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Lithium, Titanium, and Zirconium Complexes with Novel Amidinate Scorpionate Ligands

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The reaction of bis(3,5-dimethylpyrazol-1-yl)methane (bdmpzm) with Bu^{n}Li and carbodiimide derivatives, namely, *N*,*N*′-diisopropyl, dicyclohexyl, and 1-*tert*-butyl-3-ethyl carbodiimides, enables the preparation of new heteroscorpionate ligands in the form of the lithium derivatives [Li(NNN)(THF)] (NNN = pbpamd (**1**) (pbpamd = *N*,*N*′-diisopropylbis-(3,5-dimethylpyrazol-1-yl)acetamidinate); cbpamd (**2**) (cbpamd = *N*,*N*′-dicyclohexylbis(3,5-dimethylpyrazol-1-yl)-acetamidinate); and tbpamd (**3**) (tbpamd = *N*-ethyl-*N*′-*tert*-butylbis(3,5-dimethylpyrazol-1-yl)acetamidinate)), although a similar process with *N*,*N*′-dimethylcarbodiimide gave the dinuclear complex $[\mathrm{Li(bpzii)(THF)}]_2$ (**4**) (bpzii = *N*-(dimethylamino)-*N*′-[(dimethylamino)bis(3,5-dimethylpyrazol-1-yl)methylimino]imino). When this last reaction was carried out in an air atmosphere, the cluster complex $[\mathrm{Li_8}(\mu_4\text{-O})_2(\mu_4\text{-OH})_2(\mu_4\text{-pz})_2(\kappa^2\text{-bpziLi})_2(\mathrm{bpzCN})_2(\mathrm{THF})_4]$ (**5**) (bpziLi = dimethylaminobis(3,5-dimethylpyrazol-1-yl)methyliminolithium, bpzCN = bis(3,5-dimethylpyrazol-1-yl)-acetonitrile) was isolated and characterized by X-ray analysis. Finally, when the same process was carried out in the presence of water the amidine–scorpionate (bpzan) (**6**) (bpzan = *N*,*N*-dimethylbis(3,5-dimethylpyrazol-1-yl)-acetamidine) was obtained. Compounds **1** and **3** reacted with $[\mathrm{TiCl_4(THF)_2}]$ or $[\mathrm{ZrCl_4}]$ to give complexes of stoichiometry $[\mathrm{MCl_3}((\kappa^3\text{-NNN}))]$ (M = Ti, Zr) (**7**–**10**). The structures of the different compounds were determined by spectroscopic methods and, in addition, the X-ray crystal structures of **1**, **3**, **4**, **5**, and **6** were also established.

Introduction

Over the past several years, metal complexes that incorporate amidinate ligands ($[\mathrm{R^1NC(R^2)NR^3}]^-$) have been actively studied.[1] These complexes have displayed a wide range of chemistry as cyclopentadienyl replacements in transition metal chemistry,[2] support ligands in catalysis,[3] and scaffolds for bimetallic complexes.[4] Amidinate anions exhibit versatility in terms of their binding modes (Figure 1). Of these, modes **B** (bidentate chelating) and **C** (bimetallic bridging) are the most common,[5] with **B** being the expected coordination when **C** is not sterically or electronically favored, whereas examples of **A** (monodentate) are relatively scarce.[6]

One of the challenging problems in organometallic and inorganic chemistry is the search for new ancillary ligands

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(1) (a) Barker, J.; Kilner, M. *Coord. Chem. Rev.* **1994**, *133*, 219. (b) Edelmann, F. T. *Coord. Chem. Rev.* **1994**, *137*, 403.

(2) See, for example: (a) Brandsma, M. J. R.; Brussee, E. A. C.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Eur. J. Inorg. Chem.* **1998**, 1867. (b) Kincaid, K.; Gerlach, C. P.; Giesbrecht, G. R.; Hagadorn, J.; Whitener, G. D.; Shafir, A.; Arnold, J. *Organometallics* **1999**, *18*, 5360. (c) Boyd, C. L.; Guiducci, A. E.; Dubberley, S. R.; Tyrrell, B. R.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **2002**, 4175.

(3) For group 4 transition metals, monoamidinates have been used as ancillary ligands in olefin polymerization catalysis: (a) Flores, J. C.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1995**, *14*, 1827. (b) Littke, A.; Sleiman, N.; Bensimon, C.; Richeson, D. S. *Organometallics* **1998**, *17*, 446. (c) Averbuj, C.; Tish, E.; Eisen, M. S. *J. Am. Chem. Soc.* **1998**, *120*, 8640.

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(5) For bidentate chelating mode see, for example: (a) Schmidt, J. A. R.; Arnold, J. *Organometallics* **2002**, *21*, 2306. (b) Brussee, E. A. C.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Chem. Commun.* **2000**, 497. (c) Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Schooler, P. *J. Chem. Soc., Dalton Trans.* **2000**, 2001. For bimetallic bridging mode see, for example: (a) Chen, W. Z.; Ren, T. *Inorg. Chem.* **2003**, *42*, 8847. (b) Cotton, F. A.; Daniels, L. M.; Murillo, C. A. *J. Am. Chem. Soc.* **2003**, *125*, 5436. (c) Cotton, F. A.; Daniels, L. M.; Huang, P.; Murillo, C. A. *Inorg. Chem.* **2002**, *41*, 317.

