Formation of Zirconium(III) Complexes by Thermolysis of $(\eta^5\text{-}C_5H_5)_2ZrH(CH_2PPh_2)$

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E.s.r. spectra obtained when the thermolytic reduction of $(\eta^5\text{-}C_5H_5)_2ZrH(CH_2PPh_2)$ in the presence of a phosphine PR_3 is monitored, compared with those obtained from $(\eta^5\text{-}C_5H_5)_2ZrH_2$, led to the characterization of a monophosphine zirconium(III) hydride formulated as the adduct $(\eta^5\text{-}C_5H_5)_2ZrH(PR_3)$ and a new species assumed to be a metallated complex such as $(\eta^5\text{-}C_5H_5)_2\overline{ZrC_6H_4P}R_2$.

Studies on homolytic cleavage of zirconium–carbon and zirconium–hydrogen bonds afford valuable information on radical processes involving complexes of early transition metals. The formation of zirconium(III) complexes on photolysis (or thermolysis) of $(\eta^5\text{-}C_5H_5)_2ZrR_2$[1] and $(\eta^5\text{-}C_5H_4Me)_2ZrH_2$[2] has been recently reported; when the reactions were performed in the presence of a tertiary phosphine, a zirconium(III) monophosphine adduct was detected. In previous work, the reaction of $(cp)_2ZrHR$ (cp = $\eta^5\text{-}C_5H_5$) with phosphines was found to lead to reduction to Zr^{II} and the formation of $(cp)_2Zr(PR_3)_2$ which may be oxidized to Zr^{III} complexes [$(cp)_2ZrR$ and $(cp)_2ZrX$] by the action of RX.[3]

In this work, we report the synthesis of $(cp_2)ZrH(CH_2PPh_2)$ (**1**) which, in contrast to the analogous $(cp)_2ZrH(alkyl)$, does not give rise to zirconium(II) species by ligand-induced elimination of alkane. Surprisingly, we found that thermolysis of (**1**) at *ca.* 60 °C in toluene containing a phosphine, PR_3, yielded paramagnetic species containing zirconium(III), the formation of which was followed by e.s.r. spectroscopy. The identification of the new complexes generated by this way was made possible by comparison with the e.s.r. spectra obtained on thermolysis of the dihydride $(cp)_2ZrH_2$ under similar conditions and by reference to the literature data concerning the few zirconium(III) complexes previously characterized.[4]

The new complex $(cp)_2ZrH(CH_2PPh_2)$ (**1**) was obtained as a white polymeric solid from $(cp)_2ZrCl(CH_2PPh_2)$ (**2**) and $LiAlH(OBu^t)_3$ in tetrahydrofuran and characterized by analytical data (C, H, Zr, and P) and a broad, strong i.r. absorption at 1355 cm^{-1} (970 cm^{-1} for the deuteride).† Insolubility in usual solvents prevented any further spectroscopic characterization. When a suspension of (**1**) in benzene or toluene was heated, a dark red paramagnetic solution was obtained which was studied by e.s.r. spectroscopy.

For instance, thermolysis of 40 mg of (**1**) in toluene (1.5 ml) in a sealed tube at *ca.* 60 °C resulted in a doublet with *g* 1.985 [$A(^{91}Zr)$ 13.5 G;‡ $a(^{31}P)$ 19.5 G] attributed to

