Syntheses and single-crystal X-ray structures of $[(Bu^tNP)_2(Bu^tN)_2]MCl_2$ (M = Zr, Hf): the first transition-metal bis(alkylamido)cyclodiphosphazane complexes

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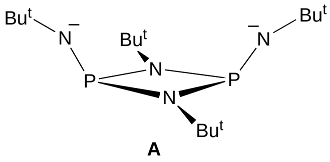
The interaction of $[(Bu^tNP)\{Bu^tNLi(thf)\}_2]$ with $ZrCl_4$ and $HfCl_4$ produces the remarkably stable monomeric $[(Bu^tNP)_2(Bu^tN)_2]MCl_2$ (M = Zr, Hf) complexes.

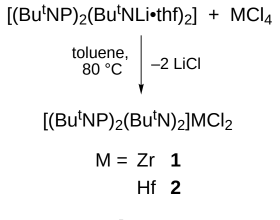
The organometallic chemistry of the group 4 metals is dominated by compounds of the type $(\eta\text{-}C_5H_5)_2MCl_2$ and variations thereof.[1] The ubiquity of these bent metallocenes is largely due to the cyclopentadienyl ligand's ability to stabilise large, electropositive metals sterically and electronically and to create monomeric complexes with a well defined coordination environment. Because of the success of the 'constrained-geometry catalysts', *i.e.*, hybrid complexes with a mixed $(\eta\text{-}C_5Me_4)SiMe_2NBu^t$ ligand, in the Ziegler–Natta polymerization alkenes,[2] there has in recent years been a tremendous synthetic interest in group 4 amide complexes. This research has produced a large number of early-transition-metal complexes with bi-, tri-, and tetra-dentate amide ligands.[3] Many of these new compounds are structurally interesting and some have shown outstanding reactivity.[4] Due to their small bite angles most of these chelating amides are unable to stabilize the heavier group 4 metals as monomeric complexes, however, thereby reducing potential catalytic activity.

To synthesise monomeric amide complexes of zirconium and hafnium we have used bis(*tert*-butylamido)cyclodiphosphazane, **A**, as a ligand.[5] Although these cyclic phosphorus–nitrogen molecules have been known for some time,[6] their metal chemistry is not well developed and their use as chelating bis(amide) ligands is all but unknown.[7] The obscurity of cyclodiphosphazanes is surprising, because their flexible bite angle and multidentate nature make them ideal ligands for transition- and main-group-metals alike.



A

The prolonged (24 h) interaction of $[(Bu^tNP)_2(Bu^tNLi{\cdot}thf)_2]$ with MCl_4 in hot toluene (Scheme 1) afforded $[(Bu^tNP)_2(Bu^tN)_2]MCl_2$ (M = Zr **1**, Hf **2**), in yields of *ca.* 80%.† These colourless compounds have remarkable thermal and chemical stability, being unaffected by oxygen and sulfur in hot toluene solutions even after 12 h. NMR spectral data show conclusively that the metal complexes have C_{2v} symmetry in solution. Thus, for example, the ^1H NMR spectra of **1**(**2**) display two singlets at δ 1.41(1.40) and 1.27(1.27), for the amido and imido *tert*-butyl groups, respectively, while the $^{31}P\{^1H\}$ NMR spectra consist of only one sharp singlet at δ 101.7 and 99.9, respectively, indicative of equivalent P^{III} centres.



Scheme 1

A single-crystal X-ray analysis confirmed the solid-state structure of **1** as that shown in Fig. 1;‡ the hafnium analogue is isostructural. These compounds crystallise racemically twinned as discrete molecules in the acentric orthorhombic space group $P2_12_12_1$. The metal–chloride and metal–amide bonds define to a first approximation a pseudo-tetrahedral coordination geometry about the zirconium atom. An additional fifth, long Zr–N(1) interaction, however, reduces the molecular symmetry from C_{2v} to C_s in the solid state to create a highly distorted trigonal-bipyramidally coordinated zirconium atom. Alternatively the central moiety of the molecule may be described as two almost perpendicular inorganic heterocycles, consisting of phosphorus, nitrogen and zirconium atoms. Symmetry-related zirconium–nitrogen and phosphorus–nitrogen bonds are, within experimental errors, equivalent. Thus, the two zirconium–nitrogen bonds are 2.060(3) and 2.067(3) Å long, making them quite comparable to those in related compounds with monodentate

