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Complexes of zirconium with aryl substituted triamidoamines: molecular structures of amide and alkyl derivatives

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Abstract

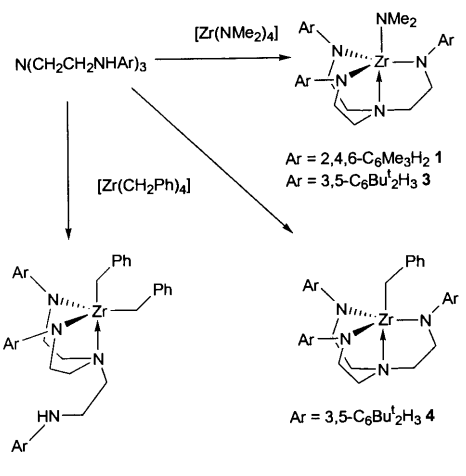
Reactions of the arylated TREN derivatives $N(CH_2CH_2NHAr)_3$ [Ar = 2,4,6-$C_6Me_3H_2$ (H_3TMT), 3,5-$C_6Bu^t_2H_3$ (H_3TDT)] individually with $Zr(NMe_2)_4$ and $Zr(CH_2Ph)_4$ give the azazirconatranes [Zr(TMT)(NMe_2)], [Zr(TDT)(NMe_2)] and [Zr(TDT)(CH_2Ph)] and unexpectedly [Zr(HTMT)($CH_2Ph)_2$]. The molecular structures of [Zr(TMT)(NMe_2)] and [Zr(TDT)(CH_2Ph)] show that the triamidoamine ligand is arranged with the usual three-fold symmetry about the metal and that the aryl substituents form a bowl cavity with the apical ligand at the base. The reactions of the alkyl with dihydrogen lead to decomposition, and a hydride species such as that proposed in earlier studies could not be detected.

Keywords: Zirconium; Azametallatrane; Amide; Alkyl; TREN; X-ray structure

1. Introduction

Synthetic and catalytic chemistry involving amido R_2N– complexes of the early transition metals and f elements is currently an area of intense study [1]. The triamidoamines constitute an important class of such complexes [2]. These formally trianionic quadridentate ligands are usually disposed in a symmetric (C_3) orientation leaving a sterically protected fifth coordination site at the apex of an approximate trigonal bipyramid. The geometric and electronic structure promotes the formation of M–L multiple bonds at this site [3]. Also, the (triamidoamine)lanthanide fragment is unusually Lewis acidic [4].

Zirconium triamidoamines or azazirconatranes were first reported by Verkade [5]. The titanium derivatives have been more extensively studied [6]. Our recent contribution [7] focussed on the synthesis of organometallic derivatives such as [Zr(NN'_3)CH_2Ph] (**I**) and subsequent attempts to synthesise a hydride derivative [Zr(NN'_3)H] by hydrogenation. This reaction led instead to clean metalation of the amide substituent $SiMe_2Bu^t$ groups to give **II**. This type of chemistry had previously been observed in titanium [6c,d], molybdenum [2e], uranium and thorium [8] systems and is quite commonplace for SiMe groups. We mentioned that Schrock's more recently introduced aryl substituted triamidoamine ligands [2f] may be more resistant to this type of reaction and we present here our investigations in this area.



Scheme 1. Synthesis of complexes **1**–**4**.

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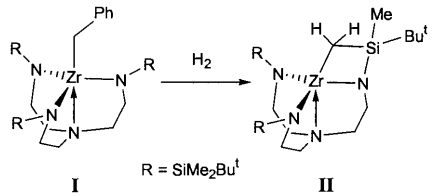


Scheme 2.

