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SOME COORDINATION COMPOUNDS OF PHENYLZIRCONIUM TRICHLORIDE

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Summary

Phenylzirconium trichloride has been isolated as its tetrahydrofuran adduct $PhZrCl_3 \cdot 3thf$ (I). The reaction of I with a range of nitrogen, phophorus and sulphur ligands gave products of stoichiometry $PhZrCl_3 \cdot thf \cdot L$ (L = 2,2′-bipyridyl, 4,4′-bipyridyl, 2-methylpyridine or triphenylphosphine) and $PhZrCl_3 \cdot thf \cdot 2L'$ (L′ = pyridine, PhCN or 1,4-thioxan). Reaction of I with methyl cyanide gave $PhZrCl_3 \cdot 2CH_3CN$, which reacted with bidentate donors to give complexes of formula $PhZrCl_3 \cdot L$ (L = 2,2′-bipy, 4,4′-bipy or $Ph_2PCH_2CH_2PPh_2$). The adducts were characterised by analysis, NMR and infrared spectroscopy.

Introduction

A range of adducts of $RTiCl_3$ are known, the most widely studied being $MeTiCl_3$ [1—3], but in contrast there are few reports of analogous zirconium species. $RZrCl_3$ (R = CH_3, C_2H_5 and C_3H_7) have been reported to be formed in toluene at 0° and $R_2ZrX_2 \cdot 2,2'$-bipy has been isolated [4]. Our attempts to synthesise CH_3ZrCl_3 were unsuccessful but we were able to prepare $PhZrCl_3$ as its tris-tetrahydrofuran adduct. The only related reports of phenylzirconium species discuss the preparation of Ph_4Zr (which was not isolated because of its thermal instability) and the etherate of Ph_2Zr [5].

Results and discussion

$PhZrCl_3 \cdot 3thf$ (I) is formed when equimolar amounts of zirconium tetrachloride and phenylmagnesium chloride are reacted in toluene at 0°. The yellow-brown solid I is extremely sensitive to air and moisture so that carbon and hydrogen analyses were precluded. However, the compound showed no measureable decomposition when stored under nitrogen at room temperature over a period of several hours. This thermal stability is in contrast to that reported

TABLE 1

Ligand; adduct	Analysis found (calcd.) (%)			Colour	Reaction time (h)	Infrared bands of coördinated thf(cm^{-1})		ν(Zr—C)
	Zr	Cl	N			$\nu_{asym}(COC)^a$	$\nu_{sym}(COC)^a$	
Tetrahydrofuran								
$PhZrCl_3 \cdot 3thf$	18.5 (18.4)	21.6 (21.4)		Yellow-brown	4	1025	860	475
2,2′-Bipyridyl								
$PhZrCl_3 \cdot thf \cdot 2,2'$-bipy	18.0 (18.0)	21.4 (21.0)	6.7 (5.6)	Yellow	2	*b*	886	471
$PhZrCl_3 \cdot 2,2'$-bipy	21.8 (21.2)	24.5 (24.6)	6.2 (6.5)	Yellow	2			469
4,4′-Bipyridyl								
$PhZrCl_3 \cdot thf \cdot 4,4'$-bipy	18.0 (18.0)	21.2 (21.0)	6.3 (5.6)	White	2	1010	840	*c*
$PhZrCl_3 \cdot 4,4'$-bipy	20.5 (21.2)	23.6 (24.6)	7.5 (6.5)	Yellow	2			*c*
Pyridine								
$PhZrCl_3 \cdot thf \cdot 2py$	18.0 (18.0)	20.7 (20.9)	5.3 (5.5)	Yellow	2	1009	870	*c*
2-Methylpyridine								
$PhZrCl_3 \cdot thf \cdot (2\text{-mpy})$	20.5 (20.6)	23.9 (24.0)	2.8 (3.2)	Yellow	2	1020	865	470
Triphenylphosphine								
$PhZrCl_3 \cdot thf \cdot tpp$	14.0 (14.9)	17.7 (17.4)		Yellow	2	1020	860	*c*
PhCN								
$PhZrCl_3 \cdot thf \cdot 2PhCN$	17.0 (16.4)	19.9 (19.1)	6.1 (5.1)	Brown	2	1025	878	*c*
Thioxan								
$PhZrCl_3 \cdot thf \cdot 2thiox$	15.6 (16.4)	19.3 (19.1)		Orange	2	1002	844	*c*
MeCN								
$PhZrCl_3 \cdot 2CH_3CN$	27.2 (25.6)	31.0 (29.8)	8.5 (7.9)	Grey	48			450^d
$Ph_2PCH_2CH_2PPh_2$								
$PhZrCl_3 \cdot dppe$	13.3 (13.5)	16.0 (15.8)		Yellow	2			474

