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Synthesis and characterization of titanium and zirconium complexes bearing diphenyltriazenido ligands

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Abstract—Treatment of tetrakis(dimethylamido)titanium(IV) and tetrakis(diethylamido)titanium(IV) with two equivalents of 1,3-diphenyltriazene in hexane afforded bis(dimethylamido)bis(1,3-diphenyltriazenido)titanium(IV) (62%) and bis(diethylamido)bis(1,3-diphenyltriazenido)titanium(IV) (68%), respectively, as deep red crystalline solids. Reaction of tetrakis(dimethylamido)titanium(IV) with more than two equivalents of 1,3-diphenyltriazene in refluxing toluene did not lead to substitution of more than two dimethylamido ligands, but only gave extensive decomposition. Treatment of tetrakis(dimethylamido) zirconium(IV) with four equivalents of 1,3-diphenyltriazene in hexane afforded tetrakis(1,3-diphenyltriazenido)-zirconium(IV) (79%) as a deep red crystalline solid. Crystal structures of bis(dimethylamido) bis(1,3-diphenyltriazenido)titanium(IV), bis(diethylamido)bis(1,3-diphenyltriazenido)titanium(IV), and tetrakis(1,3-diphenyltriazenido)zirconium(IV) were determined. The titanium complexes exhibit octahedral coordination spheres with cis-dialkylamido ligands, while the zirconium complex is eight-coordinate with η^2-1,3-diphenyltriazenido ligands. Solution molecular weight measurements for tetrakis(1,3-diphenyltriazenido)zirconium(IV) indicated a monomeric structure in benzene, consistent with the structural results. © 1997 Elsevier Science Ltd

Keywords: titanium; zirconium; diphenyltriazenido; chemical vapor deposition.

We are interested in early transition metal complexes with nitrogen coordination spheres for use as precursors to metal nitride films [1]. Triazenido ligands (RNNNR) are promising candidates for such applications, since they coordinate by the nitrogen atoms and may exhibit low energy ligand decomposition pathways. Triazenido ligands have a rich structural chemistry and can be two- or four-electron donors depending on their coordination mode. They act as unidentate ligands (two electron donors) in $Pd(PPh_3)_2Cl$(1,3-di-*p*-tolyltriazenido) [2], $PtH(PPh_3)_2$ (1,3-di-*p*-tolyltriazenido) [3], and *cis*-[$Pt(PPh_3)_2$(1,3-diphenyltriazenido)$_2$] [4], as bridging ligands (four electron donors) in Cu_2(1,3-diphenyltriazenido)$_2$ [5]. Cu_4(1,3-dimethyltriazenido)$_4$ [6], M_2(1,3-diphenyltriazenido)$_4$ (M = Ni [7], Cu [7], Pd [7], Cr [8], Rh [9]), Zn_4O(1,3-diphenyltriazenido)$_6$ [10], Pd_2(1,3-di-*p*-tolyltriazenido)$_2$(allyl)$_2$ [11], Pd_2(1,3-dimethyltriazenido)(methallyl)$_2$ [12], and RhCuCl(1,3-dimethyltriazenido)(CO)$(PPh_3)_2$ [13], and as bidentate ligands (four electron donors) in M(1,3-diphenyltriazenido)$_3$ (M = Cr [8], Rh [9], Co [14–16]), Mo $(CO)_2Cp$(1,3-di(3,5-bis(trifluoromethyl)-phenyl) triazenido) [17], $Re(CO)_2(PPh_3)_2$(1,3-di-*p*-tolyltriazenido) [18], $Re(PPh_3)_2Cl_2$(1,3-dimethyl-triazenido) [20], $M(py)_2$(1,3-diphenyltriazenido)$_2$ (M = Co, Ni) [21], $Ru(PPh_3)_2L_2$ (L = 1,3-di-*p*-tolyltriazenido, 1,3-diphenyltriazenido) [21], and *trans*-[RuH(1,3-di-*p*-tolyltriazenido)(CO)-$(PPh_3)_2$] [22]. Surprisingly there have been no reports of triazenido ligand coordination by the Group 4 or Group 5 metals. Since the focus of our film deposition work is on Group 4 and Group 5 metal nitrides, we sought to examine the preparation of triazenido complexes to assess if this ligand could provide useful precursors.