10.1021/ic062093c CCC: $37.00

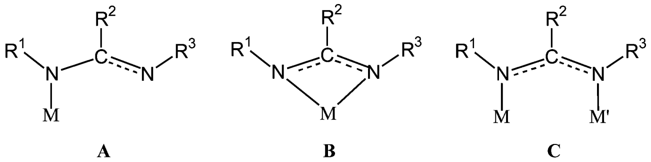
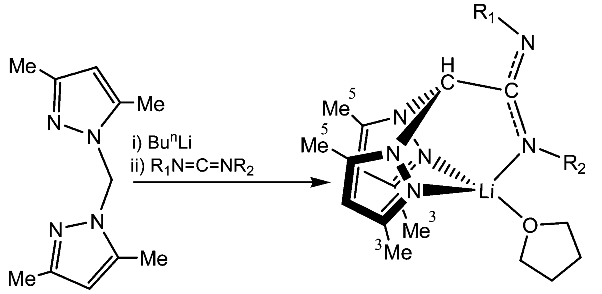


Figure 1. The three common amidinate coordination classes.

that are capable of supporting a wide variety of catalytic processes and that can be easily tuned, both sterically and electronically, to form complexes that exhibit unusual structures and reactivity. During the past decade our research group has contributed widely to this field, designing new “heteroscorpionate” ligands[7] related to the bis(pyrazol-1-yl)-methane system[8] and incorporating several pendent donor arms such as carboxylate,[9] dithiocarboxylate,[10a] methoxy,[10,11] cyclopentadienyl,[12] and, more recently, acetamidate and thioacetamidate groups.[13] We have developed a synthetic route for the preparation of these ligands[9a] based on the deprotonation of bis(pyrazol-1-yl)methanes at the methylene group with Bu^{n}Li, followed by an insertion reaction of a heterocumulene into the lithium−carbon bond to yield the lithium salts of these ligands. In the study described here we used this approach to explore the synthetic route with a series of carbodiimides[14] and, with some of these compounds, we prepared a new type of tridentate ligand as the lithium salt. These represent the first amidinate scorpionate ligands in which the amidinate moiety presents a monodentate coordination mode, a situation that is relatively unusual. However, the lower steric demand associated with *N*,*N*′-dimethylcarbodiimide led to an unusual type of behavior in these reactions, which led to the isolation of the first diimino−scorpionate compound and, in an air atmosphere, to an unprecedented lithium cluster that contains two new types of heteroscopionate ligands. Finally, we prepared neutral titanium and zirconium complexes that contain amidinate scorpionate ligands by treatment of MCl_4 with some of these lithium compounds.

Scheme 1. Synthesis of Lithium Compounds **1**−**3**



$R_1 = R_2 = {}^iPr$ (pbpamd, **1**)
$R_1 = R_2 = Cy$ (cbpamd, **2**)
$R_1 = Et$, $R_2 = {}^tBu$ (tbpamd, **3**)

Results and Discussion

A mixture of a cooled (−70 °C) solution of bis(3,5-dimethylpyrazol-1-yl)methane (bdmpzm)[15] in THF and 1 equiv of Bu^{n}Li, under an atmosphere of dry nitrogen, was treated with a series of symmetric carbodiimides (*N*,*N*′-diisopropyl- and dicyclohexylcarbodiimide) and an asymmetric carbodiimide such as 1-*tert*-butyl-3-ethylcarbodiimide. These reactions gave rise to the lithium acetamidinates [Li(pbpamd)(THF)] (**1**) (pbpamd = *N*,*N*′-diisopropylbis(3,5-dimethylpyrazol-1-yl)acetamidinate), [Li(cbpamd)(THF)] (**2**) (cbpamd = *N*,*N*′-dicyclohexylbis(3,5-dimethylpyrazol-1-yl)-acetamidinate), and [Li(tbpamd)(THF)] (**3**) (tbpamd = *N*-ethyl-*N*′-*tert*-butylbis(3,5-dimethylpyrazol-1-yl)acetamidinate) as white solids in good yield (ca. 85%) after the appropriate workup (see Scheme 1). However, when the same reaction was carried out with *N*,*N*′-dimethylcarbodiimide a new dinuclear complex $[Li(bpzii)(THF)]_2$ (**4**) (bpzii = *N*-(dimethylamino)-*N*′-[(dimethylamino)bis(3,5-dimethylpyrazol-1-yl)methylimino]imino) was obtained along with the starting bdmpzm compound. When the reaction was carried out with 2 equiv of the *N*,*N*′-dimethylcarbodiimide, compound **4** was the only product and was obtained as an orange solid in good yield (80%) (Scheme 2). The proposed reaction pathway leading to the unprecedented diimino−scorpionate compound **4** is shown in Scheme 3.

