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Synthesis of cationic Group 4 metal compounds by protonolysis of amide precursors: crystal structure of $[Ti(NMe_2)_3(NC_5H_5)_2][BPh_4]$

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Abstract

Protonation of $[M(NMe_2)_4]$ with $NHEt_3BPh_4$ in tetrahydrofuran (THF) gave the cationic compounds $[M(NMe_2)_3(THF)_x][BPh_4]$ (M = Ti and $x = 1$; M = Zr or Hf and $x = 2$); similar treatment of $[M(cp)_2(NMe_2)_2]$ (M = Zr or Hf, cp = η-C_5H_5) afforded the cations $[M(cp)_2(NMe_2)(NMe_2H)_{1-x}(THF)_x]^+$ which were transformed into $[M(cp)_2(NMe_2)(NC_5H_5)]^+$ in pyridine. The trigonal bipyramidal crystal structure of $[Ti(NMe_2)_3(NC_5H_5)_2][BPh_4]$ has been determined.

Keywords: Group 4; Amide; Cationic

1. Introduction

Recently we described the novel protonolysis reaction of a U–NR_2 bond by means of $NHEt_3BPh_4$, which proved to be an efficient synthesis of mono- and dicationic uranium compounds [1,2]. For testing the potential of reaction (1) in the synthesis of cationic complexes of the d transition metals, we first considered its application to some representative amide derivatives of the Group 4 elements. Here we report on the cationic compounds which were obtained from $[M(NMe_2)_4]$ and $[M(cp)_2(NMe_2)_2]$ (M = Ti, Zr or Hf; cp = η-C_5H_5); we also describe the crystal structure of $[Ti(NMe_2)_3(NC_5H_5)_2][BPh_4]$.

$$[\{M\}\text{–}NR_2] + NHEt_3BPh_4 \rightarrow [\{M\}][BPh_4] + NHR_2 + NEt_3 \quad (1)$$

2. Results and discussion

2.1. Syntheses

Protonolysis of $[Ti(NMe_2)_4]$ by means of $NHEt_3BPh_4$ in tetrahydrofuran (THF) led to the formation of the cationic tris-amide compound $[Ti(NMe_2)_3(THF)][BPh_4]$ **1** which was isolated as an ochre powder in 87% yield. This reaction proceeded by the intermediacy of the amine adduct $[Ti(NMe_2)_3(NMe_2H)][BPh_4]$ and several consecutive evaporations of THF solutions were necessary for complete replacement of the NMe_2H ligand. Yellow crystals of $[Ti(NMe_2)_3(NC_5H_5)_2][BPh_4]$ **2**, obtained by slow diffusion of pentane into a solution of **1** in pyridine, were suitable for an X-ray diffraction study (vide infra). Treatment of $[Zr(NMe_2)_4]$ and $[Hf(NMe_2)_4]$ with $NHEt_3BPh_4$ readily afforded white microcrystalline powders of $[M(NMe_2)_3(THF)_2][BPh_4]$ (M = Zr, **3** or Hf, **4**) in 97 and 88% yield respectively; in that case, the amine molecule was not firmly attached to the less hard metal centre and was easily eliminated. After

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the tris[bis(trimethylsilyl)amido] compounds $[M\{N(SiMe_3)_2\}_3Cl]$ (M = Zr or Hf) [3], which have a peculiar chemistry due to the distinct electronic and steric effects of the $N(SiMe_3)_2$ ligand, complexes **3** and **4** are, to our knowledge, unique examples of tris(dialkylamido) derivatives of zirconium and hafnium.

Reaction (1) was also applied to the bis(cyclopentadienyl) bis(amide) complexes $[M(cp)_2(NMe_2)_2]$ (M = Zr or Hf; cp = η-C_5H_5) which were transformed into the cations $[M(cp)_2(NMe_2)(NMe_2H)_{1-x}(THF)_x]^+$; after addition of pyridine, pale yellow microcrystals of $[M(cp)_2(NMe_2)(NC_5H_5)][BPh_4]$ (M = Zr, **5** or Hf, **6**) were respectively obtained in 93 and 66% yield. The new complexes **1–6** have been characterized by their elemental analyses and ^1H NMR spectra (Table 1).

