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Preliminary communication

Synthesis and reactions of the tungsten nonheteroatom-stabilised carbene anion $[CpW(CO)_2(=CHPh)]^-$

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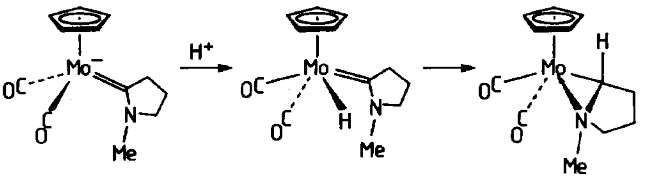
Abstract

Treatment of $CpW(SnPh_3)(CO)_2(=CHPh)$ with I_2 gives the new nonheteroatom-stabilised carbene complex $CpWI(CO)_2(=CHPh)$, whose reduction by $NaC_{10}H_8$ gives the nonheteroatom stabilised carbene anion $[CpW(CO)_2(=CHPh)]^-$, the first member of a new class of such complexes.

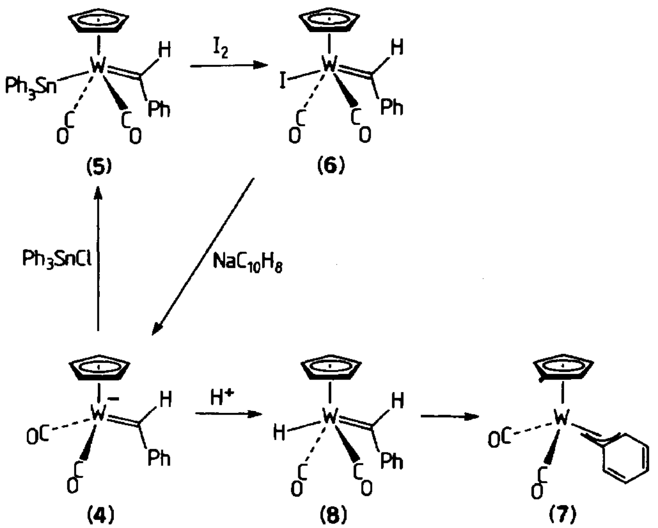
The migrations of groups such as hydride or alkyl to carbene ligands represent C–H or C–C bond formations and are important in that regard [1,2].

Recent work demonstrates the directly observable migration of the hydride ligand in $CpMoH(CO)_2\{=\overline{C(CH_2)_3N}Me\}$ (1) to the heteroatom stabilised carbene, to give ultimately complex **2** (Scheme 1) [2]. The ability of various groups to migrate to a coordinated carbene ligand and of the types $=CRX$, where X = heteroatom or hetero-group, should differ from that of the same groups to migrate to nonheteroatom-stabilised carbene ligands (some of which are frequently referred to as alkylidenes) in otherwise similar environments. The precursor of the hydride **1** is the anion $[CpMo(CO)_2\{=\overline{C(CH_2)_3N}Me\}]^-$ (3) [2,3]. Therefore, to make direct comparisons of the migratory abilities, sources of anions of the type $[CpM(CO)_2(=CR^1R^2)]^-$ (M = Mo, W; R^1, R^2 = H or carbon substituents) are required. We report here the synthesis of $[CpW(CO)_2(=CHPh)]^-$ (4), the first member of a new anionic class of nonheteroatom stabilised carbene complexes.



(3) (1) (2)

Scheme 1.



Scheme 2.

The reaction of iodine with the previously reported nonheteroatom stabilised carbene complex CpW(SnPh$_3$)(CO)$_2$(=CHPh) (5) [4] in CH$_2$Cl$_2$ at ambient temperature results in cleavage of the W–Sn bond to give Ph$_3$SnI and CpWI(CO)$_2$(=CHPh) (6) (Scheme 2) (61%) *. These compounds are separable by chromatography. The spectroscopic properties of 6 are comparable to those of CpWI(CO)$_2$(=CHtol) [5] (tol = *p*-tolyl) made previously by the reaction of aqueous HI with CpW(CO)$_2$(≡Ctol). Rather unexpectedly, reaction of iodine with CpW(SnPh$_3$)(CO)$_2$(=CMePh) does not proceed analogously, and the only isolated products are traces of starting material.

Sodium naphthalide reduction of the iodide in 6 in THF results in cleavage of the W–I bond and formation of the nonheteroatom stabilised carbene anion 4. The IR spectrum of 4 in the carbonyl region (ν(CO) (THF) 1849s and 1713s cm^{-1}) is indicative of an anionic dicarbonyl, and the associated frequencies correspond closely to those of related anions such as [CpMo(CO)$_2${P(OPh)$_3$}]$^-$ (ν(CO) (THF) 1832s and 1732s cm^{-1}) [6] and 3 (ν(CO) (THF) 1786s and 1666s cm^{-1}) [3], suggesting a similar electron density at the metal.

Reinforcing this, addition of Ph$_3$SnCl to solutions of 4 results in attack by the Ph$_3$SnCl at the metal and reformation of 5 (38%). Addition of acid to solutions of the anion 4 results in the rapid formation of the η^3-benzyl-CpW(CO)$_2$(η^3-C$_6$H$_5$CH$_2$) (7). This compound was previously known, but made by a very different method [7]. We envisage this reaction as proceeding by protonation at the metal to give CpWH(CO)$_2$(=CHPh) (8) (undetected at ambient temperature), followed by a very facile H to =CHPh migration. The phenyl ring enters the coordination sphere of the metal to maintain the 18-electron count.

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* CpWI(CO)$_2$(=CHPh) (6): IR: (CO)(CH$_2$Cl$_2$) 2005m, 1935s cm^{-1}; ^{1}H NMR: δ(CDCl$_3$) 13.15 (1 H, s, *J*(WH) 9.5, =CH), 7.83–7.71 (2 H, m, Ph-*o*); 7.60–7.44 (3 H, m, Ph-*m* + *p*), 6.11 (5 H, s, Cp); ^{13}C NMR δ(CDCl$_3$, −50 °C): 269.8 (s, *J*(WC) 74, W=C), 207.4 (s, *J*(WC) 161, CO), 148.6 (Ph-*i*) 133.2 (Ph-*p*), 131.8 (Ph-*o*), 129.4 (Ph-*m*), 97.6 (Cp).

Earlier studies have demonstrated the migration of $SnPh_3$ to =CHPh in $CpMo(SnPh_3)(CO)_2$(=CHPh) [4]. It therefore appears that migrations to =CHPh are more facile than those to heteroatom stabilised carbenes (for which there is no sign of $SnPh_3$ migration) in $CpMX(CO)_2$(carbene) (M = Mo, W) systems [4]. We consider it likely that protons attack at the metal of **4** rather than directly at the =CHPh group, since Ph_3SnCl attacks at the metal of **4** and protons clearly attack a number of anions $[CpM(CO)_2(=CRX)]^-$ directly at the metal [2,3]. We are therefore currently seeking to identify the hydride **8** (and/or its *cis* isomer) by chemical derivation and low temperature spectroscopy.

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