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FULL PAPER

Ansa-di(phosphaneiminato)titanium chelates: novel isolobal analogues of *ansa*-titanocene derivatives

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$(Me_3SiN)Bu^t_2P(CH_2)_3PBu^t_2(NSiMe_3)$ (**1**) was obtained by the Staudinger reaction from Me_3SiN_3 and $Bu^t_2P(CH_2)_3PBu^t_2$. Metathesis of **1** with $TiCl_4$ in boiling toluene afforded the chelate $[(NBu^t_2P(CH_2)_3PBu^t_2N)TiCl_2]$ (**2**). $[(NBu^t_2P(CH_2)_3PBu^t_2N)TiMe_2]$ (**3**) and $[(NBu^t_2P(CH_2)_3PBu^t_2N)Ti(CH_2Ph)_2]$ (**4**) were obtained from **2** by reaction with methyllithium and benzylmagnesium chloride, respectively. The crystal structures of **3** and **4** were determined. Both compounds exhibit two quite different bond angles at their respective nitrogen atoms (*ca.* 140° *vs. ca.* 160°).

Introduction

The polymerisation of α-olefins by titanocene- and zirconocene-based catalysts is of great technological relevance.[1] Nevertheless, there is increasing interest in the development of novel non-metallocene catalysts for olefin polymerisation, since these may allow, *inter alia*, an even greater control over polymer properties. Several new catalyst families have been described in this context.[2]

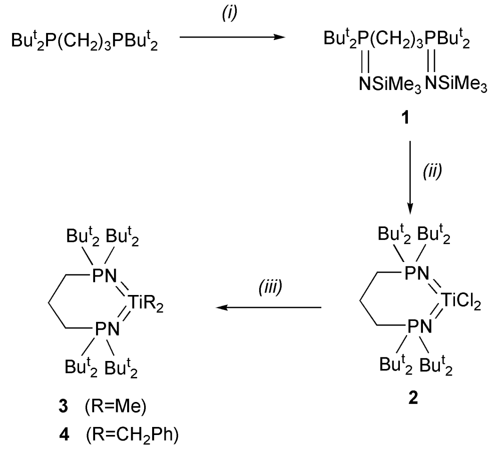
Di(phosphaneiminato)titanium(IV) complexes of the type $[(Bu^t_3PN)_2TiX_2]$ (X = Cl, Me) represent the first non-cyclopentadienyl, single-site catalysts competitive with derivatives of metallocenes under commercially relevant polymerisation conditions.[3] Similar to di(organoimido) complexes of the Group 6 metals, they are isolobal analogues of bent metallocene derivatives of the Group 4 metals.[4]

Ansa-metallocene derivatives are essential for the stereospecific polymerisation of α-olefins, and hence their isolobal analogues are of great current interest in this context. We recently reported the first examples of *ansa*-di(organoimido)-chromium complexes[5] and here describe the first *ansa*-di(phosphaneiminato)titanium compounds.

Results and discussion

The number of *ansa*-di(phosphaneiminato) complexes known to date is very small,[6] and no such compound has been described in the chemistry of the Group 4 metals. A convenient method for the synthesis of phosphaneiminato complexes is the metathesis of silylated iminophosphoranes with metal halides.[7] For example, the reaction of two equivalents of $Ph_3P(NSiMe_3)$[8] and $Bu^t_3P(NSiMe_3)$,[3] respectively, with $TiCl_4$ affords $[(Ph_3PN)_2TiCl_2]$ and $[(Bu^t_3PN)_2TiCl_2]$ in 85 and 91% yield, respectively. In contrast, the reaction of $(Me_3SiN)Ph_2PCH_2CH_2PPh_2(NSiMe_3)$ with $TiCl_4$ does not lead to a di(phosphaneiminato) chelate. Instead, reaction of a CH_2 group with the strongly Lewis acidic metal halide takes place, and a bis(trimethylsilylphosphoranimino) chelate containing one carbon–titanium bond is obtained.[9] A similar reaction takes place between $[VCl_3(THF)_3]$ and $(Me_3SiN)Ph_2PCH_2PPh_2(NSiMe_3)$.[10] Dinuclear complexes containing a bridging di(phosphaneiminato) ligand are formed in the reaction of $(Me_3SiN)Ph_2P(CH_2)_nPPh_2(NSiMe_3)$ with the comparatively weak Lewis acids Cp^*TiF_3 (n = 2)[11] and Cp^*TiCl_3 (n = 1,[12] 2[13]).