After the synthesis of a series of cations from $[U(NEt_2)_4]$ and various cyclopentadienyl and cyclooctatetraene uranium amide precursors [1,2], the above results show the wider applicability of reaction (1), which can also be useful for the preparation of cationic compounds of the d transition metals. In particular, the cationic amide complexes, which are very rare and limited to $[\{M\}(NHR)]^+$ derivatives [4], might exhibit an interesting reactivity, distinct from that of their neutral precursors [5]; it was recently demonstrated that organozirconium cations with heteroatom ligands possess a potential utility in stoichiometric and catalytic processes [6]. The amide cations can also be versatile starting materials in inorganic and organometallic synthesis, as already demonstrated in uranium chemistry

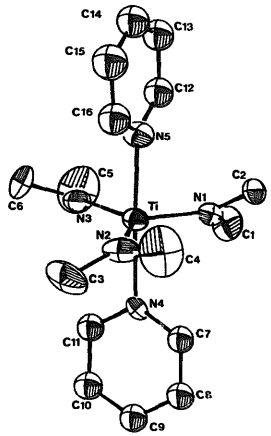

Fig. 1. ORTEP drawing of the cation of **2**.

[2,7]. In addition to the classical reactions of metal amide complexes [8], i.e. insertion of unsaturated molecules into the metal–nitrogen bond and substitution of the NR_2 group with proton acidic substrates, cations of the type $[\{M\}(NR_2)]^+$ can undergo facile addition of anionic species to give neutral derivatives. In certain

Table 1
Analytical and ^1H NMR data for the complexes

Compound	Analyses [a] (%)	NMR data [b]
1 $[Ti(NMe_2)_3(THF)][BPh_4]$	C 71.5 (71.45) H 8.05 (8.1) N 7.25 (7.35)	7.1 (8H, *o*-Ph), 6.8 and 6.6 (12H, *m*- and *p*-Ph), 3.11 (18H, Me)
2 $[Ti(NMe_2)_3(NC_5H_5)_2][BPh_4]$	C 72.9 (73.05) H 7.2 (7.35) N 10.55 (10.65)	8.26 (4H, d, *J* 4, *o*-NC_5H_5), 7.65 (2H, t, *J* 7, *p*-NC_5H_5), 7.2 (12H, *o*-Ph and *m*-NC_5H_5), 6.8 and 6.7 (12H, *m*- and *p*-Ph), 3.10 (18H, Me)
3 $[Zr(NMe_2)_3(THF)_2][BPh_4]$	C 66.2 (66.45) H 7.75 (7.9) N 5.95 (6.1)	7.1 (8H, *o*-Ph), 6.8 and 6.6 (12H, *m*- and *p*-Ph), 2.80 (18H, Me)
4 $[Hf(NMe_2)_3(THF)_2][BPh_4]$	C 58.8 (58.95) H 7.0 (7.05) N 5.3 (5.45)	7.1 (8H, *o*-Ph), 6.8 and 6.7 (12H, *m*- and *p*-Ph), 2.82 (18H, Me)
5 $[Zr(cp)_2(NMe_2)(NC_5H_5)][BPh_4]$	C 74.15 (74.2) H 6.3 (6.25) N 4.35 (4.2)	8.20 (2H, d, *J* 4, *o*-NC_5H_5), 7.65 (1H, t, *J* 7, *p*-NC_5H_5), 7.2 (10H, *o*-Ph and *m*-NC_5H_5), 6.8 and 6.7 (12H, *m*- and *p*-Ph), 6.21 (10H, cp), 3.20 (6H, Me)
6 $[Hf(cp)_2(NMe_2)(NC_5H_5)][BPh_4]$	C 65.2 (65.55) H 5.55 (5.5) N 3.75 (3.75)	8.18 (2H, d, *J* 4, *o*-NC_5H_5), 7.65 (1H, t, *J* 7, *p*-NC_5H_5), 7.2 (10H, *o*-Ph and *m*-NC_5H_5), 6.8 and 6.7 (12H, *m*- and *p*-Ph), 6.17 (10H, cp), 3.28 (6H, Me)

[a] Analytical data given as Found (Calc.) (%).
[b] At 30°C in THF-d_8; data given as chemical shift δ (relative integral, multiplicity, coupling constant *J* in hertz, assignment); when not specified, the signal is a singlet with half-height width between 10 and 30 Hz.