Table 1
Experimental data for the X-ray diffraction studies of **1** and **4**

	[Zr(TMT)(NMe_2)] (**1**)	[Zr(TDT)(CH_2Ph)]·C_5H_{12} (**4**)
Empirical formula	$C_{35}H_{51}N_5Zr$	$C_{60}H_{82}N_4Zr$
Formula weight	633.03	950.52
Crystal dimensions (mm)	$0.10\times0.10\times0.05$	$0.15\times0.10\times0.10$
Colour	Colourless	Colourless
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	11.9669(15)	16.1683(9)
b (Å)	15.755(2)	17.5095(3)
c (Å)	18.143(2)	21.652
β (Å)	102.6250(10)	109.5200(10)
Cell volume (Å^3)	3338.0(7)	5777.4(3)
Z	4	4
D_{calc} (Mg m^{-3})	1.260	1.093
$F(000)$	1344	2040
μ (mm^{-1})	0.360	0.228
Temperature (K)	180(2)	180(2)
θ_{max} (°)	28.51	22.50
Total reflections	19 491	22 655
Independent reflections	7736	7555
R_{int}	0.0720	0.0644
Parameters	403	604
T_{max}, T_{min}	0.928, 0.6934	0.928, 0.7151
Goodness-of-fit on F^2	1.083	1.079
Largest difference peak and hole (e Å^{-3})	0.660 and −0.504	1.556 and −0.491
R_1, wR_2 [$I>2\sigma(I)$]	0.0623, 0.0985	0.0599, 0.1413

2. Results and discussion

2.1. Synthesis

The triarylated proligands $N(CH_2CH_2NHAr)_3$ [Ar = 2,4,6-$C_6H_3Me_3$ (H_3TMT) [2f], 3,5-$C_6H_4Bu^t_2$ (H_3TDT)] were synthesised by palladium catalysed arylation of TREN [9]. The triamine H_3(TMT) reacted readily with $Zr(NMe_2)_4$ to give the expected amido complex [Zr(TMT)(NMe_2)] (**1**) in 77% isolated yield (Schemes 1 and 2). This complex was characterised spectroscopically and by X-ray crystallography (vide infra).

The reaction of H_3(TMT) with $Zr(CH_2Ph)_4$ unexpectedly gave the dibenzyl complex [Zr(HTMT)(CH_2Ph)$_2$] (**2**) together with two equivalents of toluene. ^{1}H-NMR spectra show inequivalent benzyl groups (axial and equatorial) in the presumed trigonal bipyramidal structure. The presence of five mesityl group methyl resonances in the ratio 6:6:6:6:3 and an apparent mirror plane through the amino nitrogen, Zr and bisecting the two amido nitrogens would indicate inequivalence of the *ortho*-methyl groups at the amide ligands on the ^{1}H chemical shift time-scale. We ascribe this to restricted rotation about amido N–C_{ipso} bonds. This behaviour has also been noted in a closely related diamidoamine complex [10]. Unfortunately the thermal instability of **2** has impeded variable temperature NMR studies.

The amide complex **1** above is analogous to several molybdenum complexes possessing various aryl N-substituents [2f]. Those without groups in the *ortho* positions of the aromatic ring readily form methyl derivatives, whereas this was not achieved for complexes of more sterically demanding ligands such as TMT. As expected, *ortho* substituents have the most significant steric influence about the metal. Nevertheless the failure of H_3TMT to be completely metalated by $Zr(CH_2Ph)_4$ when it reacts cleanly and rapidly with $Zr(NMe_2)_4$ is not explained. We conjectured however that a ligand without *ortho*-methyl substituents but with bulky groups in other positions, i.e. TDT would be better suited to the formation of a zirconium alkyl and perhaps also our target hydride.

Reaction of H_3TDT with $Zr(NMe_2)_4$ gives the amido complex [Zr(TDT)(NMe_2)] (**3**) analogous to **1** (Scheme 1). A similar reaction with $Zr(CH_2Ph)_4$ gave the monobenzyl complex [Zr(TDT)(CH_2Ph)] (**4**) which was characterised crystallographically (vide infra).

2.2. Molecular structures

Single crystals of compounds **1** and **4** were readily grown by slow cooling of saturated solutions in pentane. Their molecular structures (Table 1) are shown in Figs. 1 and 2. In both cases the triamidoamine ligand has approximate three-fold symmetry about the metal with the aryl substituents encircling the apical site and forming a bowl- like cavity. This is analogous to the structure of Schrock's pentafluorophenyl derivative [Mo(NN^F_3)Cl] [11].

