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Fulvalene titanium and zirconium complexes: synthesis and NMR study of phosphanido-, alkyl-, and alkynyl-derivatives. X-ray crystal structures of $[\{Ti(\eta^5\text{-}C_5H_5)(\mu\text{-}PPh_2)\}_2\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}]$ and $[\{Zr(\eta^5\text{-}C_5H_5)(\mu\text{-}C{\equiv}CSiMe_3)\}_2\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}]$

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Abstract

Reaction of $[\{M(\eta^5\text{-}C_5H_5)(\mu\text{-}Cl)\}_2\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}]$ (M = Ti, **1**; Zr, **2**) or $[\{M(\eta^5\text{-}C_5H_5)Cl_2\}_2\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}]$, (M = Ti, **5**; Zr, **6**) with one or two equivalents of $LiPPh_2$ afforded the new phosphanidometal(III) complexes $[\{M(C_5H_5)(\mu\text{-}PPh_2)\}_2\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}]$, (M = Ti, **3**; Zr, **4**). Reaction of **2** with $LiC{\equiv}CSiMe_3$ led to the diamagnetic zirconium(III) alkynyl derivative $[\{Zr(C_5H_5)(\mu\text{-}C{\equiv}CSiMe_3)\}_2(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4]$, **7**. Alkylation of **6** with $LiCH_2CMe_2Ph$ gave $[\{Zr(\eta^5\text{-}C_5H_5)(CH_2CMe_2Ph)_2\}_2\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}]$, **8**. A detailed NMR study of complexes **3** and **4** allowed the observation of the spectral behaviour of the eight different fulvalene protons through their coupling to the ^{31}P nucleus. The fluxional behaviour of complex **7** was studied by dynamic DNMR, and kinetic parameters for the σ–π-conversion of the alkynyl ligand were determined. The molecular structures of complexes **3** and **7** were determined by X-ray diffraction methods.

Keywords: Titanium; Zirconium; μ-Phosphanido; Alkynyl; Fulvalene; Alkyl

1. Introduction

The chemistry of organo-homodimetallic complexes of the early transition metals, containing cyclopentadienyl-bridging ligands has received particular attention during recent years [1]. A range of different metal–metal interactions, from weak short contacts to strong bonds, have been found [2] in this type of binuclear compounds. The presence of these interactions can produce important modifications of the chemical behaviour in relation to that known for mononuclear complexes and, in some circumstances, gives rise to new reactivity patterns. The use of fulvalene $[\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$ formed by reductive coupling of two cyclopentadienyl rings [3] and *ansa*-dimethylsilyl-dicyclopentadienyl [4] $[\mu\text{-}SiMe_2(\eta^5\text{-}C_5H_4)_2]$ ligands has allowed the synthesis of a variety of homo-binuclear Group IV metal complexes. These two ligands facilitate the accessibility of rare low oxidation states, providing a better knowledge of their restricted chemistry [1c,4b,5]. We were interested in studying the synthesis and reactivity of new binuclear Group IV derivatives in oxidation states (III) and (IV). Here we report the isolation and structural characterization of new titanium and zirconium(III) phosphanido complexes $[\{M(\eta^5\text{-}C_5H_5)(\mu\text{-}PPh_2)\}_2\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}]$, (M = Ti, **3**; Zr, **4**), the alkynylzirconium complex $[\{Zr(\eta^5\text{-}C_5H_5)(\mu\text{-}C{=}CSiMe_3)\}_2\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}]$, **7**, which shows a σ,π-$C{=}CSiMe_3$ disposition and the tetraalkylzirconium(IV) complex $[\{Zr(\eta^5\text{-}C_5H_5)(CH_2\text{-}CMe_2Ph)_2\}_2\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}]$, **8**. A detailed NMR and DNMR study was carried out for **3**, **4** and **7** and the molecular structures of **3** and **7** were studied by X-ray diffraction methods.

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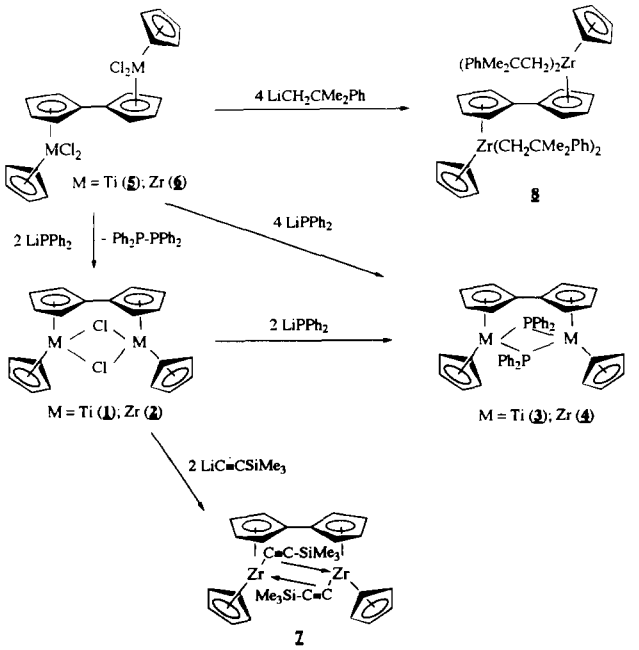
2. Discussion of synthetic and structural results

2.1. Phosphanido complexes

Reaction of $[\{M(\eta^5\text{-}C_5H_5)(\mu\text{-}Cl)\}_2\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}]$, (M = Ti, **1**; Zr, **2**) with $LiPPh_2$ at room temperature in toluene leads to metal(III) phosphanido complexes $[\{M(\eta^5\text{-}C_5H_5)(\mu\text{-}PPh_2)\}_2\{\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}]$, (M = Ti, **3**; Zr, **4**), as shown in Scheme 1. The same complexes **3** and **4** may also be obtained by reaction of the fulvalene metal(IV) chlorides $[\{M(\eta^5\text{-}C_5H_5)Cl_2\}_2\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}]$, (M = Ti, **5**; Zr, **6**) with four equivalents of $LiPPh_2$ at −78°C. The expected metal(IV) phosphanides that are probably formed in this reaction are spontaneously reduced to the titanium(III) and zirconium(III) derivatives. Similar behaviour was observed in the reaction of $[ZrCp_2Cl_2]$ with $LiPPh_2$, which was reported [6] to lead to the isolation of one of the first known zirconium(III) compounds, whereas the same reaction with $[Zr(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2]$ or $[ZrCpCp^*Cl_2]$ ($Cp^* = C_5Me_5$) led to the corresponding zirconium(IV) phosphanides [7].