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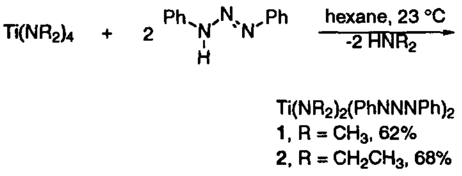
Herein we describe the synthesis and characterization of several titanium and zirconium complexes containing the diphenyltriazenido ligand and comment on their potential utility for the deposition of metal nitride films. Moreover, the crystal structures of representative 1,3-diphenyltriazenido complexes are described.

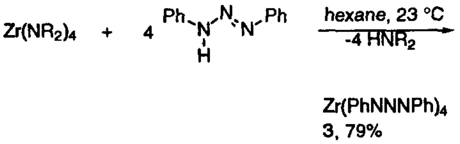
RESULTS AND DISCUSSION

Treatment of tetrakis(dimethylamido)titanium(IV) or tetrakis(diethylamido)titanium(IV) with 2 equiv. of 1,3-diphenyltriazene in hexane afforded the disubstituted products bis(dimethylamido)bis(1,3-diphenyltriazenido)titanium(IV) (**1**, 62%) and bis(diethylamido)bis-(1,3-diphenyltriazenido)titanium(IV) (**2**, 68%) as deep red crystalline solids (eq. 1). The complexes were characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, infrared spectroscopy, microanalyses, and by X-ray crystal structure determinations. The incomplete substitution of the dialkylamido groups in **1** and **2** was obvious from the NMR spectra. The ratio of the ligands was determined by integration of the ^1H NMR resonances and by obtention of acceptable microanalyses. Loss of the nitrogen-bound hydrogen of the 1,3-diphenyltriazene was evident in the infrared spectro of **1** and **2** from the lack of absorption at 3196 cm^{-1}, which is where the nitrogen–hydrogen stretch for 1,3-diphenyltriazene is observed. Treatment of tetrakis(dimethylamido)titanium(IV) with four equivalents of 1,3-diphenyltriazene in refluxing toluene for 4 h did not afford the homoleptic triazenido complex, but rather gave an intractable mixture from which a pure compound could not be isolated.



(1)

We reasoned that a larger metal center might be able to accommodate four 1,3-diphenyltriazenido ligands. Accordingly, tetrakis(dimethylamido)zirconium(IV) [23] was treated with four equivalents of 1,3-diphenyltriazene in hexane at ambient temperature to afford tetrakis(1,3-diphenyltriazenido)zirconium(IV) (**3**, 79%) as deep red crystals (eq. 2). The structure of **3** was established from a combination of ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, infrared spectroscopy, and a microanalysis, and by an X-ray crystal structure determination. The NMR spectra showed resonances attributable only to phenyl groups, indicating complete substitution of the dimethylamido ligands. The absence of a nitrogen–hydrogen stretch at or near 3196 cm^{-1} in the infrared spectrum indicated the formation of triazenido (as opposed to triazene) ligands. Freezing point depression molecular weight measurements of **3** in benzene indicated that it is monomeric in this medium.



(2)

In order to define the triazenido ligand bonding parameters, crystal structures of **1**–**3** were determined. Experimental crystallographic data are summarized in Table 1, selected bond lengths and angles are given in Tables 2–4, while perspective views are presented in Figs 1–3.