It is instructional to compare the structures of the aryl complexes **1** and **4** with the similar amido and benzyl complexes containing the $SiMe_2Bu^t$ substituted triamidoamine ligand, i.e. [Zr(NN'_3)(NMe_2)] and [Zr(NN'_3)(CH_2Ph)] which we reported recently [7]. A summary of relevant data is given in Table 2. The length of the Zr–N_{ax} bond has an inverse relationship to both the dihedral angle N_{ax}–Zr–N_{eq}–R and the anticipated degree of steric compression in the apical site (X) (Scheme 3). This can be rationalised as follows. A complex suffering steric compression about the axial site at X could relieve this by an increase in the

aforementioned dihedral angle. The resultant 'upright' conformation of the substituents R, which is more usually associated with metals of smaller radii, leads to compression of the Zr–N_{ax} bond.

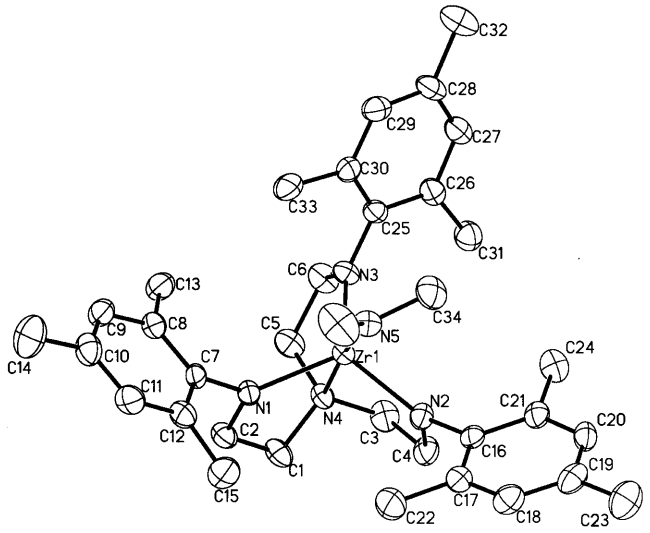


Fig. 1. Thermal ellipsoid plot of the molecular structure of [Zr(TMT)(NMe_2)] (**5**) (non-hydrogen atoms). Selected distances (Å) and angles (°): Zr(1)–N(3) 2.108(3), Zr(1)–N(1) 2.119(3), Zr(1)–N(2) 2.124(3), Zr(1)–N(5) 2.044(3), Zr(1)–N(4) 2.393(3), N(3)–Zr(1)–N(2) 109.42(13), N(3)–Zr(1)–N(1) 109.53(13), N(2)–Zr(1)–N(1) 118.23(13), N(3)–Zr(1)–N(5) 108.78(13), N(2)–Zr(1)–N(5) 101.23(13), N(1)–Zr(1)–N(5) 109.09(13), N(3)–Zr(1)–N(4) 74.81(12), N(2)–Zr(1)–N(4) 73.64(12), N(1)–Zr(1)–N(4) 72.72(11), N(5)–Zr(1)–N(4) 174.65(13).

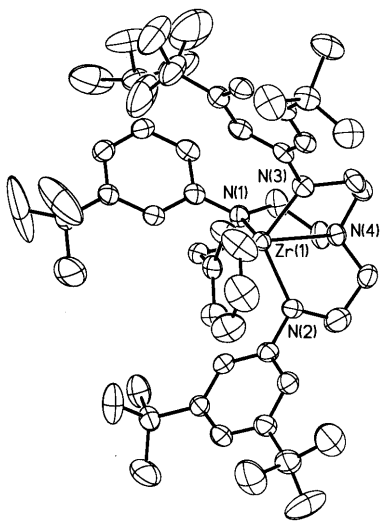


Fig. 2. Thermal ellipsoid plot of the molecular structure of [Zr(TDT)(CH_2Ph)] (**8**) (non-hydrogen atoms). Selected distances (Å) and angles (°): Zr(1)–N(2) 2.070(4), Zr(1)–N(3) 2.082(4), Zr(1)–N(1) 2.114(4), Zr(1)–C(49) 2.311(5), Zr(1)–N(4) 2.455(5), N(3)–Zr(1)–N(2) 117.23(18), N(3)–Zr(1)–N(1) 106.71(16), N(2)–Zr(1)–N(1) 111.05(17), N(3)–Zr(1)–C(49) 105.62(18), N(2)–Zr(1)–C(49) 102.36(18), N(1)–Zr(1)–C(49) 113.97(18), N(3)–Zr(1)–N(4) 71.87(15), N(2)–Zr(1)–N(4) 71.60(16), N(1)–Zr(1)–N(4) 75.43(15), C(49)–Zr(1)–N(4) 170.46(17).