Table 2
Selected bond distances (Å) and angles (°) for $[Ti(NMe_2)_3(NC_5H_5)_2][BPh_4]$ with estimated standard deviations in parentheses

Ti–N(1)	1.86(1)	Ti–N(2)	1.87(1)
Ti–N(3)	1.87(1)	Ti–N(4)	2.215(9)
Ti–N(5)	2.25(1)		
N(1)–Ti–N(2)	119.3(6)	N(1)–Ti–N(3)	120.0(5)
N(2)–Ti–N(3)	120.6(6)	N(4)–Ti–N(5)	178.4(4)
N(1)–Ti–N(4)	90.4(4)	N(2)–Ti–N(4)	89.4(4)
N(3)–Ti–N(4)	92.6(4)	N(1)–Ti–N(5)	88.4(4)
N(2)–Ti–N(5)	90.3(5)	N(3)–Ti–N(5)	88.9(4)

cases, such uranium cations were found to have a major advantage over the corresponding chloro-amide compounds $[\{U\}(NR_2)Cl]$ in their reactions with alkali metal reagents, by avoiding the problems encountered with the elimination of salts and the formation of 'ate' complexes. The cationic amide complexes **1–6** would thus represent valuable substitutes for their neutral halogeno-amide counterparts, such as the titanium tris(amide) compounds $[Ti(NR_2)_3X]$ (R = Me or Et, X = halogen) [9] and the metallocene complexes $[M(cp)_2(NMe_2)Cl]$ (M = Ti, Zr) [10] which have been isolated and served to prepare a series of derivatives by metathetical exchange of the halide ligand.

2.2. Crystal structure of $[Ti(NMe_2)_3(NC_5H_5)_2][BPh_4]$

The crystals of **2** are composed of discrete cation–anion pairs. The BPh_4 anion displays the expected geometry; an ORTEP [11] drawing of the cation is shown in Fig. 1 and selected bond distances and angles are listed in Table 2. The titanium atom is in a quite perfect trigonal bipyramidal environment. The metal centre and the three nitrogen atoms of the NMe_2 groups are coplanar, the N–Ti–N angles being equal to 120° within experimental error. The N atoms of the pyridine ligands occupy the apical positions and the pyramid axis N(4)–Ti–N(5) deviates from linearity by 2°; the N(pyridine)–Ti–N(NMe_2) angles range from 88.4(4) to 92.6(4)°. The Ti–N(amido) bond lengths average 1.867(6) Å and are at the lower limit of the range of these distances found for terminally coordinated NMe_2 ligands, which vary from 1.854(7) Å in $[Ti(OC_6H_2\text{-}2,4\text{-}^tBu_2\text{-}6\text{-}Ph)_2(NMe_2)_2]$ [12] to 2.067(12) Å in $[(\eta\text{-}C_5Me_5)(Me_2N)_2Ti\{\mu\text{-}O(Me_2N)C\}W(CO)_5]$ [13]; the $TiNC_2$ fragments are planar (within ±0.08 Å). These structural parameters are generally considered as reflecting significant nitrogen–p to metal–d π bonding. The Ti–N–C angles for each NMe_2 ligand are different by ±10°; such distortion of amide ligands has been observed in other metal dialkylamides [14]. The coordination of the pyridine ligands is unexceptional, with an average value of 2.23(2) Å for the Ti–N distances [15].

3. Experimental details

3.1. General methods

All preparations and reactions were carried out under argon (< 5 ppm oxygen or water) using standard Schlenk vessel and vacuum-line techniques or in a glove-box. Solvents were thoroughly dried and deoxygenated by standard methods and distilled immediately before use. Deuterated solvents were dried over Na–K alloy.

