A Zirconium Hydride Enolate from Carbonylation of the Alkyl Compound $[Zr\{C_5H_2(SiMe_3)_3\text{-}1,2,4\}_2(Me)_2]$

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Reaction of the hindered, substituted electron-withdrawing cyclopentadienyl zirconium complex $[Zr\{C_5H_2(SiMe_3)_3\}_2(Me)_2]$ with CO leads, *via* the acyl intermediate $[Zr\{C_5H_2(SiMe_3)_3\}_2(COMe)(Me)]$ detected during the course of the reaction, to the metal hydride enolate $[Zr\{C_5H_2(SiMe_3)_3\}_2(H)\{OC(Me)=CH_2\}]$.

The chemistry of CO is rich and complex and many different methodologies have been used to probe aspects of the reactivity of this small molecule. CO insertion into a metal–carbon bond has been extensively investigated in relation to several catalytic processes[1] and bis(cyclopentadienyl)–group 4 (Ti, Zr, Hf) or –actinoid models have been used to elucidate some significant facets of the relationship between the character of coordinated acyl groups and the nature of the alkyl group concerned.[2] CO activation in the environment of a highly oxophilic metal centre leads to different types of CO reduction, which accentuate the oxycarbenoid character of the η^2-acyls. This property is exemplified by the treatment of $[Zr(C_5H_5)_2Cl\{CH(SiMe_3)Ar\}]$ or $[Zr(C_5Me_5)_2(Me)_2]$ with CO: for the former an enolate complex $[Zr(C_5H_5)_2Cl\{OC(SiMe_3)=CHAr\}]$[3] is obtained whereas for the latter a bis(acetyl) complex forms which undergoes C–C coupling to afford $[Zr(C_5Me_5)_2\{OC(Me)=C(Me)O\}]$.[2c] Therefore, $[Zr(C_5H_5)_2(Me)_2]$ with CO gives the η^2-acyl derivative $[Zr(C_5H_5)_2(COMe)(Me)]$.[2g] Several enolate complexes have been prepared by the reaction of ketones with the titanocene methylene intermediate $[(C_5Me_5)_2Ti=CH_2]$[4a] or the titanocene vinylidene intermediate $(C_5Me_5)_2Ti=C=CH_2]$,[4b] and of acid chlorides and $[(C_5H_5)_2Ti=CH_2]$,[2i] by hydrogenation of the ketene complex $[(C_5Me_5)_2Zr(C,O\text{-}\eta^2\text{-}H_2C=CO)]$[2j] or by reaction of simple enolate salts with metal halides.[4c–f] For the more specialised case of CO activation leading to enolates, only complexes containing the pentamethylcyclopentadienyl ligand are known: $[Zr(C_5Me_5)_2(H)\{OC(H)=CH(CHMe_2)\}]$, $[Zr(C_5Me_5)_2(H)\{\overline{OC=CH(CH_2)_2(CH_2})\}]$[2c] and $[Th(C_5Me_5)(Cl)\{OC(SiMe_3)=CH_2\}]$.[2m]

We report here that carbonylation of bis[1,2,4-tris(trimethylsilyl)cyclopentadienyl]dimethylzirconium $[Zr\{C_5H_2(SiMe_3)_3\}_2(Me)_2]$ **1**[†] affords the zirconium hydride enolate $[Zr\{C_5H_2(SiMe_3)_3\}_2(H)\{OC(Me)=CH_2\}]$ **2**.[‡] In different solvents ($[^2H_8]$tetrahydrofuran, CD_2Cl_2, C_6D_6, pentane), a solution of **1** exposed to carbon monoxide (1 atm) gives the zirconium hydride enolate **2** as the sole product after one day, at room temperature. The high solubility of **2** in hexane or pentane due to the presence of trimethylsilyl substituents on the cyclopentadienyl ligand[5] has prevented the crystallization of this complex. The nature of the enolate is confirmed by comparison of ^1H and ^{13}C NMR[‡] data with data for other similar zirconium or titanium complexes.[2c,4f] The presence of an unexpected zirconium hydride, indicated by a peak at δ 5.78 (1 H) in the ^1H NMR spectrum, was confirmed by the reaction of **2** with HCl (or DCl) which gave the expected evolution of H_2 (or HD) as analysed by mass spectrometry. ^2H NMR studies with the labelled complex $[Zr\{C_5H_2(SiMe_3)_3\}_2(D)\{OC(CD_3)=CD_2\}]$ synthesised from $[Zr\{C_5H_2(SiMe_3)_3\}_2(CD_3)_2]$ and CO verified the existence of the Zr–D unit and indicated that hydride formation resulted from hydrogen abstraction of a zirconium–methyl moiety. The IR spectrum of **2** (in Nujol) shows bands due to Zr–H and C=C at 1646 and 1596 cm^{-1} respectively (in the deuteriated compound, the Zr–D stretch is observed at 1167 cm^{-1}). The reaction was also monitored at low temperatures by ^1H NMR spectroscopy ($[^2H_8]$toluene). At 10 °C, **1** reacts slowly with CO and a new species **3** is detected; signals for this new species, which disappear gradually and are replaced by those due to **2**, can be assigned to the acetyl structure $[Zr\{C_5H_2(SiMe_3)_3\}_2(COMe)(Me)]$ **3** on the basis of its ^1H NMR spectrum.[§] These results imply that the formation of **2** occurs *via* the acetyl intermediate **3**, and suggest a reaction mechanism such as is outlined in Scheme 1.

