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SOME COORDINATION COMPOUNDS OF ZIRCONIUM TETRABENZYL AND SOME REACTIONS IN WHICH THERE IS INSERTION INTO CARBON—ZIRCONIUM BONDS

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Summary

Zirconium tetrabenzyl ($ZrBz_4$) has been allowed to react with a number of nitrogen and oxygen donor ligands. Air-sensitive complexes of formula $ZrBz_4 \cdot 2L$, $ZrBz_4 \cdot L$ or $2ZrBz_4 \cdot L$ have been isolated and characterised by analysis and by NMR and IR spectroscopy. The reaction of $ZrBz_4$ with SO_2, PhNCO and MeNCS gave $ZrBz(SO_2Bz)_3$, $Zr[NPhC(=O)Bz]_4$ and $Zr(NMeC(=S)Bz)_4$ respectively.

Introduction

A substantial number of complexes of titanium(IV) in which the only metal—carbon bonds present are of the σ type are known [1]. In contrast most of the zirconium(IV) species that have been reported to contain σ-metal—carbon bonds also contain π-bonded aromatic rings e.g. π-$(C_5H_5)_2Zr(CH_3)_2$ [2]. The major exceptions are the elimination-stabilised alkyls e.g. $Zr(CH_2CMe_3)_4$ [3,4] and $ZrBz_4$ (Bz = CH_2—Ph) [5,6]. Of these two species the tetrabenzyl has received most attention. Zucchini et al. [5] reported its preparation and reaction with O_2 and CO_2, while Felten and Anderson [7] studied its NMR spectrum in solutions containing Lewis bases. Only one solid complex of $ZrBz_4$ has been previously reported, namely $ZrBz_4 \cdot 2,2'$-bipyridyl [7,8].

It has been said that the kinetic stability of early transition metal alkyls can be increased by the use of alkyl groups that do not contain β-hydrogen atoms or by the formation of Lewis acid—base complexes. Accordingly we have taken an elimination-stabilised alkyl, namely $ZrBz_4$ and prepared from it various coordination compounds to see if the kinetic stability of an elimination-stabilised alkyl is enhanced by complex formation.

There have been a number of studies of insertion reactions into zirconium—carbon bonds. SO_2 and NO have been reacted with π-$(C_5H_5)_2ZrMe_2$ to give π-$C_5H_5Zr(SO_2C_5H_5)(SO_2Me)_2$ and π-$(C_5H_5)_2Zr(O_2N_2Me)Me$ [2,9]. More recently

TABLE 1

DATA RELATING TO COORDINATION COMPOUNDS

Ligand	Complex	Analysis calcd. (%)		Analysis found (%)		Position of benzyl CH$_2$ resonance (τ) (CH$_2$Cl$_2$ soln.)	Colour	ν(M–C) (cm^{-1})	Temperature at which decomposition became apparent (°C)
		Zr	N	Zr	N				
	ZrBz$_4$	20.0		19.8		8.60 (8.47)^a	yellow	472	
2,2-Bipyridyl	ZrBz$_4$· 2,2-bipy	14.9	4.6	14.7	4.5	7.77	red	462	250
4,4-Bipyridyl	ZrBz$_4$· 4,4-bipy	14.9	4.6	15.3	4.6	^{b}	purple	465	
Pyridine	ZrBz$_4$· py				^{c}	8.10	orange (oil)		
2-Methylpyridine	ZrBz$_4$· (2mpy)	16.6	2.5	16.6	2.4	8.30	yellow	461	250
	ZrBz$_4$· 2(2mpy)	14.2	4.4	14.2	4.5	8.34	light yellow		
Quinoline	ZrBz$_4$· 2quin	12.8	3.9	12.5	4.1	(7.74)^a	brown	462	
Thioxan	2ZrBz$_4$· thiox	18.0	3.1^d	18.2	3.4^d	8.55	yellow	460	
Tetrahydrofuran	ZrBz$_4$· thf	17.2		17.2		8.50	yellow	465	
2-Cyanopyridine	ZrBz$_4$· (2-cpy)	16.4	5.0	16.7	5.1	^{b}	brown		130
3-Cyanopyridine	ZrBz$_4$· 2 (3-cpy)	13.7	8.4	13.6	8.2	^{b}	orange	450	
4-Cyanopyridine	ZrBz$_4$· 2 (4-cpy)	13.7	8.4	15.0	8.2	^{b}	yellow	450	
Pyrazine	ZrBz$_4$· pyra	17.0	5.2	16.7	5.2	^{b}	yellow	465	
Pyridazine	ZrBz$_4$· 2pyd	15.0	9.1	15.1	8.5	^{b}	brown	462	
p-Phenyline diamine	ZrBz$_4$· (*p*-NH$_2$PhNH$_2$)	16.2	5.0	15.9		^{b}	yellow	460	