2.3. Reactions of the alkyls with dihydrogen

We mentioned above that the benzyl complex [Zr(NN'_3)(CH_2Ph)] gives a metallacycle on reaction with dihydrogen. The intermediacy of a hydride species in this reaction is likely, and indeed a deuteride complex is implicated in the mechanism of exhaustive deuteration of the methylsilyl groups on exposure of the complex to D_2 [7]. The reactions of **2** and **4** with dihydrogen (1 atm) at room temperature however gave complex mixtures of products.

3. Conclusions

In an effort to synthesise a hydride derivative of zirconium we used Schrock's mesityl triamidoamine ligand H_3(TMT), but found that the *ortho*-substituents of the aryl rings prevented complete metalation by Zr(CH_2Ph)$_2$. The *meta*-substituted ligand H_3(TDT) was synthesised, and while this gave the target [Zr(TDT)X] complexes, this ligand did not support the formation of a stable hydride.

4. Experimental

4.1. General methods

All manipulations were carried out under an inert atmosphere of argon using standard Schlenk techniques and an MBraun dry-box. NMR samples were made up in the dry box and the sample tubes were sealed in vacuo or using Young type concentric stopcocks. Solvents were pre-dried over sodium wire and then distilled over sodium (toluene) and sodium–potassium alloy (diethyl ether, pentane) under an atmosphere of dinitrogen. Deuterated hydrocarbons were dried by refluxing over molten potassium in vacuo and then distilled trap-to-trap also in vacuo. NMR spectra were recorded at ca. 295 K on Bruker AC-250, AC-400 or DMX-300 spectrometers and the spectra referenced internally using residual protio solvent resonances relative to tetramethylsilane ($\delta = 0$ ppm). EI mass spectra were obtained on a VG Autospec mass spectrometer. Elemental Analyses were performed by Warwick Analytical Services. H_2 (Grade 6.0) was purchased from Air Products. Zr(NMe_2)$_4$ [12] and Zr(CH_2Ph)$_4$ [13] and H_3TMT [2f] were synthesised by literature methods.

4.2. Crystallography

Crystals were coated with inert oil and transferred to the cold N_2 gas stream on the diffractometer (Siemens

Table 2
A comparison of bond lengths and angles for **1** and **4** with related complexes

	Zr–N_{ax} (Å)	Zr–N_{eq} (Å)	Dihedral angles (°) N_{ax}–Zr–N_{eq}–R
[Zr(TMT)(NMe_2)] (**1**)	2.393(3)	2.108(3), 2.119(3), 2.124(3)	171.4, 160.9, 156.2
[Zr(TDT)(CH_2Ph)] (**4**)	2.455(4)	2.070(4), 2.082(4), 2.114(4)	169.5, 165.3, 161.4
[Zr(NN'_3)(CH_2Ph)] (Ref. [7])	2.5484(15)	2.0727(15), 2.0796(15), 2.0885(16)	133.1, 131.0, 128.8
[Zr(NN'_3)(NMe_2)] (Ref. [7])	2.509(2)	2.096(2), 2.124(3), 2.130(2)	165.3, 131.0,123.8

SMART three-circle with CCD area detector). Graphite monochromated Mo–K_α radiation $\lambda =$ 0.71073 Å was used. Absorption correction was performed by multi-scan (SADAB). The structures were solved by direct methods using SHELXS [14] with additional light atoms found by Fourier methods. Hydrogen atoms were added at calculated positions (except the hydrogen atoms on C34 and C35 in **1** which were found by Fourier methods) and refined using a riding model with freely rotating methyl groups. Anisotropic displacement parameters were used for all non-H atoms except a solvent pentane molecule in **4** which was left isotropic; H-atoms were given isotropic displacement parameters $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for methyl groups. The structures were refined using SHELXL-96 [15].