However, the fulvalene titanium(IV) complex **5** reacts with two equivalents of $LiPPh_2$ to give the known [1c] paramagnetic titanium(III) complex **1** with elimination of tetraphenyldiphosphane.

The ^1H and ^{13}C NMR data for **3** and **4** are shown in Tables 1 and 2, respectively. The ^1H NMR spectrum of **4** in benzene-d_6 shows resonances from two inequivalent phenyl rings, one singlet for the cyclopentadienyl ring protons and two multiplets from the fulvalene protons (Fig. 1).



Scheme 1.

Table 1
^1H NMR data for the titanium and zirconium phosphanido complexes **3** and **4** (C_6D_6 solution at 293 K)

Assignment		3		4
	C_p	5.33 s (10H)		5.30 s (10H)
Ph:	H_{ortho}	7.44 d,d (4H)		7.70 d,d (4H)
		7.00 d,d (4H)		7.20 d,d (4H)
	H_{meta}	7.16 t (4H)		7.15 t (4H)
		6.90 t (4H)		7.00 t (4H)
	H_{para}	7.07 t (2H)		7.10 t (2H)
		6.75 t (2H)		6.80 t (2H)
Fulv.:	H_α	4.55 br (8H) [a]	3.58 br (4H) [b]	3.85 m (4H)
	H_β		5.03 br (4H) [b]	4.70 m (4H)

[a] $H_\alpha + H_\beta$.
[b] THF-d_8.

The multiplet at δ 4.7 corresponding to H_β (Fig. 1a) shows the characteristic AA' part of a AA'BB' spin system, whereas the multiplet at δ 3.85 corresponding to H_α (Fig. 1b) contains at least one additional coupling. Eight fulvalene protons would lead to a AA'A''A'''BB'B''B''' spin system [the protons AA' and A''A''', BB' and B''B''', belong to different fulvalene rings (Fig. 2)], and under certain circumstances it should be possible to observe coupling between H_α from different rings. The $H_\alpha\{H_\beta\}$ multiplet (Fig. 1c) represents the AA'A''A''' part of a AA'A''A'''XX' spin system, where X are the ^{31}P nuclei. Fig. 1d shows the theoretical multiplet obtained using the following coupling constants: $^4J_{H-H} = 2.7$ Hz (calculated from the multiplet assigned to H_β), $^3J_{H-P} = 7.3$ Hz, $^2J_{P-P} = 40$ Hz and $^5J_{H-H} = 0$ Hz. The presence of phosphorus as a magnetically and abundant active isotope is responsible for this spectral effect. The same spectroscopic effect has been detected, although not explained, in the ^1H NMR spectrum of $[\{Zr(\eta^5\text{-}C_5H_5)(\mu\text{-}PMe_2)\}_2\{\mu\text{-}\eta^5\text{-}(C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}]$ [8], whereas complexes containing bridging ligands other than phosphorus show two pseudo triplets corresponding to an AA'BB' spin sys-

Table 2
^{13}C NMR data for the titanium and zirconium phosphanido complexes **3** and **4** (C_6D_6 solution at 293 K)

Assignment		3	4
	C_p	101.3	99.4
Fulv.:			
	C_{ipso}	106.9	97.8
	C_α	97.5	92.3
	C_β	95.8	95.9
Ph:			
	C_{ipso}	150.5	149.5
			144.5
	C_{ortho}	139.0	138.9
		133.2	133.0
	C_{meta}	128	127.9
		126.9	126.8
	C_{para}	128	128
		125.2	124.7

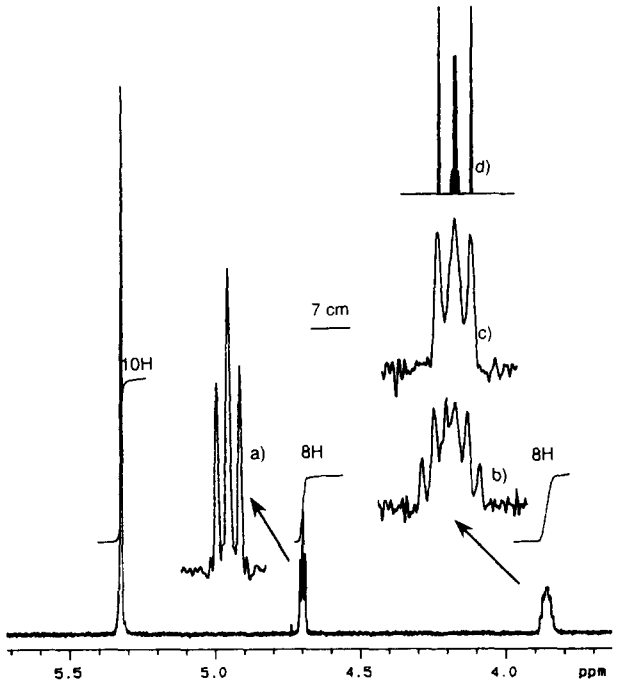


Fig. 1. ^1H NMR Spectra of **4** in C_6D_6 at 293 K. (a) H_β; (b) H_α normal; (c) H_α-{H_β}; (d) H_α theorethical.

tem [8]. Therefore, the signal at δ 3.85 corresponds to the A part of a six-spin system.

The ^1H NMR spectrum of **3** in THF-d_8 at 18°C has similar characteristics to those observed for **4**, (δ 5.03 for H_β and 3.58 for H_α), but the fulvalene proton signals are broader preventing resolution of the multiplets. However, the width of the H_α signal is more than double that of H_β, consistent with the previous discussion. The ^1H spectrum of the same complex in benzene-d_6 shows a single signal for the eight fulvalene protons (see Table 1).