^{a} NMR signal in benzene. ^{b} Species not soluble in suitable solvent for NMR. ^{c} Only an oil obtained; NMR integration ratios suggest 1/1 complex. ^{d} % S.

$ZrBz_4$ has been shown to undergo insertion reactions with CO to give polymeric products via $\{Zr\{C(=O)CH_2R\}\}$ [10]. We have extended the number of unsaturated species that have been reacted with $ZrBz_4$ and report reactions with NO, SO_2, PhNCO, and MeNCS.

Results and discussion

(i) Coordination compounds

Table 1 lists the coordination compounds prepared together with the analytical data we were able to obtain. The analytical data are repeatable but we failed to obtain reliable carbon and hydrogen analyses because of the extreme air and moisture sensitivity of the species. Attempts to obtain solid complexes with PhCN, CH_3CN, pyridine and dioxan were unsuccessful, and these results parallel those of Felten and Anderson [7] who found no shift in the benzyl methylene NMR resonance for a number of $ZrBz_4$ solutions containing weak donors.

A number of the species of the types $ZrBz_4 \cdot L$ (L = 2-cyanopyridine, pyrazine, 4,4'-bipyridyl or *p*-phenyline diamine) and $ZrBz_4 \cdot 2L$ (L = 4-cyanopyridine, 3-cyanopyridine and pyrazidine) were too insoluble in suitable solvents for NMR spectra to be obtained and in these cases only IR spectra and analytical evidence are avaiable to aid structural assignments. The IR spectra of the 1/1 adducts indicate that in every case both donor atoms are coordinated. For example, in $ZrBz_4$ (2cpy), $\nu(C{\equiv}N)$ has risen in frequency to 2270 cm^{-1}(free ligand $\nu(C{\equiv}N) = 2225$ cm^{-1}) and the bands that are associated with the ring nitrogen atom show the shifts that are expected to occur on coordination. It thus appears that 2-cyanopyridine acts as a bidentate donor most probably bridging two zirconium atoms. In contrast, for the insoluble species of the type $ZrBz_4 \cdot 2L$ the evidence from their IR spectra indicates that the ligands are acting as monodentate donors. In the complexes formed with 4-cyanopyridine and 3-cyanopyridine donation being through the ring nitrogen atom. For the species $ZrBz_4 \cdot L$ (L = 2,2'-bipyridyl, 2-methylpyridine and tetrahydrofuran) $ZrBz_4 \cdot 2$-quinoline and $2ZrBz_4 \cdot$thioxan both NMR and IR spectra were obtained. The IR spectra are typical of the coordinated ligands and in the case of 2,2'-bipyridyl and thioxan show that both donor atoms are coordinated. For the soluble species the integration ratios obtained from the NMR spectra agree with the formulation assigned to the species on the basis of analytical evidence.

The most interesting feature of the NMR spectra are the shifts of the benzyl methylene resonances (Table 1). The shifts for $ZrBz_4 \cdot 2,2'$-bipy, $ZrBz_4 \cdot$thf and $ZrBz_4 \cdot$py agree with those previously reported [7]. For the nitrogen donors the size of the shift in the methylene resonance is not directly related to the pK_a of the ligand but perhaps this is not surprising as pK_a's are measured in aqueous media and the metal—nitrogen bond length may vary in these complexes. What is rather unexpected is that the resonances shift down field. In Me_2NbCl_3 for example the alkyl resonance shifts to higher field on the formation of adducts [11]. The six-coordinate species $ZrBz_4 \cdot 2,2'$-bipy and $ZrBz_4 \cdot$ 2quin (if it were in the *cis* form) should both show two benzyl methylene resonances but we only observed singlets even at low temperature.