Elemental analyses were performed by the Analytische Laboratorien at Lindlar (Germany). The ^1H NMR spectra were recorded on a Bruker WP 60 (FT) instrument and were referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ 0). The salt $NHEt_3BPh_4$ precipitated in water by mixing $NaBPh_4$ and $NHEt_3Cl$. The compounds $[M(NMe_2)_4]$ (M = Ti, Zr [16] or Hf [17]) and $[M(cp)_2(NMe_2)_2]$ (M = Zr or Hf [17]) were prepared by published methods.

3.2. Synthesis of $[Ti(NMe_2)_3(THF)][BPh_4]$ 1

A round-bottomed flask (50 ml) was charged with $[Ti(NMe_2)_4]$ (570 mg, 2.54 mmol) and $NHEt_3BPh_4$ (957 mg, 2.27 mmol) and THF (20 ml) was condensed into it at −78 °C under vacuum. The reaction mixture was stirred for 3 h at 20 °C and, after filtration, the volume of the orange solution was reduced to 10 ml by evaporation. The yellow powder which precipitated upon addition of diethyl ether (25 ml) was filtered off and washed with Et_2O (2 × 20 ml). At this stage the ^1H NMR spectrum of the product revealed the presence of the amine NMe_2H. The yellow powder was then dissolved in THF (10 ml) and the solution evaporated to dryness; this operation was repeated three times, finally giving an ochre powder of **1** (1130 mg, 87%).

3.3. Synthesis of $[Zr(NMe_2)_3(THF)_2][BPh_4]$ 3

A round-bottomed flask (50 ml) was charged with $[Zr(NMe_2)_4]$ (172 mg, 0.64 mmol) and $NHEt_3BPh_4$ (254 mg, 0.60 mmol) and THF (20 ml) was condensed into it at −78 °C under vacuum. The reaction mixture was stirred for 1 h at 20 °C and, after filtration, the volume of the colourless solution was reduced to 10 ml by evaporation. The white powder of **2** which precipitated upon addition of diethyl ether (25 ml) was filtered off, washed with Et_2O (2 × 15 ml) and dried under vacuum (400 mg, 97%).

3.4. Synthesis of $[Hf(NMe_2)_3(THF)_2][BPh_4]$ 4

The preparation of **4** was identical to that of **3**, from $[Hf(NMe_2)_4]$ (155 mg, 0.44 mmol) and $NHEt_3BPh_4$

(175 mg, 0.42 mmol); the white powder was obtained in 88% yield.

3.5. Synthesis of $[Zr(cp)_2(NMe_2)(NC_5H_5)][BPh_4]$ 5

A round-bottomed flask (50 ml) was charged with $[Zr(cp)_2(NMe_2)_2]$ (289 mg, 0.93 mmol) and $NHEt_3BPh_4$ (383 mg, 0.91 mmol) and THF (20 ml) was condensed into it at −78 °C under vacuum. The reaction mixture was stirred for 1 h at 20 °C and, after filtration, the solution was evaporated to dryness, leaving a yellow powder of $[Zr(cp)_2(NMe_2)(NMe_2H)_{0.6}(THF)_{0.4}][BPh_4]$: δ (30 °C, THF-$d_8$) 7.2 (8H, *o*-Ph), 6.8 and 6.7 (12H, *m*- and *p*-Ph), 6.21 (10H, cp), 4.1 (0.6H, $w_{1/2}$ 35 Hz, NMe_2H), 3.14 (6H, Me), 2.14 (3.6H, NMe_2H). This latter was dissolved in a mixture of THF (15 ml) and pyridine (1 ml); after filtration, the solvents were evaporated off and 5 was isolated as a pale yellow microcrystalline powder (562 mg, 93%).