Complexes **1** and **2** exemplify distorted octahedral complexes of the general formula [M(bidentate)$_2$(monodentate)$_2$]. In such complexes, the *cis*-structure is preferred over the *trans*-configuration if the normalized bite of the bidentate ligand is reduced from 1.414 (ideal octahedron) due to more efficient $d\pi$–$p\pi$ back-bonding [24]. Complexes **1** and **2** have the expected *cis*-arrangement, since their normalized bites (calculated as $b = 2\sin\{(N(2)—Ti—N(4))/2\}$ and $b = 2\sin\{(N(1)—Ti—N(3))/2\}$) are 0.97 and 0.96, respectively. The near planarity of the TiN_3 rings indicates that there is an extensive delocalization of the electron density over each diphenyltriazenido ligand. This feature is common to other compounds with chelating triazenido ligands [8,9,14–22]. The N—N—N angles (**1**, 107.1(4); **2**, 106.7(2)°) have values similar to the corresponding angles in the related compounds: 104(1)° in Cr(diphenyltriazenido) [8], 103.6(9)° in Co(diphenyltriazenido)$_3$ [14–16], 100.8(7)° in CpMo(CO)$_2$(dibenzyltriazenido) [17], 105(1)° in Re(CO)$_2$(PPh$_3$)$_2$(di-*p*-tolyltriazenido) [18], 99(2)° in ReCl$_2$(PPh$_3$)$_2$(dimethyltriazenido)$_2$ [19], 107.2(2)° in Co(diphenyltriazenido)$_2$(py)$_2$ [20], 103.3 (4)° in Ru(PPh$_3$)$_2$(diphenyltriazenido)$_2$ [21], and 105.2(3)° in*trans*-[Ru(H)(di-*p*-tolyltriazenido)(CO)(PPh$_3$)$_2$] [22]. However, these values differ considerably from the N—N—N angles found in complexes with monodentate (avg = 114°) [2–4] or bridging (avg = 117°) [5–13] triazenido groups. This fact emphasizes the strained nature of four-membered TiN_3 metallacycles. The bite angles of the triazenido ligands in **1** and **2** (58.0(1) and 57.65(8)°, respectively) are comparable to those in the related complexes (56.8(3)–59.7(1)°) [8,14–22] and indicate severe angular distortion of the titanium coordination sphere from ideal octahedral geometry. The dihedral angles between the chelate ring and phenyl groups of the triazenido functions are 0.9 and 9.6° in **1** and 10.7 and 16.5° in **2**. Consequently, the π-systems spanning over each triazenido ligand have extensive conjugation upon coordination to the metal.

In octahedral *cis*-complexes [M(bidentate)$_2$(monodentate)$_2$] the bond lengths between the central atom and each coordination site of the bidentate

Table 1. Experimental Crystallographic Data for **1**–**3**

	1	**2**	**3**
Empirical formula	$C_{28}H_{32}N_8Ti$	$C_{32}H_{40}N_8Ti$	$C_{48}H_{40}N_{12}Zr$
Fw	528.52	584.62	876.14
Space group	*C*2/*c*	*C*2/*c*	$P4_2/n$
a(Å)	15.5973(4)	17.340(3)	15.1784(10)
b(Å)	11.4507(3)	11.416(2)	
c(Å)	17.0082(2)	18.374(4)	9.6216(8)
α (deg)			
β (deg)	111.4700(10)	92.08(3)	
γ (deg)			
V (Å^3)	2826.88	3226.5(11)	2216.7(3)
Z	4	4	2
T (K)	223(2)	295(2)	295(2)
λ (Å)	0.71073	0.71073	0.71073
ρ calcd (g cm^{-3})	1.242	1.204	1.313
μ (cm^{-1})	3.34	2.99	2.96
R(F) (%)	3.19	3.82	6.91
Rw(F) (%)	9.83	8.27	14.03

Table 2. Selected bond lengths (Å) and angles (°) for **1**

Ti—N(1)	1.895(2)	N(2)—N(3)	1.307(2)
Ti—N(4)	2.130(2)	N(3)—N(4)	1.324(2)
Ti—N(2)	2.232(2)		
N(1) # 1—Ti—N(1)	105.45(10)	N(1)—Ti—N(2)	93.11(6)
N(1) # 1—Ti—N(4)	100.67(6)	N(4)—Ti—N(2)	58.00(6)
N(1)—Ti—N(4)	99.98(7)	N(4) # 1—Ti—N(2)	93.61(6)
N(4)—Ti—N(4) # 1	145.57(8)	N(2)—Ti—N(2) # 1	75.80(8)
N(1) # 1—Ti—N(2)	154.38(6)		