4.3. Syntheses

4.3.1. [H_3(TDT)]

Toluene (100 ml) was added to a large Schlenk vessel charged with TREN (2.00 g, 13.7 mmol), 1-bromo-3,5-di-*tert*-butylbenzene [16] (11.1 g, 41.1 mmol), $Pd_2(dba)_3$ (0.19 g, 0.20 mmol), *rac*-BINAP (0.34 g, 0.55 mmol) and NaOBu^t (4.60 g, 47.5 mmol). The resulting deep-orange mixture was heated over night at 90°C with stirring. On cooling to room temperature (r.t.) the cloudy solution was filtered and the toluene was removed using a rotary evaporator. The crude yellow oil was chromatographed with a 4:1 mixture of hexane–ethyl acetate containing 5 vol% of MeOH saturated with NH_3 to give an off-white solid. Recrystallisation from a 1:1 mixture of diethyl ether–pentane (40 ml) afforded clear, colourless crystals (4.98 g, 51%).

^{1}H-NMR (293 K, $CDCl_3$): δ 6.78 (s, 3H, Ph), 6.44 (s, 6H, Ph), 4.12 (s, 3H, NH), 3.25 (q, 6H, CH_2), 2.86 (t, 6H, CH_2), 1.24 (s, 54H, Bu^t). ^{13}C{^{1}H}-NMR (293 K, $CDCl_3$): δ 152.06 (s, Ph), 148.05 (s, Ph), 112.75 (s, Ph), 107.99 (s, Ph), 54.02 (s, CH_2), 42.45 (s, CH_2), 35.16 (s, CMe_3), 31.85 (s, CMe_3). MS (EI): m/z 712 (65%, $M^+ + 1$)

4.3.2. [Zr(TMT)(NMe_2)] (**1**)

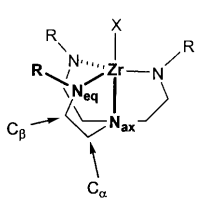
Toluene (20 ml) was added to a mixture of [H_3(TMT)] (0.20 g, 0.40 mmol) and [Zr(NMe_2)$_4$] (0.11 g, 0.40 mmol). The reaction was then heated at 80°C for 18 h under static reduced pressure. After evaporation of volatiles, the residue was dissolved in diethyl ether–pentane (10 ml) and filtered. Cooling overnight to −30°C afforded colourless crystals (0.19 g, 77%).

Anal. Calc. for $C_{35}H_{51}N_5Zr$: C, 66.41; H, 8.12; N, 11.06. Found: C, 65.41; H, 7.99; N, 11.04%. ^{1}H-NMR (293 K, benzene-d_6): δ 6.94 (s, 6H, Ph), 3.49 (t, 6H, CH_2), 2.85 (t, 6H, CH_2), 2.52 (s, 18H, Me), 2.20 (s, 9H, Me), 2.04 (s, 6H, NMe_2). ^{13}C{^{1}H}-NMR (293 K benzene-d_6): δ 149.24 (s, Ph), 134.95 (s, Ph), 132.65 (s, Ph), 129.86 (s, Ph), 53.67 (s, CH_2), 53.49 (s, CH_2), 39.72 (s, NMe_2), 21.22 (s, Me), 20.66 (s, Me). MS (EI): m/z 632 (5%, $M^+ + 1$), 587 (11%, $M^+ - NMe_2$).

4.3.3. [Zr(TMT)($CH_2Ph)_2$] (**2**)

Toluene (20 ml) was added to a mixture of [H_3(TMT)] (0.20 g, 0.40 mmol) and [Zr(CH_2Ph)$_4$] (0.19 g, 0.40 mmol) at r.t. The ampoule was wrapped in aluminium foil and the solution was stirred at ambient temperature for 3 days. After removal of volatiles, the residue was extracted with diethyl ether (50 ml), filtered and cooled to −30°C. Standing overnight afforded a yellow microcrystalline precipitate (0.12 g, 39%).