3.6. Synthesis of $[Hf(cp)_2(NMe_2)(NC_5H_5)][BPh_4]$ 6

A round-bottomed flask (50 ml) was charged with $[Hf(cp)_2(NMe_2)_2]$ (98 mg, 0.25 mmol) and $NHEt_3BPh_4$ (100 mg, 0.24 mmol) and THF (20 ml) was condensed into it at −78 °C under vacuum. The reaction mixture was stirred for 1 h at 20 °C and, after filtration, the solution was evaporated to dryness, leaving a white powder of $[Hf(cp)_2(NMe_2)(NMe_2H)_{0.6}(THF)_{0.4}][BPh_4]$: δ (30 °C, THF-$d_8$) 7.2 (8H, *o*-Ph), 6.8 and 6.7 (12H, *m*- and *p*-Ph), 6.19 (10H, cp), 4.5 (0.6H, $w_{1/2}$ 35 Hz, NMe_2H), 3.20 (6H, Me), 2.20 (3.6H, NMe_2H). This latter was dissolved in a mixture of THF (15 ml) and pyridine (1 ml) and, after 15 min, the volume of the pale

Table 3
Crystallographic data and experimental details for $[Ti(NMe_2)_3(NC_5H_5)_2][BPh_4]$

Formula	$C_{40}H_{48}BN_5Ti$
M	657.57
Crystal size (mm³)	0.60×0.50×0.40
Colour	Yellow
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	9.771(5)
b (Å)	11.715(3)
c (Å)	17.271(7)
α (°)	107.01(3)
β (°)	93.84(4)
γ (°)	91.05(3)
U (Å³)	1885(2)
Z	2
D_c (g cm⁻³)	1.159
μ(Mo Kα) (cm⁻¹)	2.551
F(000)	700
θ limits (°)	1, 20
Scan type	ω–2θ
Scan width	0.8 + 0.35 tan θ
Range *h*, *k*, *l*	−9 to 9, −11 to 11, 0 to 16
Reflections collected	
total	3764
unique	3511
with $I > 3\sigma(I)$	1735
No. of parameters	249
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.070
$Rw = [\Sigma w\|\|F_o\| - \|F_c\|^2 / \Sigma w(\|F_o\|)^2]^{1/2}$	0.074
Max. residual electron density (e Å⁻³)	0.343

Table 4
Fractional atomic coordinates with estimated standard deviations in parentheses for $[Ti(NMe_2)_3(NC_5H_5)_2][BPh_4]$

Atom	*x*	*y*	*z*	B(Å²)
Ti	0.7138(2)	0.4487(2)	0.8090(1)	3.80(5) [a]
N(1)	0.8675(9)	0.4848(7)	0.7612(5)	4.4(2) [a]
N(2)	0.734(1)	0.3610(8)	0.8836(5)	6.2(3) [a]
N(3)	0.5428(9)	0.5058(8)	0.7859(6)	5.0(3) [a]
N(4)	0.6764(8)	0.2794(7)	0.7098(5)	3.8(2) [a]
N(5)	0.758(1)	0.6201(7)	0.9100(5)	5.0(3) [a]
C(1)	0.864(1)	0.486(1)	0.6779(7)	6.8(4) [a]
C(2)	1.002(1)	0.517(1)	0.7999(9)	7.5(4) [a]
C(3)	0.626(2)	0.285(1)	0.8954(8)	11.2(6) [a]
C(4)	0.857(2)	0.335(1)	0.9220(9)	13.7(7) [a]
C(5)	0.500(2)	0.549(1)	0.7217(9)	11.26(6) [a]
C(6)	0.440(1)	0.523(1)	0.8431(9)	9.9(6) [a]
C(7)	0.781(1)	0.2114(9)	0.6834(6)	4.5(3)
C(8)	0.763(1)	0.099(1)	0.6291(6)	5.1(3)
C(9)	0.635(1)	0.056(1)	0.6003(7)	5.2(3)
C(10)	0.527(1)	0.123(1)	0.6253(7)	5.2(3)
C(11)	0.552(1)	0.236(1)	0.6795(6)	4.8(3)
C(12)	0.786(1)	0.721(1)	0.8942(8)	6.1(3)
C(13)	0.807(1)	0.831(1)	0.9516(7)	6.4(3)
C(14)	0.790(1)	0.836(1)	1.0291(8)	7.1(4)
C(15)	0.760(1)	0.737(1)	1.0484(9)	8.7(4)
C(16)	0.749(1)	0.627(1)	0.9858(8)	7.0(4)
C(20)	0.019(1)	0.1417(8)	0.3115(6)	3.3(2)
C(21)	0.092(1)	0.0766(9)	0.2465(6)	4.5(3)
C(22)	0.235(1)	0.090(1)	0.2474(7)	5.6(3)
C(23)	0.306(1)	0.166(1)	0.3112(7)	5.9(3)
C(24)	0.243(1)	0.226(1)	0.3749(7)	5.2(3)
C(25)	0.099(1)	0.2152(9)	0.3761(6)	4.1(2)
C(26)	−0.226(1)	0.1161(8)	0.2229(6)	3.2(2)
C(27)	−0.170(1)	0.1643(9)	0.1665(6)	4.7(3)
C(28)	−0.245(1)	0.168(1)	0.0947(7)	5.4(3)
C(29)	−0.375(1)	0.122(1)	0.0788(7)	5.5(3)
C(30)	−0.437(1)	0.0733(9)	0.1302(6)	4.8(3)
C(31)	−0.360(1)	0.0729(9)	0.2023(6)	4.0(2)
C(32)	−0.164(1)	−0.0066(8)	0.3312(5)	2.9(2)
C(33)	−0.138(1)	−0.0147(9)	0.4092(6)	4.0(2)
C(34)	−0.142(1)	−0.1236(9)	0.4268(7)	4.6(3)
C(35)	−0.166(1)	−0.227(1)	0.3655(7)	5.0(3)
C(36)	−0.191(1)	−0.224(1)	0.2883(7)	5.6(3)
C(37)	−0.188(1)	−0.1145(9)	0.2708(7)	4.6(3)
C(38)	−0.217(1)	0.2302(8)	0.3762(6)	3.0(2)
C(39)	−0.321(1)	0.2165(9)	0.4235(6)	3.8(2)
C(40)	−0.381(1)	0.3124(9)	0.4759(7)	4.8(3)
C(41)	−0.337(1)	0.425(1)	0.4838(6)	5.0(3)
C(42)	−0.235(1)	0.443(1)	0.4391(7)	5.7(3)
C(43)	−0.177(1)	0.3491(9)	0.3848(6)	4.4(3)
B	−0.146(1)	0.120(1)	0.3096(7)	2.8(3)