Symmetry transformations used to generate equivalent atoms: #1 $-x, y, -z+1/2$

Table 3. Selected bond lengths (Å) and angles (°) for **2**

Ti(1)—N(4)	1.883(2)	N(1)—N(2)	1.323(3)
Ti(1)—N(1)	2.128(2)	N(2)—N(3)	1.303(3)
Ti(1)—N(3)	2.238(2)		
N(4)—Ti(1)—N(4) # 1	105.25(14)	N(4) # 1—Ti(1)—N(3)	91.67(9)
N(4)—Ti(1)—N(1) # 1	99.28(9)	N(1) # 1—Ti(1)—N(3)	95.26(8)
N(4)—Ti(1)—N(1)	100.83(9)	N(1)—Ti(1)—N(3)	57.65(8)
N(1) # 1—Ti(1)—N(1)	146.57(13)	N(3)—Ti(1)—N(3) # 1	79.13(11)
N(4)—Ti(1)—N(3)	155.06(8)		

Symmetry transformations used to generate equivalent atoms: #1 $-x, y, -z+1/2$

Table 4. Selected bond lengths (Å) and angles (°) for **3**

Zr—N(1)	2.293(4)	Zr—N(2)	2.779(4)
Zr—N(3)	2.249(3)	N(1)—N(2)	1.305(4)
N(2)—N(3)	1.331(5)		
N(3)—Zr—N(1)	56.02(13)	N(2)—N(1)—Zr	97.3(3)
N(2)—N(3)—Zr	98.6(2)	N(1)—N(2)—N(3)	108.0(3)

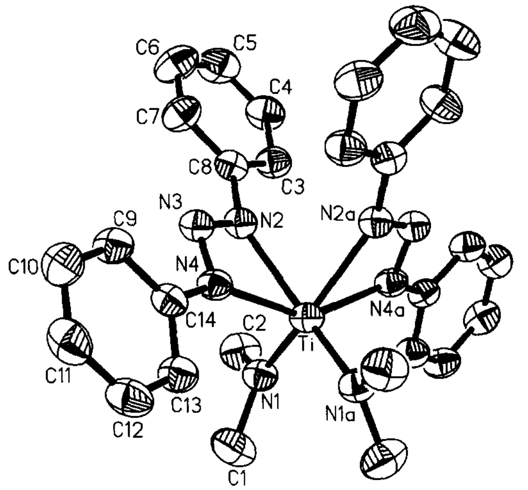


Fig. 1. Perspective view of **1** with 30% probability ellipsoids.

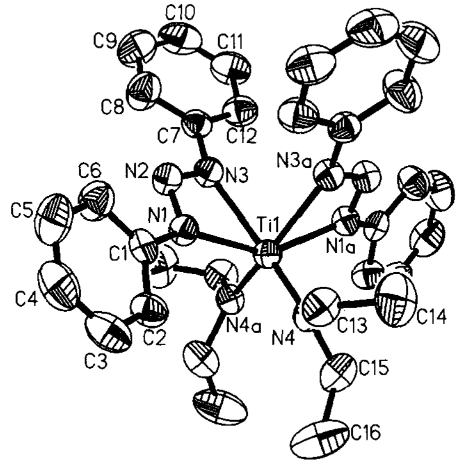


Fig. 2. Perspective view of **2** with 30% probability ellipsoids.

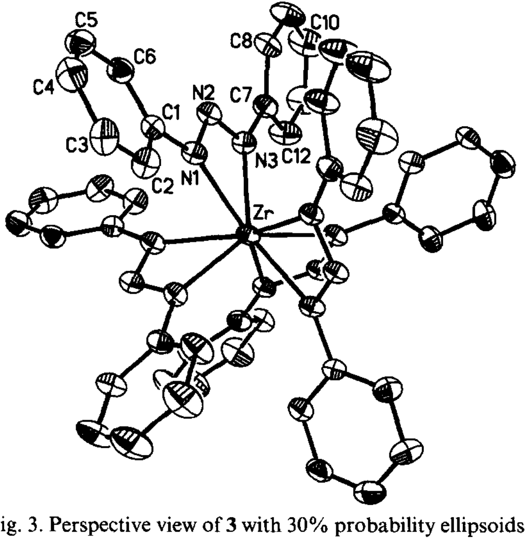


Fig. 3. Perspective view of **3** with 30% probability ellipsoids.

ligand become inequivalent. This is observed in **1** and **2**: the titanium–nitrogen bonds *trans* to the amido ligand [2.130(2) in **1** and 2.128(2) Å in **2**] are longer than the titanium–nitrogen distance *cis* to the amido ligand (2.232(2) in **1** and 2.238(2) Å in **2**). The nitrogen–nitrogen bond lengths are essentially identical within experimental error.

