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Preliminary communication

Formation of a hydrido diphenylphosphinomethylzirconium(III) species by reduction of $(C_5H_4-t-Bu)_2Zr(CH_2PPh_2)_2$

Robert Choukroun *, Danièle Gervais and Charaf-Eddine Rifai

Laboratoire de Chimie de Coordination du CNRS, Unité no. 8241, liée par conventions à l'Université Paul Sabatier et à l'Institut National Polytechnique, 205, route de Narbonne, 31077 Toulouse Cedex (France)

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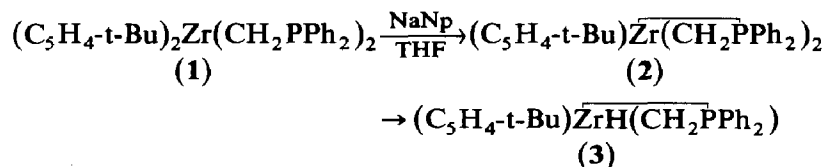
Abstract

Chemical reduction of $(C_5H_4-t-Bu)_2Zr(CH_2PPh_2)_2$ (**1**) was monitored by ESR and 1H NMR spectroscopy. A labile Zr^{III} species, $(C_5H_4-t-Bu)\overline{Zr}(CH_2PPh_2)_2$ (**2**), was first characterized by its ESR signal (triplet of quintet; $a(^1H)$ 3.5 G; $a(^{31}P)$ 11.0 G). Evolution of **2** at room temperature afforded another species, **3** (doublet of doublet, $a(^1H)$ 6.0 G; $a(^{31}P)$ 25.5 G), which was shown by its reaction with CH_3I to be a hydride (by formation of CH_4) to contain a $\overline{ZrCH_2PPh_2}$ moiety (by formation of PPh_2MeEtI), and formulated as $(C_5H_4-t-Bu)\overline{ZrH}(CH_2PPh_2)$ (**3**).

An important feature of the chemistry of hydrides is their potential reactivity towards a wide range of compounds. In particular C-H activation has attracted considerable interest in the last years. Part of this interest is centred on the behaviour of Group 4 hydrides and various types of C-H bond activation have been identified [1].

Our interest in zirconium(III) species is associated with the fact that promising catalytic activity in hydrogenation can be achieved with complexes containing the diphenylphosphinomethyl ligand [2,3]. Catalysis of hydrogenation of olefins by Zr^{IV} [4] or Zr^{II} [1i] complexes has been little studied.

We have now found that the chemical reduction of the new complex $(C_5H_4-t-Bu)_2Zr(CH_2PPh_2)_2$ (**1**) provides an easy route to a substituted monocyclopentadienyl zirconium(III) hydride catalytically active in hydrogenation [5]. This new species is obtained by reduction of **1** with sodium naphthalide in stoichiometric amount or in excess in THF solution, according to:



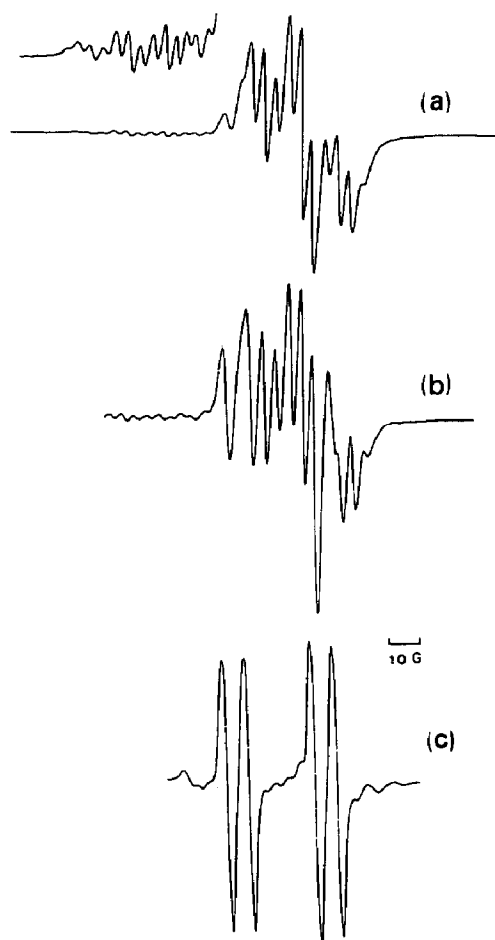


Fig. 1. Solution ESR spectra of sodium naphthalide reduction of **1** in THF: (a): **2**; (b): **2+3** mixture; (c): **3**.

When the reaction was monitored by ESR spectroscopy, a complex intense spectrum was first observed (Fig. 1a). This was successfully analyzed, by computer simulation, in terms of triplet of quintet, which we assigned to coupling of an unpaired electron on the zirconium atom to 2 equivalent phosphorus atoms and 4 equivalent protons in complex **2** ($g = 1.985$; $a(^1\text{H})$ 3.5 G; $a(^{31}\text{P})$ 11.0 G; $A(^{91}\text{Zr})$ 21.0 G). The reaction of Cp_2ZrR_2 with sodium naphthalide normally leads to monocyclopentadienyl complexes CpZrR_2 [6,7] and we recently described the chemical reduction of analogous systems, e.g. $\text{Cp}_2\text{M}(\overline{\text{CH}_2\text{PPh}_2})_2$ ($\text{Cp} = \eta\text{-C}_5\text{H}_5$; $\text{M} = \text{Ti}, \text{Zr}$), giving $\text{CpM}(\overline{\text{CH}_2\text{PPh}_2})_2$ [8].

