of **3**, with a reversible β-elimination path affording *trans*-**4**.

This compares to our recently reported migration of a methyl to a *heteroatom*-stabilized carbene in the reaction of MeI with [Mo(CO)$_2${ = C(NMe$_2$)Ph}(η-C$_5$H$_5$)]$^-$. This reaction gives [Mo(CO)$_2${η^2-CH$_2$CH(Ph)NMe$_2$}(η-C$_5$H$_5$)][9] in which the heteroatom rather than the phenyl becomes coordinated to the metal in a reaction complete after only *ca.* 1 min at −70 °C. Because of the very fast reaction, no intermediates were identified. The proposed multistep mechanism involves initial formation of [MoMe{=C(NMe$_2$)Ph}(CO)$_2$(η-C$_5$H$_5$)] which rearranges by methyl to carbene migration to give [Mo{η^1-CMe(NMe$_2$)Ph}(CO)$_2$(η-C$_5$H$_5$)]. Subsequent β-elimination/migration processes and nitrogen coordination lead to the final product.

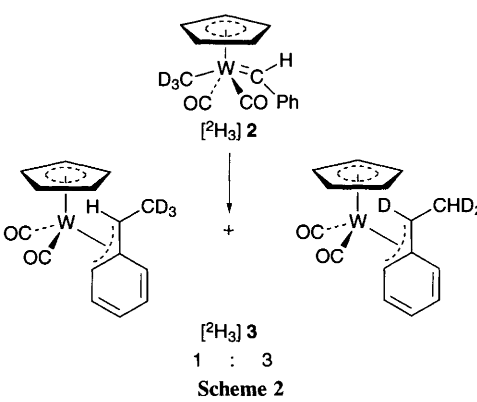
Isotopic labelling studies for the rearrangement of **2** are revealing. Treatment of **1** with CD$_3$I results in [^{2}H$_3$]**2** with the deuterium label contained *only* within the metal methyl group. The rearrangement of [^{2}H$_3$]**2** results in some loss of the label from the methyl group, but only into the exocyclic position of the benzyl ligand of [^{2}H$_3$]**3** (Scheme 2). This distribution of the label in [^{2}H$_3$]**3** is consistent with the reversible β-elimination process invoked in Scheme 1.

The rearrangement of *trans*-**2** into **3** is monitored conveniently by IR spectroscopy in the carbonyl region as a function of time. Under the conditions of the study, the disappearance of *trans*-**2** occurs with a first-order rate constant of $(7.23 \pm 0.18) \times 10^{-4}$ s^{-1} at 298 K in thf. The rate constant is invariant over a near threefold range of concentration indicating that the methyl to carbene migration is intramolecular. For activation parameters, rates determined at four temperatures (298–323 K) lead to $\Delta H^‡ = 61 \pm 2$ kJ mol^{-1} and $\Delta S^‡ = -101 \pm 5$ J K mol^{-1}.

Scheme 1 involves a *trans*/*cis* isomerisation prior to an irreversible migration step (the migration step is irreversible since dissolving either **3** or *trans*-**4** does not yield any detectable *trans*-**2**.[8]) The magnitude and sign of this value of $\Delta S^‡$ are inconsistent with the *trans*/*cis* isomerisation step being rate determining. The activation parameters therefore would seem to relate to the methyl to carbene migration. The greater ordering



Scheme 1



Scheme 2

within the transition state corresponds to the three-centre two-electron bond proposed for migrations to carbene.[10] The solvent does not appear to play a prominent role in the rearrangement as similar rates and activation parameters are found in toluene and thf, solvents with very different coordinating abilities.

The corresponding reaction of H^+ with **1** in thf at −80 °C results in a solution containing [W{η^3-CH_2Ph}$(CO)_2$(η-C_5H_5)].[11] Reaction occurs with CBr_4 immediately after protonation but unfortunately the product was not isolable. This does, however, suggest that a hydride, probably [WH(=CHPh)$(CO)_2$(η-C_5H_5)], is formed in that reaction and that it undergoes a very facile hydride to carbene migration. The migratory aptitude H ≫ Me is again consistent with the three-centre two-electron bond of the transition state where better overlap of the less directional 1s orbital of hydrogen affords greater stability.

Finally, we note that reaction of LiMe with [WI(=CHPh)$(CO)_2$(η-C_5H_5)] **6** in thf at −80 °C results in a solution containing only **3** as soon as an IR spectrum could be recorded. No evidence was found for the formation of any **2**, suggesting the organolithium reagent attacks directly at the electrophilic carbene centre of **6** and not at the metal centre.

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Footnotes

† *trans*-[WMe(=CHPh)$(CO)_2$(η-C_5H_5)] **2**, red. Found: C, 43.84; H, 3.39%. $C_{15}H_{14}O_2W$ requires C, 43.93; H, 3.44%; *m/z* 410 (M^+). IR [ν_{CO}(thf)] 1983m, 1912s cm^{-1}. ^1H NMR (C_6D_6) δ 12.17 (s, 1H, J_{WH} 8.5 Hz, =C*H*Ph), 7.75 (m, 2H, Ph), 7.20 (m, 2H, Ph), 7.08 (m, 1H, Ph), 4.99 (s, 5H, C_5H_5), 0.50 (s, 3H, Me). ^{13}C NMR (CD_2Cl_2, −50 °C) δ 256.3 (=C), 214.2 (CO), 148.4 (*ipso*-C, Ph), 132.0 (*o*- or *m*-C, Ph), 129.6 (*p*-C, Ph), 128.8 (*o*- or *m*-C, Ph), 98.1 (C_5H_5), −16.8 (Me).

‡ *trans*-**4**: IR [ν_{CO}(cyclohexane)]: 1976m and 1899s cm^{-1}. ^1H NMR ($C_6D_5CD_3$, −50 °C) δ −5.7 (s, 1H, W–H).

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