[a] Free thf ν_{asym}(COC) 1069 cm^{-1}; ν_{sym}(COC) 911 cm^{-1}. [b] The presence of two bands in the 1000—1040 cm^{-1} region prevented a definite assignment. [c] Band too weak to be observed or obscured by ligand vibration. [d] Band extremely broad.

TABLE 2

NMR SPECTRA IN CH_2Cl_2[a]

Compound	Zr—Ph	Ligand resonances (assignments in brackets)[b]
Tetrahydrofuran		
$PhZrCl_3 \cdot 3thf$	2.64[c]	5.90 (α-protons), 8.04 (β-protons)
$ZrCl_4 \cdot 2thf$		5.93 (α-protons), 7.97 (β-protons)
2,2′-Bipyridyl		
$PhZrCl_3 \cdot thf \cdot 2,2'$-bipy	d	6.20 (α-protons), 8.30 (β-protons)
Pyridine		
$PhZrCl_3 \cdot thf \cdot 2py$	2.64	6.00 (α-protons), 8.04 (β-protons)
2-Methylpyridine		
$PhZrCl_3 \cdot thf \cdot (2\text{-}mpy)$	2.67	5.95 (α-protons), 8.04 (β-protons), 7.27 (CH_3)
Triphenylphosphine		
$PhZrCl_3 \cdot thf \cdot tpp$	d	5.90 (α-protons), 8.02 (β-protons)
Phenyl cyanide		
$PhZrCl_3 \cdot thf \cdot 2PhCN$	2.70[d]	6.10 (α-protons), 8.10 (β-protons)
Thioxan		
$PhZrCl_3 \cdot thf \cdot 2thiox$	2.69	6.00 (α-protons), 8.15 (β-protons), 6.10 (CH_2—O), 7.20 (CH_2S)
1,2-Bis(diphenylphosphino)ethane		
$PhZrCl_3 \cdot dppe$	2.65[d]	6.75[e] (CH_2—P)

[a] CH_2Cl_2 used as an internal standard (τ 4.67), see ref. 10. [b] α—β protons refer to thf resonances. [c] Phenyl resonance appeared as a broad singlet. C_6H_6 in CH_2Cl_2 resonance at (τ 2.57). [d] Aromatic protons of phenyl bonded to zirconium indistinguishable from ligand resonances. [e] Signal observed as a complex multiplet.

for tetraphenylzirconium [5] and adducts of methyltitanium trichloride [2]. From its formulation the most likely stereochemistries for I are a seven-coordinate complex (of which there are a number of examples known for zirconium(IV) [6]), or six-coordinate species with either an uncoordinated molecule of tetrahydrofuran, or an ionic species with Cl^- in the lattice. Unfortunately throughout this study we were unable to obtain molecular weight or conductivity measurements because I and the other products are not soluble in suitable solvents. The infrared spectrum of I indicates that all three molecules of tetrahydrofuran are coordinated (Table 1). Thus ν_{asym}(COC) is found at 1025 cm^{-1} and ν_{sym}(COC) at 860 cm^{-1} (free ligand bands at 1069 and 911 cm^{-1}). The NMR spectrum also indicates that coordination has taken place (Table 2). The α methylene resonances have shiften by τ 0.50 and β methylene resonances of τ 0.20 and indeed the positions of the resonances exhibited by I are comparable with those of $ZrCl_4 \cdot 2thf$ (Table 2).