During a period varying from 10 min to about 2 h, at room temperature, the ESR signal changed to an intense doublet of doublets, attributed to **3** ($g = 1.989$; $a(^1\text{H})$ 6.0 G; $a(^{31}\text{P})$ 25.5 G; $A(^{91}\text{Zr})$ 7.4 G) (Fig. 1c) which persists in a sealed tube for at least 4 weeks. The form of this spectrum is attributed to the coupling of the unpaired electron on the zirconium to one hydrogen nucleus and to one phosphorus nucleus, by comparison with $a(^1\text{H})$ and $a(^{31}\text{P})$ data observed for similar complexes [9,10]. This assignment was confirmed by Q-band ESR experiments. Small observable distortions in the spectrum presumably arise from ^1H superhyperfine coupling

(ca. 0.6 G) of the unpaired electron with the 4 ring protons of the C_5H_4 -t-Bu ligand, providing good evidence that one ring remains bonded to zirconium in **3** [11–13]. The frozen ESR solution spectrum does not show the triplet state characteristics that would be expected for a dimeric structure [14].

The ESR spectrum of **3** does not exhibit any splitting of the methylenephosphine ligand, but the previously reported analogues $(C_5H_5)_2ZrCH_2PR_2$ ($R = Me, Ph$) have the same behaviour [10c]. Other ESR control experiments (involving thermolysis of $((C_5H_4-t-Bu)_2ZrH_2)_2$ in the presence or absence of PPh_2Me) rule out definitively species such as $(C_5H_4-t-Bu)_2ZrH$ ($g = 1.980$; $a(^1H) 7.25$ G) and monophosphinezirconium(III) species ($g = 1.979$; $a(^{31}P) 15.7$ G; $A(^{91}Zr) 20$ G) [15].

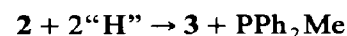
To investigate the possible presence of Zr^{IV} species in this reaction, we monitored the process accompanying evolution of ESR signals $2 \rightarrow 3$ by 1H NMR spectroscopy (at 250 MHz) in the presence of sodium naphthalide (1 equivalent) in deuterated THF- d_8 . No change was observed in the ESR spectra, proving that the solvent is not directly implied in the formation of the hydride. During the evolution $2 \rightarrow 3$, the 1H NMR spectrum remains unchanged: the resonances from naphthalene, phosphine, PPh_2Me , and NaC_5H_4 -t-Bu, were identified by comparison with those from authentic samples. In addition, small sets of unresolved resonances were detected in the 7.25, 5.5–5.0 and 1.5 ppm regions, associated with the phenyl, substituted cyclopentadienyl and t-butyl groups. No signals from **1** are present in the spectrum.

Identification of **3** was provided by its reaction with an excess of CH_3I which confirmed the presence of a Zr–H bond by evolution of an almost stoichiometric amount of CH_4 (identified by IR spectroscopy).

At the same time **3** was converted into $(C_5H_4-t-Bu)_2ZrI_2$, as revealed by its mass spectrum ($m/e = 586$) and by 1H NMR spectroscopy (by comparison with data for an authentic sample prepared from **1** + CH_3I [5]). The formation of a dicyclopentadienyl complex can be attributed to redistribution of the unstable $(C_5H_4-t-Bu)ZrI_3$ (derivatives $(C_5H_4R)ZrX_3$ with $X = Cl, Br, I$ having so far not been isolated. Furthermore the insoluble phosphonium salts PPh_2Me_2I (due to free PPh_2Me) and PPh_2MeEtI were isolated, confirming the presence of a Zr– CH_2PPh_2 bond (the phosphonium salts were recovered in ca. 95% yield based on **1**).

In view of all these findings, viz. one hydrogen atom per zirconium atom, one aromatic ligand bonded to zirconium, a Zr– CH_2PPh_2 bond still intact in **3**, we suggest the following structure for **3**: $(C_5H_4-t-Bu)ZrH(CH_2PPh_2)$ (or $(C_5H_4-t-Bu)ZrH(CH_2PPh_2), PPh_2Me$ (**3'**)). Both **3** and **3'** are 13-electron complexes (whereas **2** is a 15-electron complex) and coordination of one or two molecules of THF to the metal is quite probable.

The reaction $2 \rightarrow 3$ may be formulated as:



Of interest is the origin of the two H atoms required in this equation. A process involving activation of C–H bonds in the cyclopentadienyl ligand was recently demonstrated for diphenylphosphinomethylzirconium compounds [16] and in thermolysis of $(C_5H_5)_2ZrD(CH_2PPh_2)$ in THF- d_8 which gave only $Zr^{III}H$ species (along with $(C_5H_5)_2Zr(CH_2PPh_2)$), which was detected by ESR spectroscopy [17].

We are currently examining the reduction of other diphenylphosphinomethylzirconium complexes in order to throw light on the mechanism.

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