The position of a band tentatively assigned to $\nu(M{-}C)$ are recorded in

Table 1. It is noticeable that the band shifts to lower frequency on the formation of adducts. ν(M—C) have been assigned for similar elimination-stabilised zirconium alkyls [4] and the positions found for $Zr(Me_3CCH_2)_4$, ν(M—C) 530, 488 cm^{-1}, and $Zr(Me_3SiCH_2)_4$, ν(M—C) 457 cm^{-1}, make our assignment reasonable.

The thermostability of three of the complexes was studied by gradually warming the species on a vacuum line. The temperatures at which decomposition became apparent are recorded in Table 1. The 4,4'-bipyridyl and 1/1 2-methylpyridine adduct are remarkably stable compared with the parent alkyl [8] and only show appreciable decomposition at 250°C.

From this study we have shown that despite the poor Lewis acceptor properties of $ZrBz_4$ (by comparison with $ZrCl_4$) complexes can be prepared by reaction with strong donor molecules. It also appears that the stability of the elimination-stabilised alkyl is enhanced by the formation of adducts thus suggesting that some of the products formed during the thermal decomposition of $ZrBz_4$ [8] arise from a bimolecular process.

(ii) Insertion reactions

(a) Reaction with SO_2. When $ZrBz_4$ is dissolved in liquid sulphur dioxide a compound $ZrBz(SO_2Bz)_3$ is formed. Reaction of this species with acid failed to liberate sulphur dioxide thus showing the species to be as formulated and not to be an adduct of SO_2. Unfortunately we were unable to obtain NMR spectra because the species is insoluble in suitable solvents. However, its IR spectrum shows absorbances in the range 800—1100 cm^{-1} (at 900 and 1040 cm^{-1}) thus indicating that the species is an O-sulphinate [9,12]. Similar behaviour is seen with π-$(C_5H_5)_2ZrMe_2$ and π-$(C_5H_5)_4Zr$ both of which only take up three moles of SO_2. However, $Zr(SO_2Me)_4$ can be prepared thus the failure to substitute all four metal carbon bonds in $ZrBz_4$ is probably due to steric rather than electronic reasons.

(b) Reaction with PhNCO. Excess PhNCO reacted with $ZrBz_4$ to yield a compound that IR measurements indicated was $Zr[NPhC(=O)Bz]_4$. The IR spectrum of the white species does not show a band ca. 2300 cm^{-1} attributable to ν_{asym}(N=C=O) but there is a strong carbonyl band at 1560 cm^{-1} as shown by coordinated carbonyl groups. The NMR spectrum (in $CDCl_3$) shows a singlet at τ 6.50 assignable to a benzyl methylene group bound to the carbon of N=C=O. The integration ratio of the NMR spectrum agrees with the formulation. The species is stable and it can be stored indefinitely at room temperature. Its melting temperature is 85°C and it can be maintained at 118°C for sometime before visible decomposition occurs.

(c) Reaction with MeNCS. The reaction of $ZrBz_4$ with methylisothiocyanate parallels that with phenylisocyanate in that insertion occurs and four mols of MeNCS are taken up to give $Zr[MeNC(=S)Bz]_4$. The nature of the compound is indicated by its IR spectrum; there being no band at 2150 cm^{-1} (ν_{asym}(N=C=S)) but a characteristic band at 1540 cm^{-1} and thioacetamide bands at 1240 and 720 cm^{-1} [14,15]. The NMR spectrum (in $CDCl_3$) shows aliphatic proton resonances at τ 6.14 (benzylmethylene) and τ 6.90 (N—CH_3).