We assume that initially a new and unstable lithium acetamidinate compound similar to isolated complexes **1**−**3**

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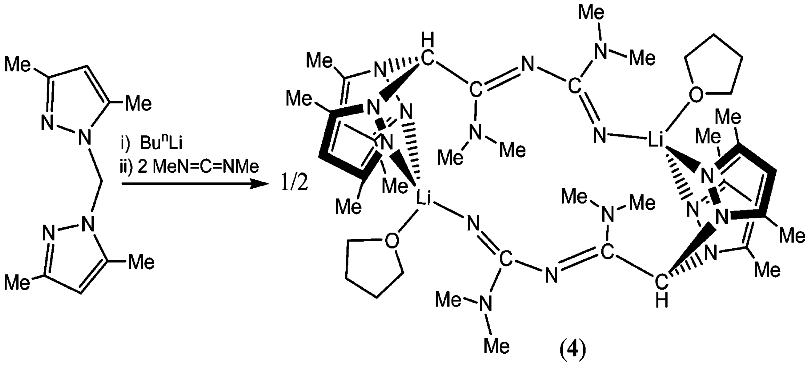
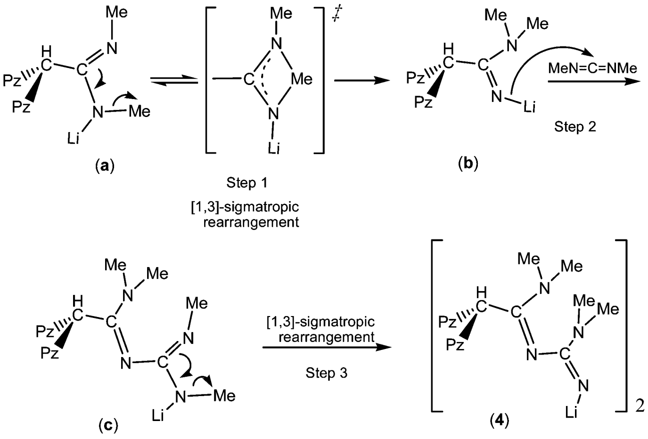
Scheme 2. Synthesis of Lithium Compound **4**



(**4**)

Scheme 3. Different Steps Proposed for the Synthesis of Complex **4**



would be formed (**a**). It is then proposed that **a** evolves through a first step where a sigmatropic [1,3]-shift of a methyl group[16] would occur through a four-membered heterocyclic transition state, giving rise to an imino−lithium intermediate such as **b**. In step 2, a nucleophilic addition of the nitrogen atom of the imino group to another molecule of dimethylcarbodiimide would take place to give a new amidinate compound (**c**). Finally, a further [1,3]-sigmatropic rearrangement would occur to produce the dinuclear di-imino−lithium complex **4**. One point that must be addressed is the reason for the instability of the proposed intermediate **a** in comparison to the stability of the similar complexes (**1**−**3**). On considering our proposed route, the answer to this question lies in the different steric demand of the substituent groups of the amidinate moiety to be considered in the formation of the four-membered cyclic transition state that gives the proposed sigmatropic [1,3]-shift process. However, the possibility that electronic factors are responsible for the different behavior cannot be definitively ruled out. The different lithium compounds were characterized spectroscopically. The ^{1}H and ^{13}C-{H} NMR spectra of **1**−**3** each show a single set of resonances for the pyrazole rings, indicating that both pyrazole rings are equivalent. These data confirm a tetrahedral disposition for the lithium atom with κ^3-NNN-coordination of the heteroscorpionate ligand, a situation in which a plane of symmetry exists and contains the amidinate group and the THF ligand (Scheme 1). The NMR signals due to the amidinate moiety of the lithium compounds **1**−**2** (where $R_1 = R_2$) show two sets of resonances for these substituents. This observation is indicative of a monodentate binding of the amidinate moiety to the lithium atom—a phenomenon that has previously been observed in only one type of lithium amidinate.[17] ^{1}H NOESY-1D experiments were also performed to confirm the assignment of the signals for the R^3, R^5, and H^4 groups. Furthermore, in the case of compound **3** (where $R_1 \neq R_2$), the response in the ^{1}H NOESY-1D experiment from the Me^5 protons of the pyrazolyl rings on irradiation of the ethyl group of the amidinate moiety suggests that this group is in the R$_1$ position, whereas the *tert*-butyl group is in the R$_2$ position (see Scheme 1). ^{1}H−^{13}C heteronuclear correlation (g-HSQC) experiments were carried out and allowed us to assign the resonances corresponding to C^4, Me^3, and Me^5 of the pyrazole ring. Finally, the ^{7}Li NMR spectra of these compounds exhibit a singlet at $\delta = 1.50-1.60$ ppm for the lithium atom.

