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Preliminary communication

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

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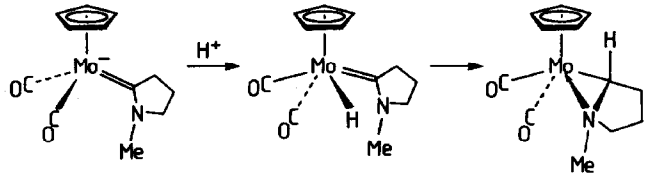
Abstract

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].

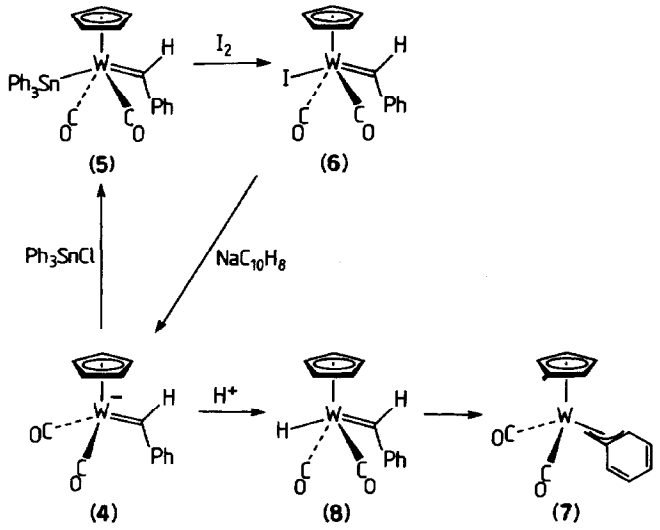
Recent work demonstrates the directly observable migration of the hydride ligand in $CpMoH(CO)_2\{=\overline{C(CH_2)_3N}Me\}$ (**1**) to the heteroatom stabilised carbene, to give ultimately complex **2** (Scheme 1) [2]. The ability of various groups to migrate to a coordinated carbene ligand and of 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.

0022-328X/89/$03.50



Scheme 2.

The reaction of iodine with the previously reported nonheteroatom stabilised carbene complex $CpW(SnPh_3)(CO)_2(=CHPh)$ (**5**) [4] in CH_2Cl_2 at ambient temperature results in cleavage of the W–Sn bond to give Ph_3SnI 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_3SnCl to solutions of **4** results in attack by the Ph_3SnCl 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-$CpW(CO)_2(\eta^3\text{-}C_6H_5CH_2)$ (**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.

* $CpWI(CO)_2(=CHPh)$ (**6**): IR: $(CO)(CH_2Cl_2)$ 2005m, 1935s cm^{-1}; ^1H NMR: $\delta(CDCl_3)$ 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 $\delta(CDCl_3, -50\,°C)$: 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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