The geometric features intrinsic to complexes **1** and **2** have not been observed in the three similar triazenido complexes of the type [M(bidentate)$_2$(monodentate)$_2$]. The pyridine analogs M(PhNNNPh)$_2$(py)$_2$, M = Co, Ni [20], possess *cis* geometries but the M—N$_{\text{bidentate}}$ bonds *trans* to pyridine ligands are 0.098 Å shorter than those *cis* to them. The *trans* influence was not recognized and the difference in M—N(bidentate) distances was explained on the basis of different degree of crowding around the terminal nitrogen atoms [20]. The third adduct, Ru(PhNNNPh)$_2$(PPh$_3$)$_2$ [20] exhibits *trans* geometry due to the bulkiness of the triphenylphosphine ligands.

Complex **3** crystallizes with distorted dodecahedral geometry about zirconium. Alternatively, the geometry can be viewed as tetrahedral, with each point of the tetrahedron being an η^2-diphenyltriazenido ligand. A small number of eight-coordinate zirconium complexes with bonds only to nitrogen has been crystallographically characterized [25]. There is a crystallographic four-fold inversion axis through the zirconium atom, which results in only one unique 1,3-diphenyltriazenido ligand. The 1,3-diphenyltriazenido ligands are bonded to zirconium by the phenyl-bearing nitrogens, with zirconium–nitrogen bond lengths of 2.293(4) Å [Zr—N(1)] and 2.249(3) Å [Zr—N(3)]. The distance from zirconium to the central nitrogen [2.779(4) Å] is short, but is constrained to be such by the triazazirconacycle. The nitrogen–nitrogen bond lengths [N(1)—N(2) 1.305(4) Å, N(2)—N(3) 1.331(5) Å] are identical within experimental error and indicate delocalization of the negative charge over the N$_3$ framework. The N—N—N angle [108.0(3)°] is similar to the related values in **1** and **2**. The bite angle of the trizenido ligands in **3** [N(1)—Zr—N(3)] is 56.02(13)°, which is slightly smaller than analogous values in **1** and **2**. The higher coordination number in **3**, as compared to **1** and **2**, may result in a slight compression of the bite angle to alleviate steric crowding. Alternatively, the slightly longer metal–nitrogen bond lengths in **3**, relative to **1** and **2**, would afford a slightly smaller bite angle than those encountered in titanium complexes. The dihedral angles between the chelate ring and phenyl groups of the triazenido functions are 15.2 and 21.7° in **3**. These values are larger than the analogous angles for **1** and **2**, which probably reflects a higher degree of crowding in the zirconium coordination sphere.

Since our long term goal is the preparation of new source compounds for metal nitride film depositions, the volatility of compounds **1**–**3** was probed. In preparative sublimation experiments, **1**–**3** failed to sublime at temperatures below 250°C and pressures of about 0.01 mmHg. Instead, black residues were obtained, indicating extensive decomposition. Hence, **1**–**3** are not promising molecular precursors for film depositions. Compound **2** was sufficiently volatile to allow its mass spectrum to be determined. It showed a molecular ion and daughter ions reflecting loss of diethylamido and diphenyltriazenido ligands. In addition, a prominent peak was observed for diphenylamine, which would result from loss of dinitrogen from a diphenyltriazenido ligand. It is possible, based upon the observation of diphenylamine, that the diphenyltriazenido ligand decomposes by loss of dinitrogen to afford a diphenylamide ligand. If this course is followed, it is unlikely that diphenyltriazenido ligands would make useful molecular precursors to high purity metal nitride films, since Gordon and Hoffman have demonstrated that use of homoleptic titanium(IV) amides as single-source precursors affords titanium nitride films that are heavily contaminated with carbon [26].