The IR spectra of **1**−**3** show two strong bands at ca. 1615 and 1380 cm^{-1}, which are assigned to $\nu_a(CN_2^-)$ and $\nu_s(CN_2^-)$, respectively.[18] A characteristic band at 1570 cm^{-1} is also observed in the IR spectra, and this corresponds to ν(C═N) of the pyrazole rings. The mass spectra (FAB) of these compounds indicate a mononuclear formulation (see Experimental Section), which was corroborated by means of X-ray crystal structure determinations.

The crystal structures of complexes **1** and **3** were determined by X-ray structure analyses and are shown in Figures 2 and 3. Selected bond lengths and angles are listed in Table 1. In both complexes the geometry around the Li atom can be described as a distorted tetrahedron. This distortion is due to the heteroscorpionate ligand, which acts in a κ^3-NNN-coordination mode with, for example, in complex **3**, N(1)−Li(1)−N(4), N(1)−Li(1)−N(6), and N(4)−Li(1)−N(6) angles of 94.0(4)°, 95.1(4)°, and 92.5(5)°, respectively, and O(1)−Li(1)−N(1), O(1)−Li(1)−N(6), and O(1)−Li(1)−N(4) angles of 139.0(7)°, 108.4(5)°, and 117.2-

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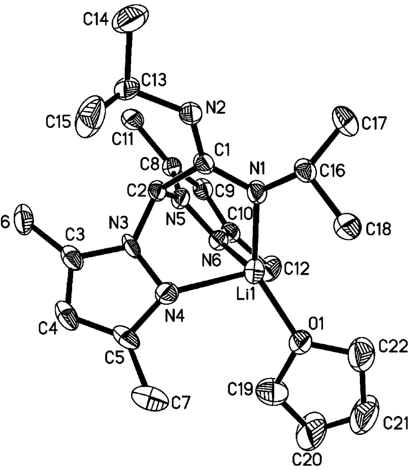

Figure 2. ORTEP view of [Li(pbpamd)(THF)] (**1**). Ellipsoids are at the 30% probability level, and hydrogen atoms have been omitted for clarity.

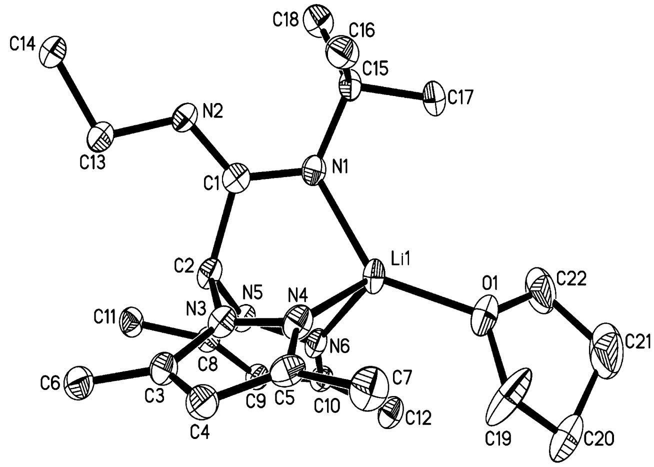

Figure 3. ORTEP view of [Li(tbpamd)(THF)] (**3**). Ellipsoids are at the 20% probability level, and hydrogen atoms have been omitted for clarity.

(5)°, respectively. Both of the Li−N distances (2.07(1) and 2.13(1) Å for **1** and 2.05(1) and 2.10(1) Å for **3**) of the bis(pyrazol-1-yl)methane moiety are in good agreement with others determined for lithium scorpionate or bis(pyrazol-1-yl)methane complexes.[9a,12,13,19] The solid-state structures of these compounds confirm that the amidinate is coordinated in a monodentate fashion to the Li atom, a situation consistent with the disposition suggested by solution NMR for these complexes. The delocalization is evident in the N−C−N core, with C(1)−N(1) values of 1.325(9) and 1.345(7) Å for **1** and **3**, respectively, and C(1)−N(2) values of 1.32(1) and 1.301(7) Å for **1** and **3**, respectively. The amidinate N−Li bond length (1.93(2) Å for **1** and 1.98(1) Å for **3**) is consistent with that reported for the only previously known monodentate amidinate lithium compound.[17] However, the distance is shorter than those observed in other Li amidinate complexes with bidentate chelating coordination, and the N−C−N angle is substantially more obtuse (125.3(8)° for **1** and 127.9(6)° for **3**) than in these species.[20]