[a] $B_{eq} = (4/3)\Sigma_i\Sigma_j \beta_{ij} \mathbf{a}_i \mathbf{a}_j$.

yellow solution was reduced to 5 ml. The white powder of **6** which precipitated upon addition of diethyl ether (25 ml) was filtered off and dried under vacuum (117 mg, 66%).

3.7. X-ray crystal structure of $[Ti(NMe_2)_3(NC_5H_5)_2][BPh_4]$

A selected single crystal was introduced into a thin-walled Lindeman glass tube in the glove-box. Data were collected at room temperature on an Enraf–Nonius CAD4 diffractometer equipped with a graphite monochromator [λ(Mo Kα) = 0.71073 Å]. The cell parameters were obtained by a least-squares refinement of the setting angles of 25 reflections with θ between 8 and 12°. Three standard reflections were measured after each hour; a decay was observed (22% in 32 h) and linearly corrected. The data were corrected for Lorentz polarization effects. The structure was solved by the heavy-atom method and refined by full-matrix least-squares on F with anisotropic thermal parameters for the titanium and nitrogen atoms and for the carbon atoms of the NMe_2 ligands. H atoms were introduced at calculated positions and constrained to ride on their C atoms. All calculations were performed on a Vax 4200 computer with the Enraf–Nonius MolEN system [18]. Analytical scattering factors for neutral atoms [19] were corrected for both $\Delta f'$ and $\Delta f''$ components of anomalous dispersion. Crystallographic data and experimental details are given in Table 3, final positional parameters in Table 4.

References

[1] J.C. Berthet, C. Boisson, M. Lance, J. Vigner, M. Nierlich and M. Ephritikhine, *J. Chem. Soc., Dalton Trans.*, (1995) 3019.

[2] J.C. Berthet, C. Boisson, M. Lance, J. Vigner, M. Nierlich and M. Ephritikhine, *J. Chem. Soc., Dalton Trans.*, (1995) 3027.