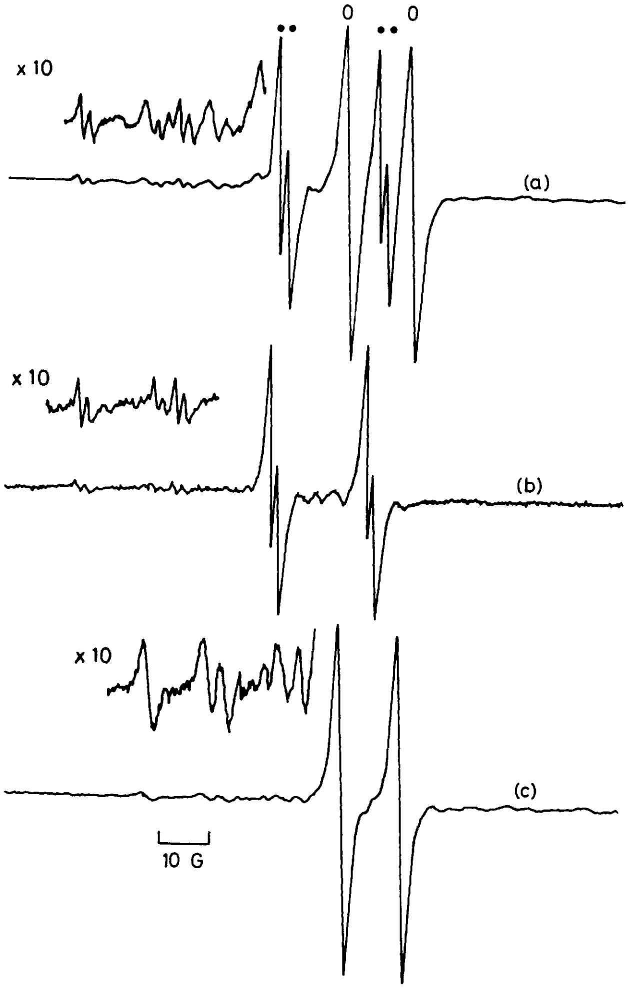

Figure 1. X band e.s.r. spectra of toluene solutions at room temperature after thermolysis at 60 °C: (a) $(cp)_2ZrH(CH_2PPh_2)$ in the presence of $PMePh_2$: ○ doublet assigned to (7), ● doublet of doublets assigned to (**6**); (b) $(cp)_2ZrH(CH_2PPh_2)$ in the presence of a very large excess of $PMePh_2$; (c) $(cp)_2ZrH_2$ in the presence of PMe_2Ph.

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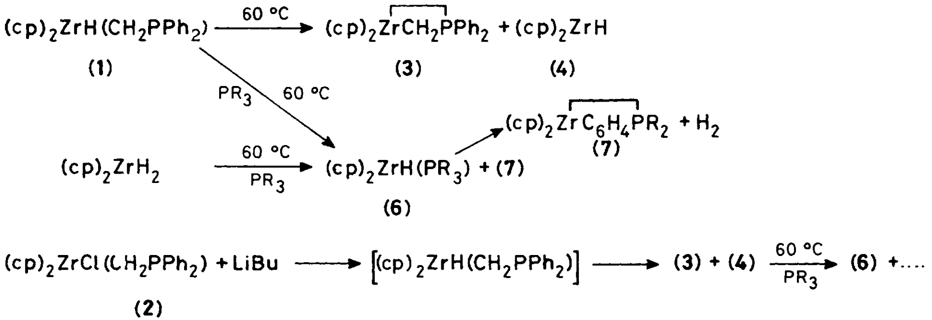
† Previously described dimeric $(cp)_2ZrHR$ complexes gave for the bridging hydride ν 1380 cm^{-1} when R = CH_2 cyclopentyl[5] and ν 1590 cm^{-1} when R = $CH(SiMe_3)_2$.[6]

‡ 1 G = 10^{-4} T.



Scheme 1

$(cp)_2ZrCH_2PPh_2$ (**3**) reported by Schore[7] and another doublet at g 1.987 [$a(^1H)$ 8 G] attributed to $(cp)_2ZrH$ (**4**) by comparison with the analogous hydrides obtained in other ways by Samuel[8] and Petersen.[2] When diphenylacetylene was added to the mixture before heating a doublet was seen at g 1.992 [$A(^{91}Zr)$ 24 G; $a(^1H)$ 5.5 G] due to $(cp)_2ZrH(PhC{\equiv}CPh)$ (**5**) also described previously.[2,8]