The ^{1}H NMR spectrum of **4** exhibits two set of resonances for H^{4}, Me^{3}, and Me^{5} and four singlets for the methyl groups of the imino moiety, indicating that the pyrazole rings are inequivalent and that an inversion center exists (see Scheme 2). In addition, the ^{13}C{H} NMR spectrum shows the corresponding signals for C^{3}, C^{4}, C^{5}, Me^{3}, and Me^{5} and the different carbon atoms of the corresponding imino moiety (see Experimental Section). The results obtained are consistent with the proposed tetrahedral disposition for the lithium atoms with a κ^3-NNN-coordination for the heteroscorpionate ligand, with the nitrogen atoms of the imino−scorpionate ligands bridging at the other lithium atom (see Scheme 2). This structural disposition was confirmed by an X-ray crystal structure determination for **4**$\cdot 2C_4H_8O$ (see Figure 4). The most important bond lengths and angles are presented in Table 1. The asymmetric unit contained half a molecule of **4** and one molecule of THF solvent. Each lithium center has a distorted tetrahedral environment with the "bpzii" ligand coordinated in a tridentate fashion through the two pyridinic nitrogen atoms of the pyrazole rings at one lithium atom and the nitrogen atom of diimino moiety at the other lithium atom. The major distortion appears in the N(2)−Li(1)−N(4) angle, which has a value of 94.0(3)°. The Li(1)−N(2) and Li(1)−N(4) bond distances of the pyrazole moiety are 2.083(7) and 2.090(7) Å, respectively, and these are similar to those in complexes **1** and **3**. The imino Li(1)−N(7) bond distance (1.950(7) Å) is in agreement with the values found in the few imino−lithium compounds described previously.[21] The bridge of the molecule consists of two imino units $Me_2NCNC(NMe_2)N$. Although the bonding within these units can be represented formally by N(6)−C(12)═N(5) and N(8)−C(15)═N(7) (see structural formula in Scheme 2), it is apparent from the bond lengths (namely, N(6)−C(12) 1.402(4), C(12)−N(5) 1.356(4), N(8)−C(15) 1.389(4), C(15)−N(7) 1.316(4), and N(5)−C(15) 1.354(4) Å) that there is considerable delocalization along the backbone. These distances can be compared with those found within an iminolithium complex of the type Ph(R)C═NLi, where R is an alkenylamino group.[21a] The essentially sp^{2} and planar nature of the imino carbon atoms C(12) and C(15) is further confirmed by the summations of the angles around them, 359.6° and 359.8°, respectively. This compound represents the first example of a diimino−lithium compound and also the first example of such an imino−scorpionate complex.

The formation of an imino−lithium compound such as the proposed intermediate (**b**) (see Scheme 3) has been established in other interesting processes between bis(3,5-dimethylpyrazol-1-yl)methane (in the presence of Bu^{n}Li) and *N,N′*-dimethylcarbodiimide. Thus, when a THF solution was slowly evaporated at room temperature in an air atmosphere,

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Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for **1**, **3**, **4**·$2C_4H_8O$, **5**, and **6**·H_2O