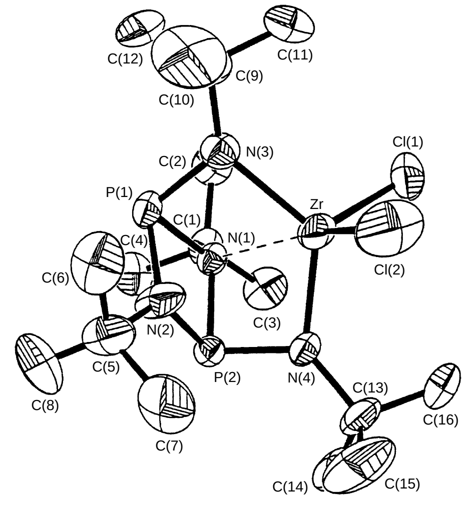


Fig. 1 Molecular structure and labeling scheme for **1**. Selected bond distances (Å) and angles (°) not mentioned in the text: P(1)–N(1) 1.790(3), P(1)–N(2) 1.729(4), P(1)–N(3) 1.682(3), P(2)–N(1) 1.780(3), P(2)–N(2) 1.743(4), P(2)–N(4) 1.681(3), Cl(1)–Zr–Cl(2) 104.51(8), N(3)–Zr–Cl(1) 110.6(1), N(3)–Zr–Cl(2) 102.4(1), N(4)–Zr–Cl(1) 110.4(1), N(4)–Zr–Cl(2) 102.6(1). The corresponding values for **2** are: P(1)–N(1) 1.785(10), P(1)–N(2) 1.734(9), P(1)–N(3) 1.632(9), P(2)–N(1) 1.790(9), P(2)–N(2) 1.752(11), P(2)–N(4) 1.665(9), Cl(1)–Hf–Cl(2) 103.7(2), N(3)–Hf–Cl(1) 110.5(3), N(3)–Hf–Cl(2) 103.0(3), N(4)–Hf–Cl(1) 109.7(3), N(4)–Hf–Cl(2) 102.4(3).

amides.[8] The zirconium–chloride bonds, however, are shorter than those in (η-C_5H_5)$_2$ZrCl$_2$, and this may reflect the lesser steric crowding of these bonds in **1**, or perhaps a small amount of Cl to Zr π-electron donation. The slight bond asymmetry, 2.375(2) and 2.397(2) Å, is presumably the result of the ring–zirconium interaction, and it is notable that the Zr–Cl bond *trans* to the Zr–N(1) bond is the longer of the two. In keeping with the trends normally observed for isostructural zirconium and hafnium species,[1] the metal–ligand bonds in the hafnium analogue are slightly shorter than those in the zirconium complex. The hafnium compound has equidistant metal–amide bonds of 2.053(9) and 2.081(10) Å, and slightly inequivalent Hf–Cl bonds of 2.355(5) and 2.382(4) Å.

Unlike the majority of the more common chelating diamides, cyclodiphosphazane **A** can effectively envelop the central metal atom through additional bonds. This is clearly demonstrated by both the secondary N(1)–Zr donor bond of 2.398(3) Å and the extremely short non-bonding distance of 2.891(1) Å between the phosphorus atoms and the zirconium centre. Because the rigidity of the ligand prevents a closer approach between metal and phosphazane ring, it is difficult to assess the strength of this ring–metal interaction. Lone-pair donation by ring–nitrogen atoms in the related cyclophosphazenes is well documented, however, and usually forms bonds of considerable strength.[9]

Only comparatively minor structural changes are displayed by the ligand upon coordination to the metals. There is a slight puckering in the cyclodiphosphazane portion of the molecule that is also observed in the pristine ligand, resulting in a slight folding along the N(1)$\cdots$N(2) line.[10] The exocyclic phosphorus–nitrogen distances are significantly shorter than the endocyclic ones, a feature we believe to be due to steric factors. The trends in the P–N bond distances of N(1) and N(2) are those expected based on the differences in their coordination numbers, the four-coordinate N(1) having the longer bonds.

Like many successful ancillary ligands, cyclodiphosphazane **A** is able to impose a well defined coordination environment on its complexes. In **1** and **2**, for example, it has produced a steric pocket that is quite reminiscent of that in bent metallocenes and related compounds. The bulky *tert*-butyl substituents of the ligand form a rather wide gap in the equatorial plane of the complexes that may allow selective access of substrate molecules to the Lewis-acidic metal centres. The cyclodiphosphazane ligand subtends identical angles of 124.6(1) and 124.8(4) Å at the metal in **1** and **2**, respectively; these values are well above that of a regular tetrahedron but comparable to those found in metallocenes.