EXPERIMENTAL

General considerations

All manipulations were performed under argon using either drybox or Schlenk line techniques. Hexane, benzene, and toluene were distilled over sodium. All NMR solvents were dried over 4 Å molecular sieves. Tetrakis(dimethylamido)titanium(IV), tetrakis(diethylamido)titanium(IV), and 1,3-diphenyltriazene were purchased and used as received. Tetrakis(dimethylamido)zirconium(IV) way prepared according to a literature procedure [23].

^{1}H NMR and ^{13}C{^{1}H} NMR spectra were obtained at 300 and 75 MHz, respectively, in benzene-d_6. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. Melting points are uncorrected. Solution molecular weight measurements were performed by measuring the freezing points of benzene solutions of **3**, using a Keithley 197A calibrated thermometer and a vacuum jacketed Schlenk flask with a volume of 12.0 mL. Errors are estimated to be ±10%.

Preparation of bis(dimethylamido)bis(diphenyltriazenido)titanium(IV) (**1**)

A 50 cm^3 Schlenk flask was charged with 1,3-diphenyltriazene (0.300 g, 0.00152 mol), hexane (30 cm^3), and was fitted with a rubber septum. Tetrakis(dimethylamido)titanium(IV) (0.20 cm^3, 0.00089 mol) was added by syringe and the flask was set aside. Red crystals of **1** separated over 20 h (0.293 g, 62%): m.p. 195.5°C; IR (Nujol, cm^{-1}) 3082 (w), 3065 (w), 3036 (w), 3023 (w), 2819 (w), 2774 (w), 1944 (w), 1869 (w), 1802 (w), 1771 (w), 1735 (w), 1717 (w), 1700 (w), 1654 (w), 1637 (w), 1592 (s), 1559 (w), 1541 (w), 1506 (w), 1483 (s), 1442 (m), 1416 (m), 1354 (s), 1327 (m), 1299 (s), 1275 (s), 1232 (s), 1213 (s), 1166 (m), 1152 (m), 1134 (m), 1074 (m), 1042 (w), 1024 (w), 995 (w), 941 (s), 903 (m), 846 (w), 834 (w), 758 (s), 693 (s), 667 (s), 612 (w), 585 (m); ^{1}H NMR (benzene-d_6, 22°C, δ) 7.63 (bs, 4H), 7.35 (bs, 2H), 7.04 (bs, 2H), 6.83 (bs, 2H), 3.22 (s, 12H); ^{13}C{^{1}H} (benzene-d_6, 22°C, δ) 148.15 (2 *ipso*-*C*), 129.50 (2 *ortho*-*C*H), 125.13 (2 *meta*-*C*H), 118.03 (2 *para*-*C*H), 46.47 (4 *C*H$_3$).

Anal. Calcd for $C_{28}H_{32}N_8Ti$: C, 63.63; H, 6.10; N, 21.20. Found: C, 63.77; H, 6.11; N, 21.20.

Preparation of bis(diethylamido)bis(diphenyltriazenido)titanium(IV) (**2**)