7.5q1		**3**		**4**·$2C_4H_8O$		**5**		**6**·H_2O	
Li(1)−N(1)	1.93(2)	Li(1)−N(1)	1.98(1)	Li(1)−N(2)	2.083(7)	Li(2)−O(1)[b]	2.08(2)	N(1)−C(11)	1.449(3)
Li(1)−O(1)	1.97(1)	Li(1)−O(1)	1.97(1)	Li(1)−N(4)	2.090(7)	Li(1)−O(2)	1.94(2)	N(3)−C(11)	1.449(3)
Li(1)−N(6)	2.07(1)	Li(1)−N(6)	2.05(1)	Li(1)−N(7)	1.950(7)	Li(2)−Li(4)	2.44(3)	N(5)−C(12)	1.275(3)
Li(1)−N(4)	2.13(1)	Li(1)−N(4)	2.10(2)	Li(1)−O(1)	1.969(7)	Li(1)−Li(4)[b]	2.79(3)	N(6)−C(12)	1.366(3)
N(1)−C(1)	1.325(9)	N(1)−C(1)	1.345(7)	N(5)−C(15)[a]	1.354(4)	Li(1)−N(51)[b]	2.05(2)	N(6)−C(14)	1.456(4)
N(1)−C(16)	1.48(1)	N(1)−C(15)	1.480(8)	N(5)−C(12)	1.356(4)	Li(2)−N(50)	2.03(2)	N(6)−C(13)	1.463(3)
N(2)−C(1)	1.32(1)	N(2)−C(1)	1.301(7)	N(6)−C(12)	1.402(4)	Li(3)−N(51)[b]	2.04(2)	C(11)−C(12)	1.530(4)
N(2)−C(13)	1.463(9)	N(2)−C(13)	1.441(7)	N(6)−C(13)	1.445(4)	Li(4)−N(50)	2.09(2)	C(12)−N(6)−C(14)	117.1(2)
C(1)−C(2)	1.54(1)	C(1)−C(2)	1.561(9)	N(6)−C(14)	1.449(4)	Li(5)−N(1)	1.97(3)	C(12)−N(6)−C(13)	123.6(2)
N(1)−Li(1)−O(1)	144.9(9)	O(1)−Li(1)−N(1)	139.0(7)	N(7)−C(15)	1.316(4)	Li(5)−N(31)	2.00(3)	C(14)−N(6)−C(13)	114.2(2)
N(1)−Li(1)−N(6)	93.4(6)	O(1)−Li(1)−N(6)	108.4(5)	N(8)−C(15)	1.389(4)	Li(5)−N(41)	2.09(3)	N(3)−C(11)−N(1)	110.6(2)
O(1)−Li(1)−N(6)	108.5(8)	N(1)−Li(1)−N(6)	95.1(4)	N(8)−C(17)	1.435(5)	N(1)−C(2)	1.30(1)	N(3)−C(11)−C(12)	112.9(2)
N(1)−Li(1)−N(4)	94.1(6)	O(1)−Li(1)−N(4)	117.2(5)	N(8)−C(16)	1.450(4)	N(2)−C(2)	1.39(1)	N(1)−C(11)−C(12)	113.6(2)
O(1)−Li(1)−N(4)	111.8(8)	N(1)−Li(1)−N(4)	94.0(4)	C(11)−C(12)	1.374(4)	N(2)−C(3)	1.44 (1)	N(5)−C(12)−N(6)	120.3(3)
N(6)−Li(1)−N(4)	91.4(6)	N(6)−Li(1)−N(4)	92.5(5)	N(7)−Li(1)−O(1)	115.5(3)	N(2)−C(4)	1.47(1)	N(5)−C(12)−C(11)	124.3(3)
C(1)−N(1)−C(16)	115.7(7)	C(1)−N(1)−C(15)	118.5(5)	N(7)−Li(1)−N(2)	114.8(3)	C(1)−C(2)	1.46(2)	N(6)−C(12)−C(11)	115.3(2)
C(1)−N(1)−Li(1)	115.6(7)	C(1)−N(1)−Li(1)	113.7(6)	O(1)−Li(1)−N(2)	103.7(3)	N(3)−C(6)	1.05(1)		
C(16)−N(1)−Li(1)	123.8(7)	C(15)−N(1)−Li(1)	120.2(5)	N(7)−Li(1)−N(4)	115.1(3)	C(5)−C(6)	1.46(1)		
C(1)−N(2)−C(13)	123.5(7)	C(1)−N(2)−C(13)	120.8(6)	O(1)−Li(1)−N(4)	111.2(3)	C(2)−N(1)−Li(5)	141(2)		
N(2)−C(1)−N(1)	125.3(8)	N(2)−C(1)−N(1)	127.9(6)	N(2)−Li(1)−N(4)	94.0(3)	C(2)−N(2)−C(3)	128(1)		
N(2)−C(1)−C(2)	120.9(8)	N(2)−C(1)−C(2)	119.9(6)	C(15)[a]−N(5)−C(12)	117.2(3)	C(2)−N(2)−C(4)	114(1)		
N(1)−C(1)−C(2)	113.8(9)	N(1)−C(1)−C(2)	112.0(5)	C(15)−N(7)−Li(1)	141.7(3)	C(3)−N(2)−C(4)	115(1)		
N(3)−C(2)−N(5)	110.1(7)	N(3)−C(2)−N(5)	110.0(4)	N(5)−C(12)−C(11)	120.2(3)	C(6)−N(3)−Li(1)	138(1)		
N(3)−C(2)−C(1)	113.1(7)	N(3)−C(2)−C(1)	110.8(5)	N(5)−C(12)−N(6)	120.2(3)	N(1)−C(2)−N(2)	126(1)		
N(5)−C(2)−C(1)	113.2(7)	N(5)−C(2)−C(1)	115.4(5)	C(11)−C(12)−N(6)	119.1(3)	N(1)−C(2)−C(1)	118(1)		
				N(7)−C(15)−N(5)[a]	128.0(3)	N(2)−C(2)−C(1)	116(1)		
				N(7)−C(15)−N(8)	118.1(3)	N(3)−C(6)−C(5)	176(2)		
				N(5)[a]−C(15)−N(8)	113.7(3)				

[a] Symmetry transformations used to generate equivalent atoms: $-x + 1/2$, $-y + 1/2$, $-z + 1$. [b] Symmetry transformations used to generate equivalent atoms: $-x + 1$, $-y + 1$, $-z + 1$.