$(Me_3SiN)Bu^t_2P(CH_2)_3PBu^t_2(NSiMe_3)$ (**1**), obtained by the Staudinger reaction from Me_3SiN_3 and $Bu^t_2P(CH_2)_3PBu^t_2$,[14] reacts with $TiCl_4$ in boiling toluene under dilution conditions, affording the di(phosphaneiminato) chelate $[(NBu^t_2P(CH_2)_3PBu^t_2N)TiCl_2]$ (**2**) (Scheme 1). The hydrocarbyl derivatives $[(NBu^t_2P(CH_2)_3PBu^t_2N)TiMe_2]$ (**3**) and $[(NBu^t_2P(CH_2)_3PBu^t_2N)Ti(CH_2Ph)_2]$ (**4**) were obtained from **2** by reaction with methyllithium and benzylmagnesium chloride, respectively (Scheme 1). Both compounds are very air-sensitive.



Scheme 1 Reagents and conditions: (i) Me_3SiN_3, toluene, *ca.* 80 °C; (ii) $TiCl_4$, toluene, reflux; (iii) **3**: methyllithium (>2 equiv.), diethyl ether; **4**: benzylmagnesium chloride (> 2 equiv.), diethyl ether.

A single-crystal X-ray structure analysis was performed for **3** (Fig. 1) and **4** (Fig. 2). Selected bond lengths and angles are collected in Table 1. The crystal which was selected for the structure determination of **4** showed some benzyl/chlorine disorder with Cl occupying 7.5% of the benzyl positions, although an excess of benzylmagnesium chloride had been used in the synthesis of **4**. The disorder could be modelled satisfactorily (see Experimental).

The Ti–N [**3**, 183.5(2) and 181.0(2) pm; **4**, 180.7(2) and 182.3(2) pm] and P–N distances [**3**, 158.9(3) and 156.9(2); **4**, 158.7(3) and 158.4(3) pm] are very similar to the respective values found for $[(Bu^t_3PN)_2TiMe_2]$[3] and compatible with bond

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Table 1 Selected bond lengths (pm) and angles (°) for **3** and **4**

3		**4**	
Ti(1)–C(4)	212.4(3)	Ti(1)–C(4)	215.7(5)
Ti(1)–C(5)	212.8(3)	Ti(1)–C(11)	216.5(4)
P(1)–C(1)	181.3(3)	P(1)–C(1)	180.5(3)
P(1)–C(6)	186.9(3)	P(1)–C(18)	187.0(3)
P(1)–C(10)	186.6(3)	P(1)–C(22)	187.4(3)
P(2)–C(3)	184.7(3)	P(2)–C(3)	184.0(3)
P(2)–C(14)	186.7(3)	P(2)–C(26)	186.0(3)
P(2)–C(18)	185.9(3)	P(2)–C(30)	186.3(3)
C(1)–C(2)	155.3(5)	C(1)–C(2)	153.2(4)
C(2)–C(3)	152.3(4)	C(2)–C(3)	154.7(4)
C(4)–Ti(1)–C(5)	107.00(15)	C(4)–Ti(1)–C(11)	105.47(19)
P(1)–C(1)–C(2)	115.8(2)	P(1)–C(1)–C(2)	116.6(2)
C(1)–C(2)–C(3)	110.5(3)	C(1)–C(2)–C(3)	111.8(3)
C(2)–C(3)–P(2)	114.1(2)	C(2)–C(3)–P(2)	113.7(2)

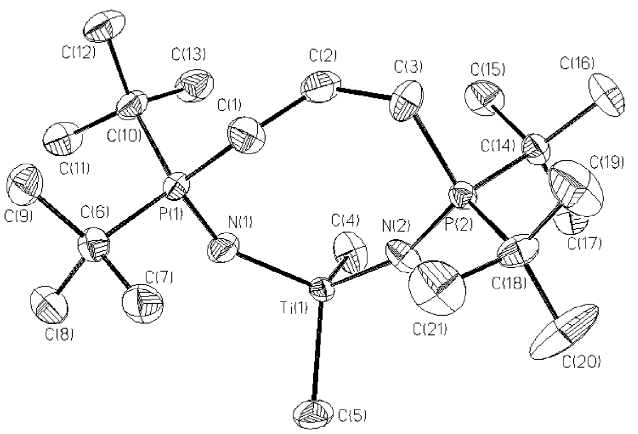

Fig. 1 Molecular structure of **3** in the crystal.