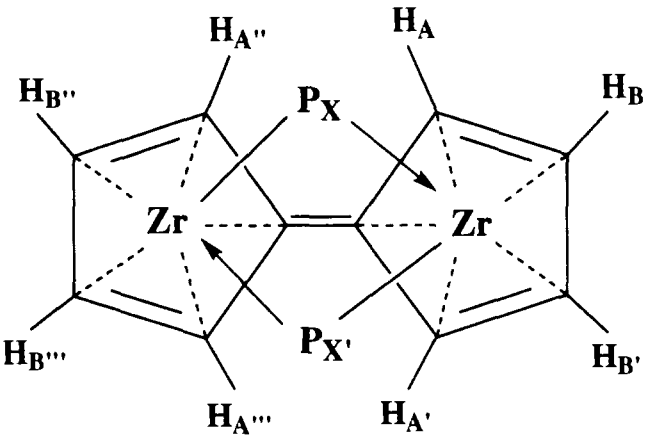


Fig. 2.

2.2. Alkynyl and alkyl complexes

When **2** is treated with LiC≡CSiMe$_3$ a reaction parallel to that reported [9] for LiC≡CPh takes place, leading to the related diamagnetic [9b] complex **7**, as shown in Scheme 1.

The ^1H and ^{13}C NMR data for **7** at 293 K are shown in Table 3. They show that protons and carbons on each fulvalene cyclopentadienyl ring are not equivalent, although both rings are equivalent. All the fulvalene ^1H NMR signals are broad. When the temperature is increased all the ^1H NMR signals broaden and move together. Coalescence of H_α signals (δ 4.80 and δ 4.39) is observed at 323 K ($\Delta G^{\#}323$ K = 15.1 kcal mol^{-1}), whereas the H_β signals (δ 5.43 and δ 4.69) coalesce at 333 K ($\Delta G^{\#}333$ K = 15.0 kcal mol^{-1}). A similar behaviour has been reported[9a] for the analogous zirconium complex with μ-C≡CPh. Kinetic parameters for this process were calculated (together

Table 3
^1H and ^{13}C NMR data for alkynyl- and alkyl-zirconium compounds **7** and **8** (C_6D_6 solution at 293 K)

Assignment		^1H				^{13}C	
		7		**8**		**7**	**8**
	C_p	5.53	10H	5.51	10H	101.0	109.9
Fulvalene.:		5.43 br	2H	5.56 t	4H	107.1	106.4
		4.80 br	2H	5.67 t	4H	100.6	109.3
		4.69 br	2H			97.3	
		4.39 br	2H			95.0	
						104.8 C_{ipso}	
Me_3Si		0.26	18H			1.4	
Acetylene:	$C\alpha$					231.9	
	$C\beta$					138.9	
Neophyl				0.72 d 4H,CH_2			34.3 C-CH_3
				J = 11.5 Hz			35.4 C-CH_3
				1.08 d 4H,CH_2			43.1 C-CH_3
				J = 11.7 Hz			74.5 CH_2
				1.37 s 12H,Me			106.4 C_5H_4
				1.38 s 12H,Me			109.3 C_5H_4
				7.26, 7.37 m,Ph			109.9 C_5H_5
							126–130 Ph

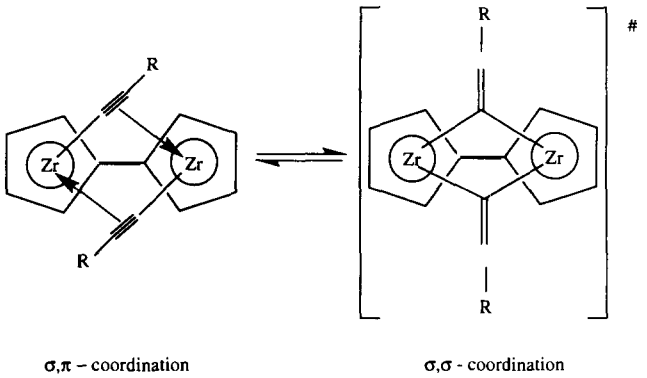


Fig. 3.

with similar data obtained for [{Zr(η^5-C_5H_5)(μ-C≡CPh)}$_2$(μ-(η^5-C_5H_4-η^5-C_5H_4)}] [9a] by using the dynamic NMR data and a complete line-shape analysis [10], as shown in Table 4.

The measured log A values indicate [10] that the process is an intramolecular transformation through a transition state characterized by C_s symmetry, instead of the C_{2v} symmetry corresponding to the ground state. Moreover, the almost zero values of $\Delta S^{\#}$ indicate that no bond breaking is required to reach the transition state. Therefore the dynamic process is related only to the mode of coordination of the alkynyl, changing from a σ–π-bonded group in the ground state to a σ–σ-bonded group in the transition state, as shown in Fig. 3.

A similar dynamic process has been observed [11] for methyl- and phenyl-alkynyl zirconium complexes [{ZrCpR}$_2$]. The $SiMe_3$ derivative, and the methyl complexes [11], require higher $\Delta G^{\#}$ than phenyl compounds, because of the lower total energy required by the phenyl complexes to reach the transition state, which is stabilized by the phenyl π electrons (Fig. 4).

Very few fulvalene titanium and zirconium(IV) alkyls are known because of the low reactivity [1a,1c] of the insoluble starting products **5** and **6**. Reaction of **6** with four equivalents of $LiCH_2CMe_2Ph$ in toluene at −78°C gives a yellow crystalline solid characterised as [{Zr(η^5-C_5H_5)(CH_2CMe_2Ph)$_2$}$_2$(μ-(η^5-C_5H_4-η^5-C_5H_4)}], **8**, as shown in Scheme 1. The mass spectrum confirms the formulation proposed for **8**. Complex **8** is very soluble in aromatic hydrocarbons, but slightly soluble in alkanes, from which it can be crystallized on cooling. It is sensitive to air, but remains unaltered for weeks under argon. Further studies on the reactivity of this and related species will be reported.