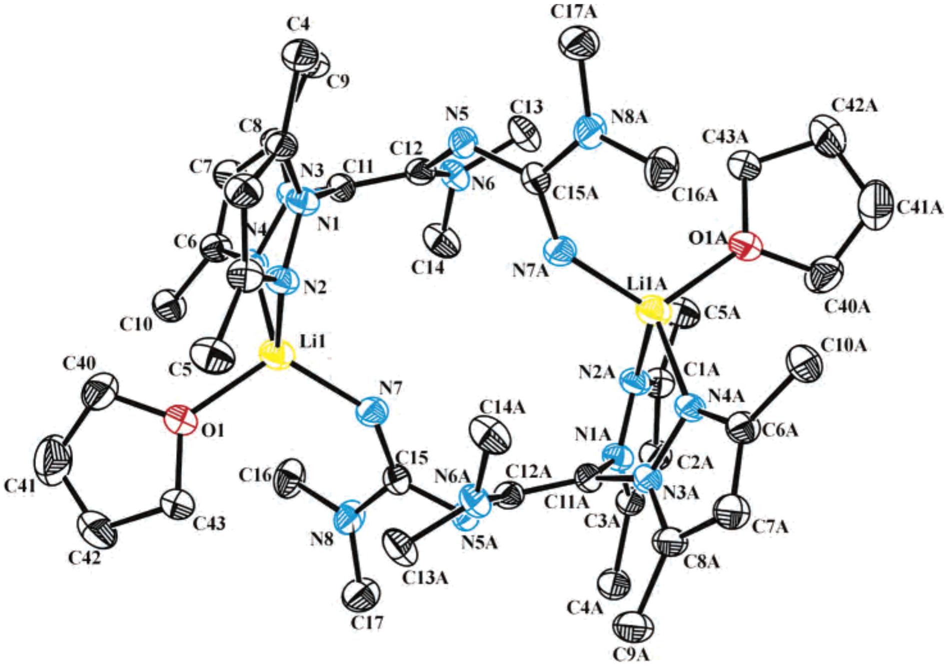

Figure 4. ORTEP view of $[Li(bpzii)(THF)]_2$ (**4**). Ellipsoids are at the 30% probability level, and hydrogen atoms have been omitted for clarity.

white crystals were deposited from the solution after 72 h, and these were identified by an X-ray crystal structure determination as the cluster complex $[Li_8(\mu_4\text{-}O)_2(\mu_4\text{-}OH)_2(\mu_4\text{-}pz)_2(\kappa^2\text{-}bpziLi)_2(bpzCN)_2(THF)_4]$ (**5**) (bpziLi = dimethylaminobis(3,5-dimethylpyrazol-1-yl)methyliminolithium, bpzCN = bis(3,5-dimethylpyrazol-1-yl)acetonitrile). The formation of **5** may be the final result of a series of complex hydrolytic processes along with other types of transformations. Thus, the presence in the cluster of these entities can be explained in terms of the transformation of the initially formed amidinate scorpionate lithium intermediate. The formation of the imino−lithium unit (bpziLi) would be the result of the previously mentioned sigmatropic [1,3]-shift of the methyl group, and the formation of the acetonitrile-scorpionate ligand would take place by elimination of lithium dimethylamide (see Scheme 4). The latter type of transformation has previously been described in the literature.[22]

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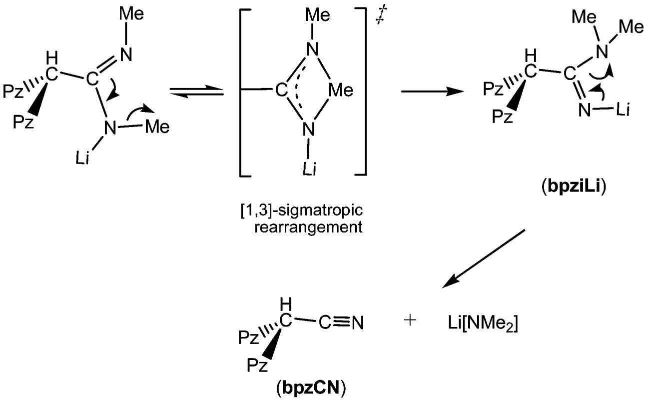
(22) (a) Coles, M. P.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1997**, *16*, 5183. (b) Foley, S. R.; Zhou, Y.; Yap, G. P. A.; Richeson, D. S. *Inorg. Chem.* **2000**, *39*, 924.

Scheme 4. Proposed Transformations of an Amidinate Scorpionate Lithium Compound in the Formation of the Cluster **5**