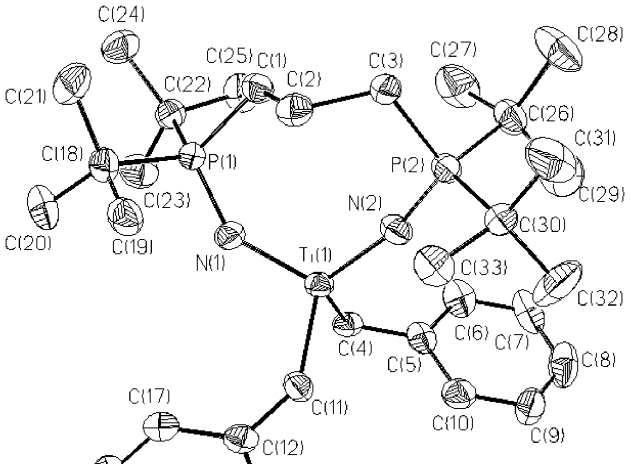

Fig. 2 Molecular structure of **4** in the crystal.

orders close to two. The N–Ti–N bite angle is 114.81(12)° for **3** and 114.17(12)° for **4**, which is only slightly smaller than the value of 117.24(11)° found for $[(Bu^t_3PN)_2TiMe_2]$.[3] This finding suggests that the eight-membered titanacycle present in **2**–**4** is essentially unstrained. Two quite different Ti–N–P angles are found for both **3** [140.30(19)° *vs.* 159.82(19)°] and **4** [140.95(17)° *vs.* 162.35(17)°], while angles of 171.2(2) and 175.3(2)° have been reported for $[(Bu^t_3PN)_2TiMe_2]$.[15] This lends further credence to the quantum-chemical result that the potential energy well for the angle at the nitrogen atom is very shallow for such compounds.[4b] A similar structural feature has previously been observed for $[(FcPh_2N)_2NbCl_3]$ (Fc = ferrocenyl), exhibiting Nb–N–P angles of 145.3(5) and 168.6(5)°.[16]

Conclusion

We have prepared the first Group 4 metal di(phosphaneiminato) chelates, showing that, contrary to previous beliefs,[13] chelating bis(trimethylsilyl)iminophosphoranes need not undergo C–H activation in preference to dehalosilylation with titanium tetrachloride. The markedly different Ti–N–P angles (*ca.* 140° *vs.* *ca.* 160°) found in the structurally characterised alkyl derivatives **3** and **4** should not be interpreted in terms of linear *vs.* bent phosphaneiminato ligands, but instead reflect the "softness" of the angle at the nitrogen atom. Studies concerning the use of compounds **2**–**4** in olefin polymerisation are currently underway.

Experimental

General

All manipulations were performed in an inert atmosphere (purified argon or dinitrogen) by using standard Schlenk and cannula techniques or a conventional glovebox. Solvents and reagents were appropriately dried and purified by using standard procedures. NMR spectra were recorded at 300 K with a Bruker DRX 500 spectrometer operating at 500.13 MHz for ^1H. Mass spectra were obtained with a VG Autospec instrument. Elemental analyses were performed by the Microanalytical Laboratory of the Universität Bielefeld and by the Microanalytical Laboratory Beller (Göttingen).