I is soluble in tetrahydrofuran and by its reaction with a range of ligands compounds of formula $PhZrCl_3 \cdot thf \cdot L$ (L = 2,2′-bipyridyl, 4,4′-bipyridyl, 2-methylpyridine or triphenylphosphine) and $PhZrCl_3 \cdot thf \cdot 2L'$ (L′ = pyridine, PhCN, or 1,4-thioxan) were obtained. (See Table 1 for analytical data.) As with I it is difficult to assign stereochemistries to these species. In all cases the ligand infrared spectra show L and L′ to be coordinated. For example in the pyridine type bases the infrared bands that are ca. 1580 cm^{-1} in the free ligands move to higher frequency. 1,4-Thioxan is capable of a number of modes of coordination. These are, as a bidentate donor through both the oxygen and sulphur atoms, or singly through either of the two donor atoms. The infrared spectrum of $PhZrCl_3 \cdot thf \cdot 2thiox$ shows the COC modes to be in the position observed in the free ligand thus indicating that the oxygen atom is not coordinated, while the CSC modes are too weak to establish whether any significant shift in frequency has taken place. The NMR spectrum (Table 2), although complicated by the close proximity of the α methylene resonances of tetrahydrofuran and the resonance of the methylene groups adjacent to oxygen in 1,4-thioxan, clearly indicates that coordination through sulphur has taken place. Thus the resonance of the methylene group adjacent to oxygen has shifted by τ 0.10 while that of the group adjacent to sulphur is altered by τ 0.30.

The single molecule of tetrahydrofuran that appears in $PhZrCl_3 \cdot thf \cdot L$ and $PhZrCl_3 \cdot thf \cdot 2L'$ is coordinated, since the infrared spectra show changes in the COC modes (Table 1) while the NMR spectra exhibit changes in the α and β methylene resonances (Table 2). With these species we were again unable to make molecular weight measurements.

In order to synthesise from I adducts containing no tetrahydrofuran it was allowed to react in non-donor solvents with a range of donor ligands. All these attempts failed, the products being either non-stoichiometric or the same as those formed by reaction in tetrahydrofuran. However, prolonged reaction of I in neat methyl cyanide afforded a grey coloured solid, $PhZrCl_3 \cdot 2CH_3CN$. This methyl cyanide adduct is insoluble in methyl cyanide and dichloromethane accordingly we were unable to obtain a NMR spectrum. The infrared spectrum shows the expected increase in ν(CN) (ca. 25 cm^{-1}). From $PhZrCl_3 \cdot 2CH_3CN$ attempts were made to prepare other compounds by ligand replacement reactions. The only successful experiments involved strong bidentate donors which gave $PhZrCl_3 \cdot L$ (L = 2,2′-bipyridyl, 4,4′-bipyridyl and $Ph_2PCH_2CH_2PPh_2$). The 2,2′-bipyridyl adduct unlike $PhZrCl_3 \cdot thf \cdot$ 2,2′-bipy is completely insoluble in dichloromethane thus precluding NMR measurements. The infrared spectra of al three $PhZrCl_3 \cdot L$ are as expected and indicate coordination has taken place. The species $PhZrCl_3 \cdot thf \cdot L$ (L = 2,2′-bipy or 4,4′-bipy) can be obtained by dissolving $PhZrCl_3 \cdot L$ (L = 2,2′-bipy or 4,4′-bipy) in tetrahydrofuran.

Table 2 records the position of the phenyl—zirconium NMR resonance. The NMR resonance occurred as a rather broad singlet in contrast to the multiplet reported for $(\pi\text{-}C_5H_5)_2ZrPh_2$ [7]. The suggestion that decomposition to benzene is taking place can be discounted as the benzene resonance occurs at τ 2.57 in dichloromethane. (See Table 2.)