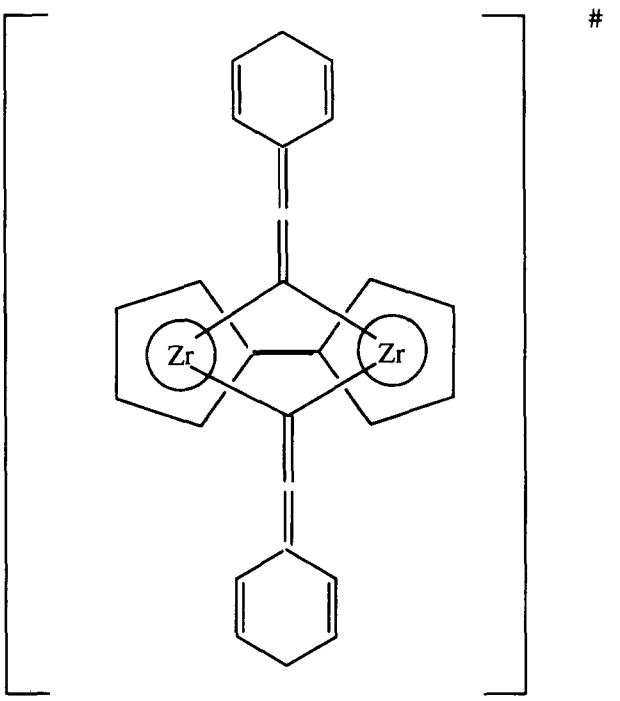


Fig. 4.

The ^1H spectrum for **8** in benzene-d_6 (Table 3) shows the AA'BB' spin system corresponding to the fulvalene group. This indicates the existence of a plane of symmetry containing the two metal and the two fulvalene C_{ipso} atoms. The methylene protons of the alkyl group show the expected diastereotopic [12] character because of the presence of a prochiral zirconium centre, giving rise to two doublets of doublets at δ 1.37 and 1.38.

The structures of [{TiCp(μ-X)}$_2$(μ-(η^5-C_5H_4-η^5-C_5H_4)}] (X = H, O, or Cl) were reviewed when the structure of the di-hydrido compound was determined [13]. It was found that all of the structures have the same form. The refinement of structure **3** is not very good, but is sufficient for the structure to be elucidated. Complex **3** has the same structure as earlier doubly bridged complexes, but is unusual in that there is no symmetry within the molecule itself, which is probably because of the larger bulk of the bridging group.

Table 4
Kinetic parameters of dynamic processes for alkynyl zirconium derivatives [M(C_5H_5)(μ-C≡CR)]$_2$(μ-η^5-η^5-$C_{10}H_8$)

R	E_a kcal mol^{-1}		log A	$\Delta H^{\#}$ kcal mol^{-1}		$\Delta S^{\#}$ u.e	$\Delta G^{\#298\,K}$
Ph	12.8 ± 0.4		13.8 ± 0.5	12.5 ± 0.4		−2.3 ± 1.8	13.7
		r = 0.998			r = 0.998		
Me_3Si	15.4 ± 0.4		13.4 ± 0.2	14.8 ± 0.4		+0.8 ± 1.2	14.6
		r = 0.999			r = 0.999		

Table 5
Fractional atomic coordinates for **3**

Atom	x	y	z
Ti(1)	0.3383(3)	0.0589(4)	0.2936(2)
Ti(2)	0.1154(3)	−0.0049(4)	0.3591(2)
P(1)	0.1900(4)	−0.0529(5)	0.2551(3)
P(2)	0.2823(4)	−0.0165(6)	0.3998(3)
C(1)	0.2086(9)	−0.2167(11)	0.2281(9)
C(2)	0.2264(9)	−0.2396(11)	0.1679(9)
C(3)	0.2478(9)	−0.3599(11)	0.1494(9)
C(4)	0.2515(9)	−0.4574(11)	0.1912(9)
C(5)	0.2338(9)	−0.4346(11)	0.2515(9)
C(6)	0.2123(9)	−0.3142(11)	0.2699(9)
C(11)	0.1280(13)	−0.0025(14)	0.1847(6)
C(12)	0.0370(13)	−0.0298(14)	0.1799(6)
C(13)	−0.0121(13)	−0.0049(14)	0.1261(6)
C(14)	0.0297(13)	0.0472(14)	0.0772(6)
C(15)	0.1207(13)	0.0744(14)	0.0820(6)
C(21)	0.3160(12)	−0.1733(14)	0.4302(11)
C(22)	0.3375(12)	−0.2719(14)	0.3925(11)
C(23)	0.3541(12)	−0.3903(14)	0.4168(11)
C(24)	0.3491(12)	−0.4100(14)	0.4788(11)
C(25)	0.3277(12)	−0.3113(14)	0.5165(11)
C(26)	0.3111(12)	−0.1930(14)	0.4923(11)
C(31)	0.3175(16)	0.0769(15)	0.4683(8)
C(32)	0.4048(16)	0.1219(15)	0.4731(8)
C(33)	0.4324(16)	0.1965(15)	0.5221(8)
C(34)	0.3727(16)	0.2261(15)	0.5663(8)
C(35)	0.2854(16)	0.1811(15)	0.5615(8)
C(36)	0.2578(16)	0.1065(15)	0.5125(8)
C(16)	0.1698(13)	0.0496(14)	0.1357(6)
C(41)	0.4733(11)	0.0462(13)	0.2384(8)
C(42)	0.4179(11)	−0.0554(13)	0.2197(8)
C(43)	0.4073(11)	−0.1340(13)	0.2705(8)
C(44)	0.4562(11)	−0.0809(13)	0.3206(8)
C(45)	0.4970(11)	0.0305(13)	0.3008(8)
C(51)	0.1119(9)	−0.2166(14)	0.3917(8)
C(52)	0.0501(9)	−0.2048(14)	0.3414(8)
C(53)	−0.0202(9)	−0.1256(14)	0.3585(8)
C(54)	−0.0019(9)	−0.0883(14)	0.4194(8)
C(55)	0.0797(9)	−0.1446(14)	0.4399(8)
C(61)	0.2400(7)	0.2269(13)	0.3114(6)
C(62)	0.2579(7)	0.2292(13)	0.2490(6)
C(63)	0.3498(7)	0.2570(13)	0.2440(6)
C(64)	0.3887(7)	0.2719(13)	0.3033(6)
C(65)	0.3209(7)	0.2533(13)	0.3449(6)
C(71)	0.1559(8)	0.2023(12)	0.3345(7)
C(72)	0.0771(8)	0.1715(12)	0.2995(7)
C(73)	0.0070(8)	0.1555(12)	0.3397(7)
C(74)	0.0424(8)	0.1763(12)	0.3994(7)
C(75)	0.1344(8)	0.2052(12)	0.3963(7)