[3] C. Airoldi, D.C. Bradley, H. Chudzynska, M.B. Hursthouse, K.M.A. Malik and P.R. Raithby, *J. Chem. Soc., Dalton Trans.*, (1980) 2010.

[4] A.L. Casalnuovo, J.C. Calabrese and D. Milstein, *J. Am. Chem. Soc.*, *110* (1988) 110; G.C. Martin, G.J. Palenik and J.M. Boncella, *Inorg. Chem.*, *29* (1990) 2027; J. Feldman and J.C. Calabrese, *J. Chem. Soc., Chem. Commun.*, (1991) 134.

[5] G. Chandra, T.A. George and M.F. Lappert, *J. Chem. Soc., Chem. Commun.*, (1967) 116; M.G. Clerici and F. Maspero, *Synthesis*, (1980) 305; P.J. Walsh, A.M. Baranger and R.G. Bergman, *J. Am. Chem. Soc.*, *114* (1992) 1708.

[6] S. Collins, B.E. Koene, R. Ramachandran and N.J. Taylor, *Organometallics*, *10* (1991) 2092; Y. Hong, B.A. Kuntz and S. Collins, *Organometallics*, *12* (1993) 964; D. Röttger, G. Erker, M. Grehl and R. Fröhlich, *Organometallics*, *13* (1994) 3897.

[7] C. Boisson, J.C. Berthet, M. Lance, J. Vigner, M. Nierlich and M. Ephritikhine, *J. Chem. Soc., Dalton Trans.*, (1996) 947; C. Boisson, J.C. Berthet, M. Ephritikhine, M. Lance and M. Nierlich, *J. Organomet. Chem.*, *522* (1996) 249.

[8] M.F. Lappert, P.P. Power, A.R. Sanger and R.C. Srivastava, *Metal and Metalloid Amides: Syntheses, Structures, and Physical and Chemical Properties*, Ellis Horwood, Chichester, UK/Wiley, New York, 1980.

[9] E.P. Benzing and W.A. Kornicker, *Chem. Ber.*, *94* (1961) 2263; H. Bürger and H.J. Neese, *Z. Anorg. Allg. Chem.*, *370* (1969) 275; H. Bürger and H.J. Neese, *J. Organomet. Chem.*, *20* (1969) 129; H.J. Neese and H. Bürger, *J. Organomet. Chem.*, *32* (1971) 213; H. Bürger and K.Z. Wiegel, *Z. Anorg. Allg. Chem.*, *398* (1973) 257; H. Bürger and C. Kluess, *J. Organomet. Chem.*, *108* (1976) 69.

[10] L.J. Baye, *Synth. React. Inorg. Metal-Org. Chem.*, *2* (1972) 47; W.J. Sartain, J.C. Huffman, E.G. Lundquist, W.G. Streib and K.G. Caulton, *J. Mol. Cat.*, *56* (1989) 20; F.R. Lemke, D.J. Szalda and R.M. Bullock, *J. Am. Chem. Soc.*, *113* (1991) 8466.

[11] C.K. Johnson, ORTEP, *Report ORNL-5138*, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

[12] V.M. Visciglio, P.E. Fanwick and I.P. Rothwell, *Inorg. Chim. Acta*, *211* (1993) 203.

[13] M. Galakhov, A. Martin, M. Mena, F. Palacios, C. Yélamos and P.R. Raithby, *Organometallics*, *14* (1995) 131.

[14] W.J. Sartain and J.P. Selegue, *Organometallics*, *8* (1989) 2153 and references cited therein.

[15] P.E. Collier, S.C. Dunn, P. Mountford, O.V. Shishkin and D. Swallow, *J. Chem. Soc., Dalton Trans.*, (1995) 3743.

[16] D.C. Bradley and I.M. Thomas, *J. Chem. Soc.*, (1960) 3857.

[17] G. Chandra and M.F. Lappert, *J. Chem. Soc. A*, (1968) 1950.

[18] MolEN, *An Interactive Structure Solution Procedure*, Enraf–Nonius, Delft, Netherlands, 1990.

[19] *International Tables for X-ray Crystallography*, Vol. 4, Kynoch Press, Birmingham, UK (present distributor Academic Publishers, Dordrecht, Netherlands), 1974.