Syntheses

$(Me_3SiN)Bu^t_2P(CH_2)_3PBu^t_2(NSiMe_3)$ (1). 5 mL of a solution of Me_3SiN_3 (19.00 g, 164.9 mmol) in toluene (50 mL) were added to a stirred solution of 1,3-bis(di-*tert*-butylphosphanyl)-propane[14] (25.99 g, 75.2 mmol) in toluene (100 mL). The mixture was slowly heated until gas evolution was observed (*ca.* 80 °C). After dropwise addition of the remaining solution of Me_3SiN_3 at this temperature the mixture was heated to reflux for 2 h and was then allowed to cool to room temperature. Volatile components were removed *in vacuo*. The remaining solid was treated with diethyl ether (80 mL). The mixture was filtered and the filtrate reduced to dryness *in vacuo*, affording 37.00 g (97%) of light yellow **1**. ^1H NMR ($CDCl_3$): δ −0.04 (s, 18H, $SiMe_3$), 1.15 (d, $|J_{HP}|$ = 13.2 Hz, 36H, Bu^t), 1.58–1.64 (m, 4H, CH_2), 1.84–1.94 (m, 2H, CH_2). ^{13}C-{^1H} NMR ($CDCl_3$): δ 4.4 ($SiMe_3$), 19.0 (t, $|J_{CP}|$ = 3.8 Hz, $CH_2\mathit{C}H_2CH_2$), 25.7 (dd, $|J_{CP}|$ = 57.9 and 10.4 Hz, $\mathit{C}H_2CH_2\mathit{C}H_2$), 27.3 ($C\mathit{Me}_3$), 36.4 (d, $|J_{CP}|$ = 62.2 Hz, $\mathit{C}Me_3$). ^{31}P-{^1H} NMR ($CDCl_3$): δ 26.5. ESI-MS: *m*/*z* (%) 507 (100) $[M]^+$. Calc. for $C_{25}H_{60}N_2P_2Si_2$: C, 59.24; H, 11.93; N, 5.53%. Found: C, 59.81; H, 12.12; N, 5.65%.

$[(NBu^t_2P(CH_2)_3PBu^t_2N)TiCl_2]$ (2). A solution of **1** (4.03 g, 7.95 mmol) in toluene (100 mL) and a solution of $TiCl_4$ (1.51 g, 7.96 mmol) in toluene (100 mL) were simultaneously added dropwise over a period of 3 h to gently refluxing toluene (100 mL). The mixture was refluxed for a further 0.5 h and then allowed to cool to room temperature. The white precipitate was collected by filtration and dried *in vacuo*. A second crop was obtained from the mother liquor at −30 °C. Yield 2.54 g (67%). ^1H NMR (CD_2Cl_2): δ 1.44 (d, $|J_{HP}|$ = 15.2 Hz, 36H, Bu^t), 2.14–2.23 (m, 2H, $CH_2C\mathit{H}_2CH_2$), 2.75–2.84 (m, 4H, $C\mathit{H}_2CH_2C\mathit{H}_2$). CI-MS: *m*/*z* (%) 478 (100) $[M]^+$. Calc. for $C_{19}H_{42}N_2Cl_2P_2Ti$: C, 47.61; H, 8.83; N, 5.84%. Found: C, 47.33; H, 8.57; N, 6.17%.

$[(NBu^t_2P(CH_2)_3PBu^t_2N)TiMe_2]$ (3). Methyllithium (1.68 mL of a 1.60 M solution in diethyl ether, 2.69 mmol) was added

Table 2 X-Ray crystallographic data

Chemical formula	$C_{21}H_{48}N_2P_2Ti$	$C_{31.94}H_{54.94}Cl_{0.15}N_2P_2Ti$
Formula weight	438.45	582.22
Space group	$P2_12_12_1$	*Pbca*
a/Å	8.77800(10)	17.6750(4)
b/Å	17.1110(2)	16.6950(4)
c/Å	17.4480(3)	23.0070(6)
V/Å^3	2620.70(6)	6789.0(3)
Z	4	8
μ/mm^{-1}	0.456	0.380
F(000)	960	2521
Reflections collected	23338	48069
Independent reflections	4565 [R(int.) = 0.036]	5962 [R(int.) = 0.122]
Data/restraints/parameters	4565/0/249	5962/0/364
Final $R1^a$ [$I > 2\sigma(I)$]/$wR2^b$	0.0380/0.0956	0.0495/0.1226

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$.