Final atomic coordinates for complex **3** are displayed in Table 5, and its molecular structure is shown in Fig. 5, together with the atomic labeling scheme. Selected bond distances and angles are given in Table 6. The structural parameters were found to depend on the Ti–Ti distance, which in **3** is 3.771 Å, closer to that observed for $[\{TiCp(\mu\text{-}Cl)\}_2\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}]$, 3.638 Å [14]. Lengthening the Ti–Ti distance led to a decrease in the dihedral angle between the fulvalene ring planes, an increase in the dihedral angle between

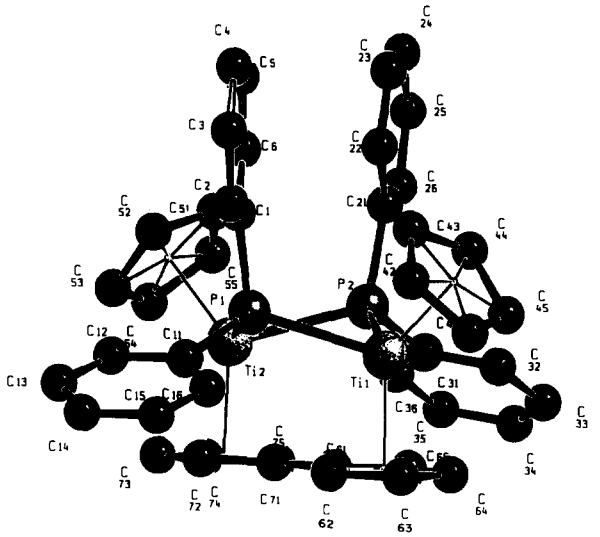


Fig. 5. View of the molecular structure of compound **3** with the atomic labeling scheme.

the C_5H_5 and C_5H_4 planes, a slight lengthening of the Ti–C(C_5H_5) and a considerable lengthening of the Ti–C(C_5H_4) bonds. For the slightly longer Ti–Ti distance in **3** the structural differences are not very large, but follow the previous pattern. The average distances to the five-membered rings were shown not to have changed; Ti–C(C_5H_5) in **3** is 2.39 Å compared to 2.38 Å in the dichloro structure and Ti–C(C_5H_4) is 2.38 Å for both compounds. The dihedral angle between the two fulvalene rings in **3** is 3.0° which is slightly smaller than the 5.3° observed for the dichloro species. The dihedral angle between the C_5H_4 and C_5H_5 planes also follows this pattern, as shown by the (C_5H_5 centroid)Ti (C_5H_4 centroid) angles of 131° and 130° compared with 134.42° in the dichloro complex.

Table 6
Selected bond distances (Å, °) and bond angles (deg) for **3**

Ti(1)–P(1)	2.633(7)	Ti(1)–P(2)	2.661(8)
Ti(1)–Ce(4)	2.07[a]	Ti(1)–Ce(6)	2.06[a]
Ti(2)–P(1)	2.659(8)	Ti(2)–P(2)	2.624(8)
Ti(2)–Ce(5)	2.08[a]	Ti(2)–Ce(7)	2.06[a]
P(2)–Ti(1)–P(1)	81.4(2)		
Ce(4)–Ti(1)–P(1)	112.0[a]		
Ce(4)–Ti(1)–P(2)	111.0[a]		
Ce(6)–Ti(1)–P(1)	106.0[a]		
Ce(6)–Ti(1)–P(2)	105.0[a]		
Ce(6)–Ti(1)–Ce(4)	130.0[a]		
P(2)–Ti(2)–P(1)	81.6(2)		
Ce(5)–Ti(2)–P(1)	112.0[a]		
Ce(5)–Ti(2)–P(2)	110.0[a]		
Ce(7)–Ti(2)–P(1)	104.0[a]		
Ce(7)–Ti(2)–P(2)	106.0[a]		
Ce(7)–Ti(2)–Ce(5)	131.0[a]		
Ti(2)–P(1)–Ti(1)	90.9(2)		
Ti(2)–P(2)–Ti(1)	91.1(3)		

[a] Ce refers to the centroids of the cyclopentadienyl rings.

Complexes involving fulvalene and Zr are more unusual. The first structure to be determined was $[(ZrCpCl)_2(\mu\text{-}O)\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}]$ [3d]. The molecular structure of complex **7** is shown in Fig. 6, together with the atomic labeling scheme. Final atomic coordinates are displayed in Table 7, and selected bond distances and angles are given in Table 8. Features of this type of structure of some interest are the nature of the Zr–C bond and the effect of the fulvalene on the structure, as compared to structures with just coordinated cyclopentadienyl groups. The Zr–C distances in **7** are 2.181 (9) Å and 2.18 (1) Å for postulated Zr–C(sp) σ-bonds and 1.25 (1) Å for both the C–C bonds. This compares with 2.280 (5) Å and 2.273 (5) Å in $[ZrCp_2(CH_3)_2]$ [15] where there is no possibility of the carbon being anything other than sp^3, and 2.187 (4) Å in $[ZrCp_2(CO)_2]$ [16] where the carbon is sp-hybridised. Two structures where there is the possibility of π-donation into the Zr–C bond are $[ZrCp_2(C{=}C - CH_3)_2]$ [11] and $[Zr_2(C_5H_4Me)_4(C{\equiv}C\text{-}Ph)_2]$ [11]. The Zr–C distances in these complexes are 2.249 (3) Å and 2.188 (2) Å, respectively, and the unsaturated C–C bonds 1.206 (4) Å and 1.261 (2) Å. The values obtained for the phenyl system are remarkably similar to those obtained for **7**. The Zr–C bond in **7** can best be described as a Zr–C(sp) bond. The unsaturated C–C bond has been slightly lengthened compared to the bond in ethyne, 1.21 Å [17]. This is probably because of the π-coordination of the bond to the second Zr in the structure. Zr–C bonds of approximately 2.4 Å are found in both structures.