Anal. Calc. for $C_{47}H_{60}N_4Zr$: C, 73.10; H, 7.83; N, 7.26. Found: C, 72.67; H, 8.06; N, 7.03%. ^{1}H-NMR (293 K, benzene-d_6): δ 6.87 (m, 18H, Ph), 6.78 (d, 2H, Ph), 6.43 (d, 2H, Ph), 3.44 (m, 2H, CH_2), 3.34 (m, 2H, CH_2), 2.90 (m, 4H, CH_2), 2.60 (m, 4H, CH_2), 2.56 (s, 6H, CH_3), 2.48 (s, 6H, CH_3), 2.23 (s, 6H, CH_3), 2.22 (bs, 9H, CH_3), 1.91 (s, 2H, CH_2Ph), 1.73 (s, 2H, CH_2Ph). ^{13}C{^{1}H}-NMR (293 K benzene-d_6): δ 147.97 (s, Ph), 145.16 (s, Ph), 143.70 (s, Ph), 135.38 (s, Ph), 135.02 (s, Ph), 134.79 (s, Ph), 132.47 (s, Ph), 130.92 (s, Ph), 130.77 (s, Ph), 130.31 (s, Ph), 130.19 (s, Ph), 130.08 (s, Ph), 129.39 (s, Ph), 127.30 (s, Ph), 123.47 (s, Ph), 121.79 (s, Ph), 67.15 (s, CH_2Ph), 63.56 (s, CH_2Ph), 55.42 (s, CH_2), 52.82 (s, CH_2), 50.84 (s, CH_2), 41.74



Scheme 3.

(s, CH_2), 21.32 (s, CH_3), 20.55 (s, CH_3), 19.67 (s, CH_3), 18.91 (s, CH_3). MS (EI): m/z 587 (28%, $M^+ - 2CH_2Ph$).

4.3.4. [Zr(TDT)(NMe_2)] (3)

Toluene (20 ml) was added to a mixture of [H_3(TDT)] (0.25 g, 0.35 mmol) and [$Zr(NMe_2)_4$] (94 mg, 0.35 mmol). The mixture was heated at 80°C for 2 days under static reduced pressure. After removal of volatiles, the residue was dissolved in pentane, filtered and cooled to −30°C. Standing overnight afforded a white microcrystalline precipitate (0.26 g, 88%).

Anal. Calc. for $C_{50}H_{81}N_5Zr$: C, 71.20; H, 9.68; N, 8.30. Found: C, 70.05; H, 9.68; N, 7.62%. ^{1}H-NMR (293 K, benzene-d_6): δ 7.23 (t, 3H, Ph), 7.17 (d, 6H, Ph), 3.78 (t, 6H, CH_2), 2.68 (t, 6H, CH_2), 2.34 (s, 6H, NMe_2), 1.44 (s, 54H, Bu^t). ^{13}C{^{1}H}-NMR (293 K benzene-d_6): δ 155.01 (s, Ph), 151.50 (s, Ph), 117.31 (s, Ph), 115.81 (s, Ph), 55.32 (s, CH_2), 53.30 (s, CH_2), 40.61 (s, NMe_2), 35.38 (s, CMe_3), 32.33 (s, CMe_3).). MS (EI): m/z 841 (6%, M^+), 797 (18%, $M^+ - NMe_2$).

4.3.5. [Zr(TDT)(CH_2Ph)] (4)

Toluene (20 ml) was added to a mixture of [H_3(TDT)] (0.25 g, 0.35 mmol) and [$Zr(CH_2Ph)_4$] (0.16 g, 0.35 mmol) at r.t. The ampoule was covered in aluminium foil and the mixture was stirred at ambient temperature for 3 days. After removal of volatiles, the residue was redissolved in pentane (5 ml), filtered and cooled to −30°C. Standing overnight afforded pale-orange crystals (0.20 g, 64%).

Anal. Calc. for $C_{55}H_{82}N_4Zr$: C, 74.18; H, 9.28; N, 6.29. Found: C, 70.41; H, 8.96; N, 6.20%. ^{1}H-NMR (293 K, benzene-d_6): δ 7.33 (t, 3H, Ph), 7.17 (d, 6H, Ph), 7.01 (m, 3H, Ph), 5.86 (d, 2H, Ph), 3.55 (t, 6H, CH_2), 2.51 (s, 2H, CH_2Ph), 2.31 (t, 6H, CH_2), 1.48 (s, 54H, Bu^t). ^{13}C{^{1}H}-NMR (293 K benzene-d_6): δ 153.41 (s, Ph), 152.64 (s, Ph), 151.68 (s, Ph), 125.36 (s, Ph), 120.63 (s, Ph), 117.37 (s, Ph), 116.53 (s, Ph), 115.63 (s, Ph), 54.93 (s, CH_2), 53.44 (s, CH_2), 35.59 (s, CMe_3), 32.50 (s, CMe_3). MS (EI): m/z 797 (42%, $M^+ - CH_2Ph$).

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC, nos. 141 097 (compound **1**) and 141 098 (**4**). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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