dropwise to a stirred suspension of **2** (0.43 g, 0.90 mmol) in diethyl ether (30 mL) at −80 °C. The mixture was allowed to warm to room temperature over the course of 12 h. Volatile components were removed *in vacuo*. The residue was extracted with toluene (2 × 10 mL) and the extracts reduced to dryness *in vacuo*. The remaining solid was washed with *n*-hexane (20 mL) and dried *in vacuo*, leaving **3** as a light yellow, microcrystalline solid. Yield 0.32 g (81%). Owing to the high sensitivity of the product towards air and moisture, no reproducible microanalytical data could be obtained. ^{1}H NMR (C_6D_6): δ 0.92, (s, 6H, $TiMe_2$), 1.06 (d, $|J_{HP}|$ = 13.3 Hz, 36H, Bu^t), 1.14–1.50 (m, 6H, CH_2). ^{13}C-{^{1}H} NMR (C_6D_6): δ 17.7 (t, $|J_{CP}|$ = 4.2 Hz, $CH_2\mathit{C}H_2CH_2$), 26.1 (dd, $|J_{CP}|$ = 47.4 and 6.7 Hz, $\mathit{C}H_2CH_2\mathit{C}H_2$), 27.9 (C*Me*$_3$), 35.1 ($TiMe_2$), 37.0 (d, $|J_{CP}|$ = 57.2 Hz, *C*Me$_3$). ^{31}P-{^{1}H} NMR (C_6D_6): δ 25.8.

[(NBu$^t_2$P(CH$_2$)$_3$PBu$^t_2$N)Ti(CH$_2$Ph)$_2$] (4). Benzylmagnesium chloride (9.39 mL of a 1.00 M solution in diethyl ether, 9.39 mmol) was added dropwise to a stirred suspension of **2** (1.50 g, 3.13 mmol) in diethyl ether (50 mL) at −80 °C. The mixture was allowed to warm to room temperature over the course of 12 h. Volatile components were removed *in vacuo*. The residue was extracted with toluene (2 × 10 mL) and the extracts reduced to dryness *in vacuo*. The remaining solid was washed with *n*-hexane (20 mL) and dried *in vacuo*, leaving **4** as a light yellow, microcrystalline solid. Yield 0.92 g (50%). Owing to the high sensitivity of the product towards air and moisture, no reproducible microanalytical data could be obtained. ^{1}H NMR (C_6D_6): δ 0.99 (d, $|J_{HP}|$ = 13.4 Hz, 36H, Bu^t), 1.25–1.43 (m, 6H, $CH_2CH_2CH_2$), 2.88 (s, 4H, C*H*$_2$Ph), 6.90 (m, 2H, Ph), 7.27 (m, 4H, Ph), 7.38 (m, 4H, Ph). ^{13}C-{^{1}H} NMR (C_6D_6): δ 17.0 (t, $|J_{CP}|$ = 4.5 Hz, $CH_2\mathit{C}H_2CH_2$), 25.8 (dd, $|J_{CP}|$ = 47.2 and 5.9 Hz, $\mathit{C}H_2CH_2\mathit{C}H_2$); 27.5 (C*Me*$_3$); 36.5 (d, $|J_{CP}|$ = 56.8 Hz, *C*Me$_3$); 65.6 (*C*H$_2$Ph); 120.3, 127.6, 128.6, 151.8 (Ph). ^{31}P-{^{1}H} NMR (C_6D_6): δ 28.2.

X-Ray crystal structure determinations

Single crystals of **3** (dimensions 0.25 × 0.17 × 0.10 mm^3) and **4** (dimensions 0.11 × 0.07 × 0.07 mm^3) were used for data collection at 100 K on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods. The program package used was SHELX 97.[17] Full-matrix least-squares refinement on F^2 was carried out anisotropically for the non-hydrogen atoms and the disordered chlorine atoms present in **4**, where they occupy 7.5% of the benzyl positions. The disorder has been modelled according to C(4)–C(10) : Cl(1) 92 : 8, C(11)–C(17) : Cl(2) 93 : 7. Hydrogen atoms were included at calculated positions using a riding model. Further X-ray structure analysis data are given in Table 2.

CCDC reference numbers 183851 and 183852.