The central portion (Zrs and Cs) of the phenyl-containing structure is planar. This is not the case in **7** where there is a dihedral angle of 13.6° between the planes containing the Zr and π-associated Cs. This twist is perhaps because of the strain imposed on the system by the coordination of the fulvalene. The fulvalene itself has become non-planar. The dihedral angle between the ring planes is 11°. The Zr–Zr vector has been decreased from 3.506 (1) Å in the phenyl-containing system to 3.405 (1) Å in **7**. Both these distances are longer than 3.1 Å, which is the sum of the van der Waals radii of the zirconium atoms.

Table 7
Fractional atomic coordinates for **7**

Atom	x	y	z
Zr(1)	0.53241(6)	0.21670(8)	0.39424(2)
Zr(2)	0.46340(5)	0.48215(7)	0.35314(2)
Si(1)	0.6662(2)	0.4260(2)	0.2831(1)
Si(2)	0.3527(2)	0.3010(3)	0.4715(1)
C(1)	0.5849(5)	0.3294(7)	0.3504(2)
C(2)	0.5994(5)	0.3977(8)	0.3242(2)
C(3)	0.6582(8)	0.2880(10)	0.2540(3)
C(4)	0.7887(6)	0.4511(11)	0.2983(3)
C(5)	0.6233(7)	0.5647(10)	0.2576(3)
C(6)	0.4389(5)	0.3982(8)	0.4052(2)
C(7)	0.4249(6)	0.3311(8)	0.4318(2)
C(8)	0.2324(7)	0.3018(16)	0.4580(3)
C(9)	0.3778(12)	0.1551(14)	0.4924(5)
C(10)	0.3717(10)	0.4213(14)	0.5049(4)
C(11)	0.3743(6)	0.1255(8)	0.3818(3)
C(12)	0.4350(8)	0.0252(9)	0.3886(3)
C(13)	0.5023(9)	0.0176(8)	0.3609(3)
C(14)	0.4853(7)	0.1123(8)	0.3371(3)
C(15)	0.4062(6)	0.1812(8)	0.3493(2)
C(17)	0.3065(5)	0.3810(9)	0.3498(3)
C(18)	0.3014(6)	0.4878(9)	0.3280(3)
C(19)	0.3598(6)	0.4725(9)	0.2987(3)
C(20)	0.4020(6)	0.3522(9)	0.3021(2)
C(16)	0.3713(5)	0.2970(8)	0.3335(2)
C(21)	0.7038(7)	0.2364(15)	0.4074(4)
C(22)	0.6834(10)	0.1123(15)	0.4090(4)
C(23)	0.6250(13)	0.1006(16)	0.4401(6)
C(24)	0.6153(10)	0.2180(25)	0.4526(4)
C(25)	0.6624(9)	0.2985(14)	0.4328(4)
C(26)	0.5782(7)	0.6617(8)	0.3528(3)
C(27)	0.4996(10)	0.7017(8)	0.3363(3)
C(28)	0.4267(8)	0.7062(9)	0.3632(5)
C(29)	0.4648(10)	0.6664(11)	0.3952(4)
C(30)	0.5557(8)	0.6389(9)	0.3891(3)

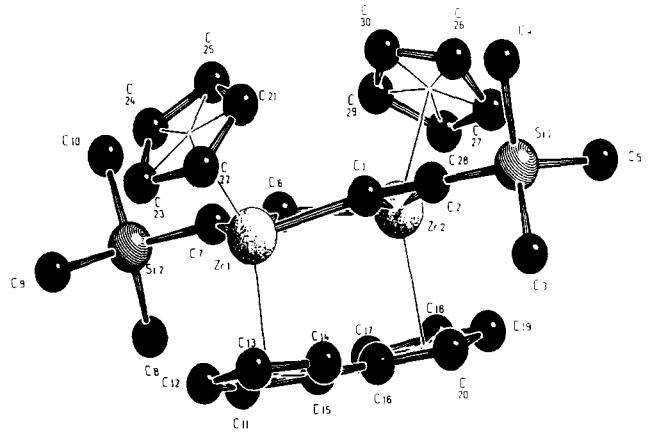


Fig. 6. View of the molecular structure of compound **7** with the atomic labeling scheme.

3. Experimental details

All manipulations were performed under dinitrogen or argon using Schlenk and high-vacuum line techniques or a VAC glove box Model HE 63P. Solvents were purified by distillation from an appropriate drying/deoxygenated agent (sodium/benzophenone for THF, sodium for toluene and sodium/potassium alloy for hexane). Lithium metal, Li^tBu, $HC{\equiv}CSiMe_3$ and $ClCH_2C(CH_3)_2Ph$ (Aldrich) were purchased and used without further purification. $LiPPh_2$ [18], $[\{M(\eta^5\text{-}C_5H_5)\mu\text{-}Cl\}_2\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}]$ (M = Ti, **1** [1c]; Zr, **2** [3d]) and $[\{M(\eta^5\text{-}C_5H_5)Cl_2\}_2\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}]$ (M = Ti, **5** [1c]; Zr, **6** [19]) were prepared according to literature procedures. NMR spectra were