(d) Reaction with NO. Nitric oxide has been shown to insert into a number of transition metal carbon bonds, two molecules inserting into each

bond [2,16]. Prolonged reaction of nitric oxide with $ZrBz_4$ formed a species in which five molecules of nitric oxide had been incorporated. The NMR spectrum exhibits two benzyl methylene resonances τ 4.9 and τ 5.0 and the IR spectrum does not show bands typical of coordinated NO but does have bands indicative of a ON(Bz)NO moiety [2,16]. Previous results [2,16] would suggest the product is a mixture of two species in which insertion has occurred in two and three bonds respectively. Variation in reaction time and attempts at purification by recrystallisation did not yield pure products. This study of insertion reactions has shown that even though the zirconium—carbon bonds of $ZrBz_4$ are thermally stable they are extremely reactive towards certain unsaturated species.

Experimental

All preparative procedures were carried out in the absence of oxygen or moisture. The adducts were isolated by filtration on an all-glass vacuum line.

Preparations

Zirconium tetrabenzyl was prepared as previously described [5]. The NMR of the product was in accord with published data.

(i) Coordination compounds

$ZrBz_4$· L (L = 2,2'-bipyridyl, 4,4'-bipyridyl, p-phenyline diamine, 2-cyanopyridine, pyrazine and 2-methylpyridine) and $ZrBz_4$· 2L (L = pyridazine, 4-cyanopyridine, 3-cyanopyridine, quinoline and 2-methylpyridine). For $ZrBz_4$· L 0.011 mol of ligand, and for $ZrBz_4$· 2L 0.022 mol of ligand, were allowed to react with a benzene solution (25 ml) that contained 0.01 mol of $ZrBz_4$. The resulting solution was stirred for 2 h. With the exception of the experiment with quinoline a solid precipitated during the stirring procedure. The solid was filtered off and pumped to dryness. The quinoline adduct precipitated on removal of some of the solvent. When 0.04 mol of 2-methylpyridine was used $ZrBz_4$(2mpy) was formed. On evaporation of the solution from which $ZrBz_4$ 2(2mpy) had precipitated $ZrBz_4$(2mpy) was obtained.

2$ZrBz_4$· thioxan and $ZrBz_4$· thf. 0.04 mol of ligand was added to 0.01 mol of $ZrBz_4$ dissolved in benzene (25 ml). The solution was stirred for 30 min and then pumped to dryness.

(ii) Insertion reactions

$ZrBz(SO_2Bz)_3$. Sulphur dioxide was condensed onto $ZrBz_4$ and the solution stirred for 1 h while the temperature was maintained at 20°C. The solvent was then allowed to evaporate leaving a yellow solid. Found: Zr, 14.0; S, 15.0; C, 50.5; H, 4.6. $ZrBz(SO_2Bz)_3$ calcd.: Zr, 14.1; S, 14.8; C, 51.9; H, 4.3%.

Zr(PhNC(=O)Bz)$_4$ and Zr(MeNC(=S)Bz)$_4$. Excess of L (L = PhNCO or MeNCS) was added to $ZrBz_4$ (0.005 mol) dissolved in 25 ml of 50/50 (v/v) n-pentane—toluene solution. The reaction was shielded from the light and stirred at −10°C for 18 h. Zr[PhNC(=O)Bz]$_4$ precipitated from the reaction medium, the other product was obtained by evaporating the reaction to dryness. The products were washed with n-pentane to remove excess L. (a) Found: Zr, 9.4; N, 6.0; C, 72.1; H, 5.9. Zr[PhNC(=O)Bz]$_4$ calcd.: Zr, 9.5; N, 6.0; C, 72.2; H, 5.2%. (b) Found: Zr, 12.6; S, 16.2; N, 7.4. Zr(MeNC(=S)-Bz)$_4$ calcd.: Zr, 12.2; S, 17.1; N, 7.5%.

The reaction of NO with ZrBz$_4$. Nitric oxide was bubbled at −80°C through 25 ml of a toluene—n-pentane solution (40/100, v/v) containing 0.005 mol of ZrBz$_4$. Immediate reactions took place and a yellow solid precipitated.

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