The infrared spectra of all the complexes in the region 6000—250 cm^{-1} contain a broad band at 300 cm^{-1} assignable to the zirconium—chlorine stretching modes. In the region ca. 475 cm^{-1} there occurs an absorption (Table 1) which we tentatively assign to a zirconium—carbon stretching mode. This band is obscured by ligand bands in some spectra but the position agrees with that assigned to ZrR_4 (R = $CH_2C(CH_3)_3$ or $CH_2{-}Si(CH_3)_3$) and $ZrBz_4$ [8,9].

This study of the coordination compounds of $PhZrCl_3$ has shown that they are kinetically more inert than the species formed by CH_3TiCl_3 [1,2] or $RZrCl_3$ (R = CH_3, C_2H_5 or C_3H_7) [4]. Presumably this decrease in reactivity is caused by the bulk of the phenyl group slowing down any bimolecular decomposition route and the lack of an easy pathway for β elimination. This is perhaps amplified by the failure of our attempts to insert SO_2, PhNCS, MeNCS into the phenyl—zirconium bond.

Experimental

General

All operations were carried out on an all-glass vacuum line. Samples for the measurement of spectra were prepared in a dry-box. NMR spectra were obtained on a Varian T60 and infrared spectra with a Perkin—Elmer 457. Analyses were carried out using conventional classical methods.

Preparations

(i) $PhZrCl_3\cdot 3thf$ *(I)*

Equimolar quantities (0.05 mol) of zirconium(IV) chloride and phenylmagnesium chloride (prepared in thf) were allowed to react in toluene (100 ml) at 0°. After four hours the resulting brown solution was filtered free from magnesium halides and any unreacted zirconium(IV) halide. The solvent was removed at the pump to give a yellow-brown solid which was stored at — 80° under nitrogen.

(ii) $PhZrCl_3\cdot thf\cdot 2,2'$*-bipy,* $PhZrCl_3\cdot thf\cdot 4,4'$*-bipy, and* $PhZrCl_3\cdot thf\cdot 2py$

Excess of the ligands (0.03 mol) were allowed to react with 0.01 mol of I in 30 ml of thf at room temperature. The solid products were filtered off and thoroughly washed with fresh thf. The products were pumped for 2—3 h.

(iii) $PhZrCl_3\cdot thf\cdot (2mpy)$*,* $PhZrCl_3\cdot thf\cdot tpp$*,* $PhZrCl_3\cdot thf\cdot 2PhCN$*,* $PhZrCl_3\cdot thf\cdot 2thioxan$

Stoichiometric amounts of ligand and I (0.01 mol) were allowed to react at room temperature for 3 h. The resulting solids were isolated by filtration, washed with n-pentane and pumped to dryness. $PhZrCl_3\cdot$thf·2thioxan was prepared similarly to the above using a 1/2 molar ratio of I to ligand with benzene as the solvent.

(iv) $PhZrCl_3\cdot 2CH_3CN$*,* $PhZrCl_3\cdot 2,2'$*-bipy,* $PhZrCl_3\cdot 4,4'$*-bipy and* $PhZrCl_3\cdot dppe$

Compound I was dissolved in neat methyl cyanide and stirred for two days at 0°. A grey solid that analyses showed to be $PhZrCl_3\cdot 2CH_3CN$ was isolated by filtration. Stoichiometric amounts of L (L = 2,2'-bipy, 4,4'-bipy or $Ph_2PCH_2CH_2PPh_2$) and $PhZrCl_3\cdot 2CH_3CN$ were allowed to react in benzene at ambient temperature for 2 h. The products $PhZrCl_3\cdot L$ (L = 2,2'-bipy, 4,4'-bipy or $Ph_2PCH_2CH_2PPh_2$) precipitated from solution and were isolated by filtration.

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