Table 8
Selected bond distances (Å, °) and bond angles (deg) for **7**

Zr(1)–Zr(2)	3.405(1)	Zr(1)–Ce(1)	2.21[a]
Zr(1)–Ce(3)	2.23[a]	Zr(1)–C(1)	2.181(9)
Zr(1)–C(6)	2.417(8)	Zr(1)–C(7)	2.433(9)
Zr(2)–Ce(2)	2.22[a]	Zr(2)–Ce(4)	2.24[a]
Zr(2)–C(1)	2.411(8)	Zr(2)–C(2)	2.421(8)
Zr(2)–C(6)	2.18(1)		
C(1)–C(2)	1.25(1)		
C(6)–C(7)	1.25(1)		
C(1)–Zr(1)–Zr(2)	44.8(2)		
C(6)–Zr(1)–Zr(2)	39.6(2)		
C(6)–Zr(1)–C(1)	82.4(3)		
C(7)–Zr(1)–Zr(2)	69.3(2)		
C(7)–Zr(1)–C(1)	111.9(3)		
C(7)–Zr(1)–C(6)	29.9(3)		
C(1)–Zr(2)–Zr(1)	39.6(2)		
C(2)–Zr(2)–Zr(1)	69.4(2)		
C(2)–Zr(2)–C(1)	29.9(3)		
C(6)–Zr(2)–Zr(1)	44.9(2)		
C(6)–Zr(2)–C(1)	82.6(3)		
C(6)–Zr(2)–C(2)	112.0(3)		
Zr(2)–C(1)–Zr(1)	95.6(3)		
C(2)–C(1)–Zr(1)	169.3(7)		
C(2)–C(1)–Zr(2)	75.5(5)		
C(1)–C(2)–Zr(2)	74.6(5)		
Zr(2)–C(6)–Zr(1)	95.5(3)		
C(7)–C(6)–Zr(1)	75.8(6)		
C(7)–C(6)–Zr(2)	169.1(7)		
C(6)–C(7)–Zr(1)	74.3(6)		
C(6)–C(7)–Si(2)	146.8(8)		

[a] Ce refers to the centroids of the cyclopentadienyl rings.

recorded on Varian FT-80 and Varian Unity FT-300 instruments (^{1}H and ^{13}C chemical shifts were referenced to Me_4Si, $\delta = 0$ ppm). IR spectra were performed (Nujol mulls) on a 883 Perkin-Elmer spectrophotometer. Mass spectra were recorded on a Hewlett Packard 5890 spectrometer. Elemental C, H analyses were carried out on a Perkin-Elmer 240B microanalyzer.

3.1. Synthesis of [{Ti(η^5-C_5H_5)(μ-PPh_2)}$_2${μ-(η^5-C_5H_4-η^5-C_5H_4)}] 3

3.1.1. Method 1

A toluene solution (50 ml) of [{Ti(η^5-C_5H_5)(μ-Cl)}$_2${μ-(η^5-C_5H_4-η^5-C_5H_4)}] (1 g, 2.35 mmol) was added at room temperature to a suspension of freshly prepared $LiPPh_2$ (0.90 g, 4.7 mmol) in hexane (10 ml). The mixture was stirred for 12 h at room temperature, the solution turning dark blue-green. After filtration and evaporation to dryness, a green solid was obtained, which was recrystallized from toluene/hexane at −78°C giving compound **3** as brown-green crystals (Yield: 1.02 g, 60%).

3.1.2. Method 2

A toluene (30 ml) solution of $LiPPh_2$ (0.54 g, 2.8 mmol) was added dropwise to a toluene (40 ml) suspension of [{Ti(η^5-C_5H_5)Cl_2}$_2${μ-(η^5-C_5H_4-η^5-C_5H_4)}] (0.35 g, 0.7 mmol) at −78°C. After stirring for 12 h at room temperature, the resulting solution was worked up as for Method 1 to give the same compound **3**. (Yield: 0.45 g, 75%).

Anal. Calc. for $C_{44}H_{38}P_2Ti_2$: C, 72.94; H, 5.29. Found: C, 72.53; H, 5.38%.

3.2. Reaction of [{Ti(η^5-C_5H_5)Cl_2}$_2${μ-(η^5-C_5H_4-η^5-C_5H_4)}] (5) with two equivalents of $LiPPh_2$

A toluene (30 ml) solution of $LiPPh_2$ (0.27 g, 1.40 mmol) was added dropwise to a toluene (50 ml) suspension of **5** (0.35 g, 0.7 mmol) at −78°C and the reaction mixture was heated and stirred for 12 h at room temperature. After filtration, the resulting solution was evaporated to dryness to give a purple residue containing complex **1** and free Ph_2P–PPh_2.

3.3. Synthesis of [{Zr(η^5-C_5H_5)(μ-PPh_2)}$_2${μ-(η^5-C_5H_4-η^5-C_5H_4)}] 4

3.3.1. Method 1

A toluene (20 ml) solution of $LiPPh_2$ (0.8 g, 4.2 mmol) was added at room temperature to a toluene (50 ml) solution containing [{Zr(C_5H_5)(μ-Cl)}$_2${μ-(η^5-C_5H_4-η^5-C_5H_4)}] (1.1 g, 2.1 mmol). It changed immediately from red to purple, and the reaction mixture was stirred for 4 h at room temperature. After filtration, the resulting solution was concentrated to 15–20 ml and cooled at −30°C for 3 d to give a purple solid. Recrystallization from toluene/hexane at −30°C yielded purple crystals which were identified as compound **4**. (Yield: 1 g, 59%).

3.3.2. Method 2

A toluene (30 ml) solution of $LiPPh_2$ (0.46 g, 2.4 mmol) was added dropwise at −78°C to a toluene (40 ml) suspension of [{Zr(η^5-C_5H_5)Cl_2}$_2${μ-(η^5-C_5H_4-η^5-C_5H_4)}] (0.35 g, 0.6 mmol). The reaction mixture was stirred for 12 h at room temperature to give a purple solution which was worked up as for Method 1, leading to compound **4** (Yield: 0.49 g, 70%).

Anal. Calc. for $C_{44}H_{38}P_2Zr_2$: C, 65.15; H, 4.72. Found: C, 64.93; H, 4.89%.

3.4. Synthesis of [{Zr(η^5-C_5H_5)(μ-C≡$CSiMe_3$)}$_2${μ-(η^5-C_5H_4-η^5-C_5H_4)}] 7

11 ml of a 1.6 M solution of Li^{t}Bu (17.6 mmol) in diethyl ether was added, at −78°C, to a solution of HC≡$CSiMe_3$ (2.68 ml, 19.36 mmol) in hexane (50 ml). The reaction mixture was warmed to room temperature and solid white LiC≡$CSiMe_3$ was formed. After filtration, the solid was washed with hexane (2 × 20 ml). (Yield: 1.4 g, 76%).