In analogy with the preparation of **1**, 1,3-diphenyltriazene (0.300 g, 0.00152 mol) and tetrakis(diethylamido)titanium(IV) (0.20 cm^3, 0.00060 mol) were reacted to afford **2** as red crystals (0.217 g, 68%): m.p. 172–173°C; IR (Nujol, cm^{-1}) 3068 (w), 3038 (w), 3023 (w), 1943 (w), 1868 (w), 1793 (w), 1735 (w), 1719 (w), 1686 (w), 1654 (w), 1592 (s), 1561 (w), 1542 (w), 1484 (s), 1459 (s), 1440 (m), 1357 (s), 1329 (w), 1299 (s), 1276 (s), 1242 (m), 1231 (s), 1211 (s), 1176 (w), 1152 (w), 1140 (w), 1095 (w), 1072 (w), 1059 (w), 1042 (w), 1023 (w), 1004 (w), 904 (w), 885 (m), 795 (w), 780 (w), 761 (s), 692 (s), 667 (s), 612 (m), 601 (m); ^{1}H NMR (benzene-d_6, 22°C, δ) 7.59 (d, 4H), 7.45 (bs, 2H), 7.14 (bs, 2H), 6.86 (bs, 2H), 4.38 (q, J = 6.9 Hz, 2H), 3.76 (q, J = 6.9 Hz, 2H), 0.76 (t, J = 6.9 Hz, 6H); ^{13}C{^{1}H} (benzene-d_6, 22°C, δ) 148.84 (*ipso*-*C*), 129.54 (2 *ortho*-*C*H), 124.12 (2 *meta*-*C*H), 118.45 (2 *para*-*C*H), 45.33 (2 *C*H$_2$), 12.66 (2 *C*H$_3$). Mass spectrum (EI, 20 eV) 584 (M$^+$, 24.4%), 512 (M$^+$—NEt$_2$, 21.1%), 440 (M$^+$—2 NEt$_2$, 14.3%), 388 (M$^+$—PhNNNPh), 169 (Ph$_2$NH$^+$, 9.1%), 77 ($C_6H_5^+$, 100%).

Anal. Calcd for $C_{32}H_{40}N_8Ti$: C, 65.72; H, 6.90; N, 19.17. Found: C, 65.92; H, 6.96; N, 19.15.

Preparation of tetrakis(1,3-diphenyltriazenido) zirconium(IV) (**3**)

A 50 cm^3 Schlenk flask was charged with 1,3-diphenyltriazene (0.295 g, 0.00150 mol), hexane (30 cm^3), and was fitted with a rubber septum. A hexane solution (0.5 cm^3) of tetrakis(dimethylamido)zirconium(IV) (0.100 g, 0.00037 mol) was carefully injected by syringe and the flask was set aside. Over 2 h, dark red crystals of **3** separated (0.170 g, 79%): m.p. 244°C; IR (Nujol, cm^{-1}) 3072 (w), 3040 (w), 3024 (w), 1949 (w), 1873 (w), 1795 (w), 1727 (w), 1596 (s), 1487 (s), 1355 (s), 1324 (m), 1311 (m), 1295 (s), 1279 (s), 1230 (s), 1194 (s), 1167 (w), 1152 (w), 1075 (w), 1025 (w), 976 (w), 903 (w), 845 (w), 827 (w), 761 (s), 725 (w), 689 (s), 659 (s); ^{1}H NMR (benzene-d_6, 22°C, δ) 7.80 (d, 4H), 6.92 (m, 4H), 6.76 (t, 2H); ^{13}C{^{1}H} (benzene-d_6, 22°C, ppm)

147.45 (Ph *ipso-C*), 129.17 (Ph *ortho-C*H), 125.83 (Ph *meta-C*H), 119.55 (Ph *para-C*H); molecular weight measurement (freezing point depression in benzene, molality in parentheses) calcd for $C_{48}H_{40}N_{12}Zr$, 875; found, 788 (0.0575), 830 (0.0968).

Anal. Calcd for $C_{48}H_{40}N_{12}Zr$: C, 65.80; H, 4.60; N, 19.18. Found: C, 64.91; H, 5.01; N, 19.07.

Crystallography

The single crystal X-ray diffraction experiments were performed on a Siemens P4/CCD diffractometer for **1** and **3**, and on a Siemens P4 diffractometer for **2**. The crystals were mounted in thin-walled capillaries in a dry box under an atmosphere of nitrogen.

The systematic absences in the diffraction data were consistent with the reported space groups. For **1** and **2**, either of the monoclinic space groups *Cc* and *C*2/*c* was indicated; the latter was preferred based on the chemically reasonable and computationally stable results of refinement. The structures were solved using direct methods, completed by subsequent different Fourier synthesis, and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions. The Ti atoms in **1** and **2** reside on crystallographic two-fold axes, while the zirconium atom in **3** resides on a crystallographic four-fold inversion axis.

All software and sources of the scattering factors are contained in the SHELXTL (version 5.03) program library (G. Sheldrick, Siemens XRD, Madison, WI).

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