See http://www.rsc.org/suppdata/dt/b2/b203606c/ for crystallographic data in CIF or other electronic format.

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References and notes

1 For leading reviews, see: (*a*) *Organometallic Catalysts and Olefin Polymerization*, eds. R. Blom, A. Follestad, E. Rytter, M. Tilset and M. Ystenes, Springer, Berlin, 2001; (*b*) W. Kaminsky, *J. Chem. Soc., Dalton Trans.*, 1998, 1413; (*c*) C. Janiak, in *Metallocenes, Vol. 2*, eds. A. Togni and R. Halterman, Wiley-VCH, Weinheim, 1998, pp. 547–623; (*d*) M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 1996, 255; (*e*) H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger and R. Waymouth, *Angew. Chem.*, 1995, **107**, 1255; H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger and R. Waymouth, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1143; (*f*) *Ziegler Catalysts*, eds. G. Fink, R. Mülhaupt and H. H. Brintzinger, Springer, Berlin, 1995.

2 For a recent review, see: G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem.*, 1999, **111**, 448; G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem., Int. Ed.*, 1999, **38**, 428.

3 D. W. Stephan, F. Guérin, R. E. v. H. Spence, L. Koch, X. Gao, S. J. Brown, J. W. Swabey, Q. Wang, W. Xu, P. Zoricak and D. G. Harrison, *Organometallics*, 1999, **18**, 2046.

4 See, for example: (*a*) U. Siemeling, T. Türk, W. W. Schoeller, C. Redshaw and V. C. Gibson, *Inorg. Chem.*, 1998, **37**, 4738; (*b*) A. Diefenbach and F. M. Bickelhaupt, *Z. Anorg. Allg. Chem.*, 1999, **625**, 892.

5 U. Siemeling, L. Kölling, A. Stammler, H.-G. Stammler, E. Kaminski and G. Fink, *Chem. Commun.*, 2000, 1177.

6 (*a*) U. Siemeling, B. Neumann, H.-G. Stammler and O. Kuhnert, *Z. Anorg. Allg. Chem.*, 2000, **626**, 825; (*b*) H. W. Roesky, K. Swerat and F. Edelmann, *Z. Naturforsch., Teil B*, 1988, **43**, 231; (*c*) K. V. Katti, U. Seseke and H. W. Roesky, *Inorg. Chem.*, 1987, **26**, 814; (*d*) K. V. Katti, H. W. Roesky and M. Rietzel, *Z. Anorg. Allg. Chem.*, 1987, **553**, 123.

7 Reviews: (*a*) K. Dehnicke, M. Krieger and W. Massa, *Coord. Chem. Rev.*, 1999, **182**, 19; (*b*) K. Dehnicke and J. Strähle, *Polyhedron*, 1989, **8**, 707.

8 T. Rübenstahl, F. Weller, S. Wocaldo, W. Massa and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1995, **621**, 953.

9 M. J. Sarsfield, M. Thornton-Pett and M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 1999, 3329.

10 G. Aharonian, K. Feghali, S. Gambarotta and G. P. A. Yap, *Organometallics*, 2001, **20**, 2616.

11 M. Sotoodeh, I. Leichtweis, H. W. Roesky, M. Noltemeyer and H.-G. Schmidt, *Chem. Ber.*, 1993, **126**, 913.

12 R. P. Kamalesh Babu, R. McDonald and R. G. Cavell, *J. Chem. Soc., Dalton Trans.*, 2001, 2210.

13 M. J. Sarsfield, M. Said, M. Thornton-Pett, L. A. Gerrard and M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 2001, 822.

14 N. Carr, B. J. Dunne, L. Mole, A. G. Orpen and J. L. Spencer, *J. Chem. Soc., Dalton Trans.*, 1991, 863.

15 Ref. 3 erroneously gives a value of 167.8(3)° for this compound. The correct angles may be found in the deposited CIF.

16 U. Siemeling, A. Stammler, H.-G. Stammler and O. Kuhnert, *Z. Anorg. Allg. Chem.*, 1999, **625**, 845.

17 G. M. Sheldrick, SHELX 97, University of Göttingen, Germany, 1997.