Recent evaluation of the electronic effects of trimethylsilyl substituents in the review by Möhring and Coville[7] shows the group to be electron-withdrawing rather than electron-donating, in agreement with the ^1H NMR results for **1** and **3** relative to those obtained from the analogous zirconocene C_5H_5 and C_5Me_5 complexes.[2c,i] This leads to an increase in the positive charge on the metal (decreasing delocalization of the d electrons from the metal centre and minimising the possibility of π back donation to the acyl group)[8] in complexes containing the $C_5H_2(SiMe_3)_3$ ligand. This renders the Zr centre even more oxophilic. η^2(CO) coordination followed by the formation of a covalent zirconium oxygen bond tends to labilize the Zr–C bond. The acyl carbon has carbenoid character[2c,9] and inserts into the second Zr–Me bond to yield the intermediate **4** (suggesting an 'outside' oxygen from a laterally coordinated CO ligand).[10] Subsequently, C–H activation of a methyl group is forced by ring strain *via* a four-centre mechanism (illustrated by the deuterium labelling study, which indicates the formation of a Zr–D bond) and affords the enolate hydride **2**.

Of note is the stability of **2** is in the presence of a large excess of CO or when heated at 140 °C in $[^2H_8]$toluene in a sealed ^1H NMR tube. No reaction of the Zr–H was observed in preliminary reactivity studies of **2** with acetone and CCl_4 respectively. We are currently exploring the reactivity of the zirconium enolate **2** towards aldehydes, with a view to produce aldol reaction products.[4c]

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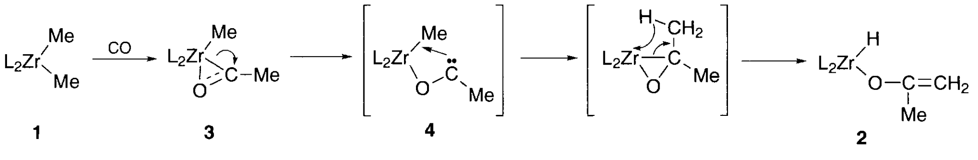

L = $C_5H_2(SiMe_3)_3$-1,2,4

Scheme 1

Footnotes

[†] This compound was prepared from $[Zr\{C_5H_2(SiMe)_3\}_2Cl_2]$[5b,6] and LiMe in diethyl ether. Satisfactory analyses (C, H, Zr) were obtained. ^1H NMR (C_6D_6), δ: 6.72 [4 H, $C_5H_2(SiMe_3)_3$]; 0.40, 0.27 (36 H and 18 H respectively, $SiMe_3$); 0.06 (6 H, Me).

‡ Satisfactory analyses (C, H, Zr) were obtained. ^{1}H NMR (C_6D_6), δ: 6.96, 6.18 [dd, J_{HH} 2 Hz, $C_5\mathit{H}_2(SiMe_3)_3$]; 5.78 (s, 1 H, ZrH); 3.90, 3.87 (s, each 1 H, diastereotopic $=CH_2$); 1.68 (s, 3 H, Me); 0.43, 0.40 and 0.36 (s, each 18 H, $SiMe_3$); ^{13}C NMR ($CDCl_3$), δ 164.5 (ZrOC); 134.1, 129.4, 120.2 [$\mathit{C}_5H_2(SiMe_3)_3$]; 129.7, 124.8 [$J_{CH}$ 166 Hz, $\mathit{C}_5H_2(SiMe_3)_3$]; 88.0 ($=CH_2$); 24.1 (Me); 1.88, 1.78 [$C_5H_2(SiMe_3)_3$].

§ ^{1}H NMR ($C_6D_5CD_3$), δ: 6.81, 6.42 [4 H, $C_5\mathit{H}_2(SiMe_3)_3$]; 0.60, 0.59 0.48 (s, each 18 H, $SiMe_3$); 0.76 (s, 3 H, Me); 2.98 (s, 3 H, CH_3CO).

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