A solution of $LiC{\equiv}CSiMe_3$ (0.41 g, 3.8 mmol) in THF (100 ml) was added at room temperature to solid $[\{Zr(\eta^5\text{-}C_5H_5)(\mu\text{-}Cl)\}_2\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}]$ (1 g, 1.9 mmol). The mixture turned orange in 4–5 h and was stirred for 2–3 d at room temperature. After evaporation of the solvent to dryness, the resulting product was extracted with hexane (2 × 30 ml). The solution was concentrated to 20 ml and cooled to −30°C to give an orange microcrystalline solid, which was recrystallized from hexane at −30°C affording orange crystals of compound **7**. (Yield: 1 g, 82.5%). Anal. Calc. for $C_{30}H_{36}Si_2Zr_2$: C, 56.56; H, 5.70. Found: C, 56.39; H, 5.72%. IR: $\nu_{C\equiv C} = 1773\ cm^{-1}$. EI-MS. (70 eV): ($[M^+]$) 31.04%.

3.5. Synthesis of $[\{Zr(\eta^5\text{-}C_5H_5)(CH_2CMe_2Ph)_2\}_2\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}]$ 8

Lithium metal (3 g, 432 mmol) was allowed to react with $ClCH_2C(CH_3)_2Ph$ (14 ml, 86.9 mmol) in hexane (75 ml). The reaction mixture was heated under reflux for 4 d. After cooling to room temperature the suspension was filtered and the solid extracted twice with hexane. The resulting hexane solution was concentrated to 20 ml and cooled to −30°C. A white crystalline solid of $LiCH_2C(CH_3)_2Ph$ was obtained (Yield: 8.5 g, 70%).

A solution containing $LiCH_2CMe_2Ph$ (0.88 g, 6.32 mmol) in toluene (30 ml) was added at room temperature to a suspension of $[\{Zr(\eta^5\text{-}C_5H_5)Cl_2\}_2\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}]$ (0.92 g, 1.58 mmol) in toluene (100 ml). The reaction mixture was stirred for 12 h at room temperature. After filtration, the resulting solution was concentrated to 30 ml and cooled to −30°C and left for 3 d, resulting in a pale-yellow crystalline solid. Recrystallization from toluene/hexane at −30°C gave the pure compound **8**. (Yield: 1 g, 65%). Anal. Calc. for $C_{60}H_{70}Zr_2$: C, 74.02; H, 7.25. Found: C, 73.73; H, 7.17%.

3.6. Crystal Structure Determinations

Crystals of **3** and **7** were mounted under argon in capillaries. An Enraf Nonius CAD4 diffractometer with graphite monochromated Mo–Kα radiation was used to collect data at room temperature (20°C). Cell parameters for **3** were obtained by refining the setting angles of 17 reflections with $14° < \theta < 17°$. For **7**, 25 reflections were used $16° < \theta < 18°$. Crystal data for both compounds are given in Table 9 together with details of the data collection and structure refinement. The data collected for **3** were found to be weak. This was thought to be because of crystal quality. Attempts to improve the quality of the crystals were unsuccessful.

Both data sets were corrected for Lorentz and polarisation effects. The intensities of three reflections were monitored over the period of both data collections, and were found not to decay significantly. Therefore a decay correction was not applied to the data.

Table 9
Crystal data, experimental data and structure refinement procedures for complexes **3** and **7**

Compound	**3**	**7**
Formula	$C_{44}H_{38}P_2Ti_2$	$C_{30}H_{36}Si_2Zr_2$
M	724.496	635.229
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$ (no. 14)	$Pbca$ (no. 61)
a, Å	15.013(5)	10.819(1)
b, Å	10.704(1)	14.427(1)
c, Å	22.132(7)	37.451(3)
β, °	92.53(2)	
V, Å^3	3552(2)	5845(1)
Z	4	8
D_c g cm^{-3}	1.353	1.44
$F(000)$	1504	2592
μ(Mo–Kα) cm^{-1}	1.19	7.71
Scan type	ω–2θ	ω–2θ
$2\theta_{max}$, °	20	22
Total no. of reflections	3684	3886
No. of unique reflections	3319	2966
R_{merg}	0.0978	0.02
No. of refl'ns with $\lvert F_{obs}\rvert > 4\sigma\lvert F_{obs}\rvert$	1488	2604
No. of variables	246	274
R	0.0982	0.0472
R_w	0.0960	0.0537
GOF	1.93	1.86
Residual density, e Å^{-3}	0.71	0.48

The structures were solved by the direct method and subsequent difference Fourier synthesis [20]. These structures were then refined by full-matrix least-squares analysis. The geometry of the cyclopentadienyl and phenyl rings was constrained with the hydrogen placed in calculated positions. The non-hydrogen atoms were given anisotropic temperature factors. The hydrogen atoms in similar environments in the individual structures were given common refined temperature factors. For **3** those on the phenyl rings 0.15 and on the cyclopentadienyl type rings 0.10. For **7**, methyl 0.16, on the cyclopentadienyl rings 0.22 and on fulvalene 0.10. In the structure of **7** some disorder in the cyclopentadienyl rings was observed which could not be resolved. The anisotropic temperature factors for these positions are therefore quite high. The final R value obtained for **3** was quite high, probably because of the weak intensities of the data.

Molecular representations of **3** and **7** are shown in Figs. 5 and 6 respectively. Final fractional atomic coordinates are given in Table 5 for **3**, and Table 7 for **7**.

Tables of fractional atomic coordinates, anisotropic and isotropic thermal parameters, bond lengths and bond angles (seven pages) for compound **3**, and of

fractional atomic coordinates, anisotropic thermal parameters, bond lengths and bond angles (five pages) and a table of least-squares planes (two pages) for compound 7 are available from the Cambridge Crystallographic Data Centre.

^{1}H NMR spectra (variable temperature) for compounds $[Zr(C_5H_5)(\mu\text{-}C{\equiv}CR)]_2(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)$ {R = $SiMe_3$ (7); Ph [9a]} are also available from the authors.

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