Because of their unique structural features, **1** and **2** appear to be excellent candidates for catalytic applications which demand low-coordinate, highly Lewis-acidic metal centres with well defined coordination environments and the desirable *cis*-arrangement of the chloride ligands. Whether ligand-centred reactions caused by the phosphorus and equatorial nitrogen centres compromise this reactivity, however, remains to be seen. Catalytic studies are currently under way, and they should provide insight into the reaction chemistry of the title compounds.

Footnotes

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† Anal. Found for **1**: C, 37.55; H, 6.89; N, 10.87. Calc. for $C_{16}H_{36}Cl_2N_4P_2Zr$: C, 37.79; H, 7.13; N, 11.02%. Mp 215 °C. Positive chemical ionisation (PCI) MS, 509.708 [M + H]$^+$. Anal. Found for **2**: C, 32.34; H, 6.05; N, 9.20. Calc. for $C_{16}H_{36}Cl_2HfN_4P_2$: C, 32.25; H, 6.09; N, 9.40%. Mp 201 °C. PCI MS, 597.1 [M + H]$^+$.

‡ *Crystal data*: for **1**: $C_{16}H_{36}Cl_2N_4P_2Zr$, M_r = 508.55; orthorhombic, space group $P2_12_12_1$, a = 9.921(2), b = 15.129(3), c = 16.331(4) Å, U = 2451.2(8) Å^3, D_c = 1.378 g cm^{-3}, Z = 4, F(000) = 1056. Intensity measurements were made with a Siemens SMART CCD (charge-coupled device) X-ray diffractometer equipped with an LT-2 low-temperature apparatus operating at 213 K using Mo-Kα radiation, λ = 0.710 73 Å and ω-scans of 0.3° per frame for 10 s, until a complete hemisphere was collected. A total of 9072 reflections in 1271 frames were collected in the 4° $< 2\theta <$ 56° range with a final resolution of 0.84 Å. Of these reflections, 4921 were unique (R_{int} = 0.0248) and observed [$I > 2\,\sigma(I)$] and used in the refinement. An absorption correction based on ψ-scans was applied to the data set, $T_{min,\,max}$ = 0.683, 0.962. The first 50 frames were recollected at the end of data acquisition to monitor for decay which was $<$1%. Cell parameters were retrieved using SMART[11] software and refined using SAINT[12] on all observed reflections. Data reduction was performed with the SAINT software which corrects for L_p and decay. The absorption correction was applied using SADABS which was supplied with the program. The structure was solved in the uniquely determined space group $P2_12_12_1$ (no. 19) by using the direct methods option of the SHELX-90[13] program and refined by least-squares on F^2 with SHELXL-93,[14] incorporated in SHELXTL-PC V 5.03.[15] Hydrogen atom positions were calculated by geometrical methods and refined as a riding model. The refinement converged at R_1 = 0.0412 and wR_2 = 0.1017 and a final GOF = 1.016. The final difference map showed no peaks(holes) greater than 0.373($-$1.039) e Å^{-3}.

For **2**: $C_{16}H_{36}Cl_2HfN_4P_2$, M_r = 595.82; orthorhombic, space group $P2_12_12_1$, a = 9.937(3), b = 15.132(4), c = 16.414(5) Å, U = 2468(1) Å^3, D_c = 1.603 g cm^{-3}, Z = 4, F(000) = 1184. Hardware configurations and software programs were identical to those used for **1.** A total of 6141 data were collected at 293 K in the range 4 $< 2\theta <$ 45°. Upon merging, R_{int} = 0.0221, these yielded 3078 unique and observed [$I > 2\,\sigma(I)$] data which were used in the refinement. An absorption correction based on ψ-scans was applied, $T_{min,\,max}$ = 0.738, 0.942. The crystal showed no decay during the data collection. Refinement converged at R_1 = 0.0472, wR_2 = 0.1138. The largest residual electron densities in the final difference map were peaks and holes of 0.774 and $-$1.795 e Å^{-3}, respectively. CCDC 182/494.

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Received in Bloomington, IN, USA, 16th April 1997; 7/02606D