When performed in the presence of a tertiary phosphine such as PPh_2Me, PMe_3, $Ph_2PCH_2PPh_2$, with a $PR_3/$(**1**) ratio of *ca.* 10, the thermolytic reduction led to variable proportions of two stable new species (**6**) [doublet of doublets at g 1.988; $A(^{91}Zr)$ 24 G] and (**7**) [doublet at g 1.981; $A(^{91}Zr)$ 23 G] as shown in Figure 1(a), possibly accompanied at the beginning of the reaction by small amounts of (3) and eventually (**4**) [the absence of $(cp)_2Zr(PR_3)_2$ was supported by ^1H and ^{31}P n.m.r. data[3]].§ The selectivity towards (**6**) may be enhanced by increasing the $PR_3/$(**1**) ratio [Figure 1(b)]. It is noteworthy that the same species (**6**) and (**7**) were obtained when the dihydride $(cp)_2ZrH_2$ was heated in toluene at 60 °C in the presence of PPh_2Me. The species (**6**) giving the doublet of doublets is assigned the monophosphine zirconium(III) hydride structure $(cp)_2ZrH(PR_3)$ on the basis of the superhyperfine coupling constants: a $(^{31}P) = 29$ G whatever the phosphine; $a(^1H) = 3$ G for PPh_2Me, 6 G for PMe_3, and 4 G for $Ph_2PCH_2PPh_2$ (acting as a monophosphine). The $a(^{31}P)$ value is not very different from those recently reported for other Zr^{III} phosphine complexes.[1,7,9,10] In fact, as far as we know, there is no example of a similar zirconium(III) hydride adduct mentioned in the literature although the analogous derivative of titanium has been known for a long time and gives a similar doublet of doublets [$a(^{31}P)$ 24.6 G; $a(^1H)$ 10.0 G].[11] Remarkably, in the photolysis of $(\eta^5\text{-}C_5H_4Me)_2ZrH_2$ in the presence of PPh_3, Petersen[2] observed the formation of a reduced species, of unknown structure, giving only a doublet [$a(^{31}P)$ 24.3 G] without any coupling to ^1H. In known zirconium hydrides, $a(^1H)$ values are generally in the range 8—5.5 G as seen above. Values as low as 4 and 3 G have not been mentioned and are probably typical of this class of adduct.

Assignment of the species (**7**) giving the doublet is more difficult. The coupling constant $a(^{31}P)$ of 17 G is indicative of one phosphorus atom bonded to Zr^{III}. Moreover thermolysis of (**1**) as well as of $(\eta^5\text{-}C_5H_5)_2ZrH_2$ in the presence of $PPhMe_2$ gave (**7**) as the predominant product [Figure 1(c)], accompanied by visually detectable evolution of H_2. On the basis of the latter experiments, we tentatively propose for (**7**) a formula corresponding to the metallation of the phosphine. For instance, in the case of $PPhMe_2$ we assume that the evolution of hydrogen may be explained by the reaction of (**6**) to give (**7**) shown in Scheme 1.

This assignment, although not completely unequivocal, is supported by numerous similar examples of metallation of alkyl and phenyl phosphines, for instance with ruthenium[12] or iridium[13] complexes, and was recently mentioned in the case of a zirconium(IV) hydride by Schwartz.[14]

Unexpectedly, we detected similar paramagnetic species in the reaction of $(cp)_2ZrCl(CH_2PPh_2)$ (**2**) with butyl-lithium. For instance, addition of a stoicheiometric amount of LiBu in hexane to (**2**) in toluene led to a paramagnetic solution containing (**3**) and (**4**) [comparable with the thermolysis of (**1**)]. Moreover, addition of PPh_2Me to the reduced solution and heating at 60 °C in a sealed tube gave rise to the formation of the hydride adduct (**6**). This may be explained by the initial formation of the unstable $(cp)_2ZrBu(CH_2PPh_2)$, which by β-elimination gives (**1**) as a short-lived intermediate under the experimental conditions, readily reduced to zirconium(III).

The main results of our work may be summarised by the reactions in Scheme 1.

A comparison between the present results concerning $(cp)_2ZrHR$ with $R = CH_2PR'_2$ and those for R = alkyl where zirconium(II) is directly obtained by reductive elimination of RH, indicates that the zirconium–carbon bond is stabilized by the presence of the phosphorus atom, Moreover, the easy cleavage of a carbon–hydrogen bond in PR_2 may be responsible for the metallation of the phosphino group in species (**7**).

Received, 24th September 1984; Com. 1349

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§ N.m.r. detection of diamagnetic species was possible although the solution was paramagnetic as previously reported in ref. 7(b).

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