The molecular structure of **5** was determined by X-ray diffraction, and the structure is shown in Figure 5. Significant bond distances and bond angles are listed in Table 1. This unusual cluster consists of eight lithium atoms in a square antiprism with two μ_4-O, μ_4-OH, and μ_4-pz groups occupying the six faces and two acetonitrile−scorpionate ligands (bpzCN) and two THF molecules in terminal positions. Finally, the rest of the lithium atoms are bridged by bpziLi ligands in a κ^2-N,N-bridging mode. This compound contains the $Li_8(\mu_4\text{-}O)_2(\mu_4\text{-}OH)_2(\mu_4\text{-}pz)_2$ cluster core with μ_4-O groups [Li_4−O(2)] capping two parallel square faces of a Li_8 cube (see Figure 6). The Li−Li distances of 2.44(3)−2.53(3) Å are in good agreement with those in other clusters[23] and with the values of 2.420 Å calculated by ab initio studies on $(MeLi)_4$.[24] However, the Li−Li distances of 2.79(3) and 2.96(3) Å between these two faces are longer than those in other clusters but shorter than those in elemental lithium (3.039 Å). The relative enlargement is probably due to the fact that rectangular faces generated with these distances are capped by two μ_4-OH (Li_4−O(1)) and two μ_4-pz (Li_4−N(50)−N(51)) groups. For the Li−O(1) and the Li−O(2) bonds, bond lengths of 1.97(2)−2.08(2) and 1.89(2)−1.96(2) Å, respectively, are observed. These distances are in agreement with structures of the square "Li_4O_4-antiprism", which are capped by an oxo or hydroxo ligand.[25] The distances of Li−N(50) and Li−N(51) of the pyrazolate group are between 2.03(2) and 2.09(2) Å, and to the best of our knowledge, this is the first observation where an μ_4-pz group is present in a structural molecular. In addition, the acetonitrile−scorpionate (bpzCN) and THF ligands are, respectively, coordinated to the Li(1) and Li(2) atoms in a terminal position (see Figures 7 and 8). The N(3)−Li(1) distance in this acetonitrile ligand (2.03(2) Å) can be compared to those typically found for terminal Li−NCR systems.[26] On the other hand, the N(3)−C(6) bond is very short (1.05(1) Å) and corresponds to a C−N triple bond. Finally, the structure of this cluster is completed with the heteroscorpionate bpziLi ligand in a κ^2-N,N-bridged coordination mode to Li3 and Li4 atoms (see Figure 8). The geometry around the Li5 atom of the bpziLi can be described as a distorted tetrahedron in which the Li atom is bonded to two pyrazol moieties of the (bpzCN) unit, the imino nitrogen (N1) of the bpziLi, and to one molecule of THF (see Figure 7). This distortion is due to the bis(3,5-dimethylpyrazol-1-yl)acetonitrile, which acts as a chelating bidentate ligand with an N(31)−Li(5)−N(41) angle of 96(1)°, whereas the angle N(1)−Li(5)−O(70) is 105(1)°. The metallacyclic ring Li−N−N−C−N−N adopts a boat conformation similar to that found with the bis(pyrazol-1-yl)methane ligand in tungsten or lithium complexes.[19]

Furthermore, when water was added to a THF solution of bdmpzm (in the presence of Bu^{n}Li) and *N*,*N*′-dimethylcarbodiimide, it was possible to isolate the amidine−scorpionate (bpzan) (**6**) (bpzan = *N*,*N*-dimethylbis(3,5-dimethylpyrazol-1-yl)acetamidine) (see Scheme 5) in good yield. This compound resulted from selective hydrolysis on the initially formed (bpziLi). This compound constitutes the first example of an amidine−scorpionate derivative.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **6** show single sets of resonances for the pyrazole rings, indicating that both pyrazoles are equivalent. The molecular structure of this compound was determined by X-ray diffraction, and the structure is shown in Figure 9. Significant bond distances and bond angles are listed in Table 1. This compound crystallizes with one molecule of water per molecule. The distance of C(12)−N(5) found in this compound (1.275(3) Å) is typical of C═N double bonds, as in Schiff bases and oximes (ca. 1.26 Å). The essentially sp^2 and planar nature of the imino carbon atom C(12) was further confirmed by the summations of the angles around it (360°).

Finally, the amidinate−lithium compounds **1** and **3** were used in the complexation of some titanium and zirconium fragments to test their coordinative capacity as scorpionate ligands. Thus, these compounds reacted with a solution of $[TiCl_4(THF)_2]$ or $[ZrCl_4]$ in THF to give complexes of stoichiometry $[MCl_3(\kappa^3\text{-NNN})]$ (M = Ti, Zr) (**7**−**10**), which were isolated as yellow or white solids after the appropriate workup (Scheme 6).

The mass spectra of these complexes indicate a mononuclear formulation (see Experimental Section). The IR spectra of **7**−**10** show two strong bands at ca. 1610 and 1380 cm^{-1}, which are assigned to $\nu_a(CN_2^-)$ and $\nu_s(CN_2^-)$, respectively. The IR spectra of all complexes show other bands of interest between 422 and 295 cm^{-1}. These bands were assigned to ν(M−Cl) of the terminal group. The ^{1}H and ^{13}C{H} NMR spectra of **7**−**10** each show a single set of resonances for the pyrazole rings, indicating that the pyrazoles are equivalent. The NMR spectra for the amidinate moiety of these complexes show two sets of resonances for

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[25] (a) Fromm, K. M.; Gueneau, E. D.; Goesmann, H. *Chem. Commun.* **2000**, 2187. (b) Lambert, C.; Hampel, F.; Schleyer, P. von R.; Davidson, M. G.; Snaith, R. *J. Organomet. Chem.* **1995**, *487*, 139. (c) Davidson, M. G.; Howard, J. A. K.; Lamb, S.; Lehmann, C. W. *Chem. Commun*. **1997**, 1607. (d) Lin, X.; Doble, D. M. J.; Blake, A. J.; Harrison, A.; Wilson, C.; Schröder, M. *J. Am. Chem. Soc.* **2003**, *125*, 9476.

[26] (a) Fei, Z.; Scopelliti, R.; Dyson, P. J. *Inorg. Chem.* **2003**, *42*, 2125. (b) Zi, G.; Li, H-W.; Xie, Z. *Organometallics* **2002**, *21*, 5415.

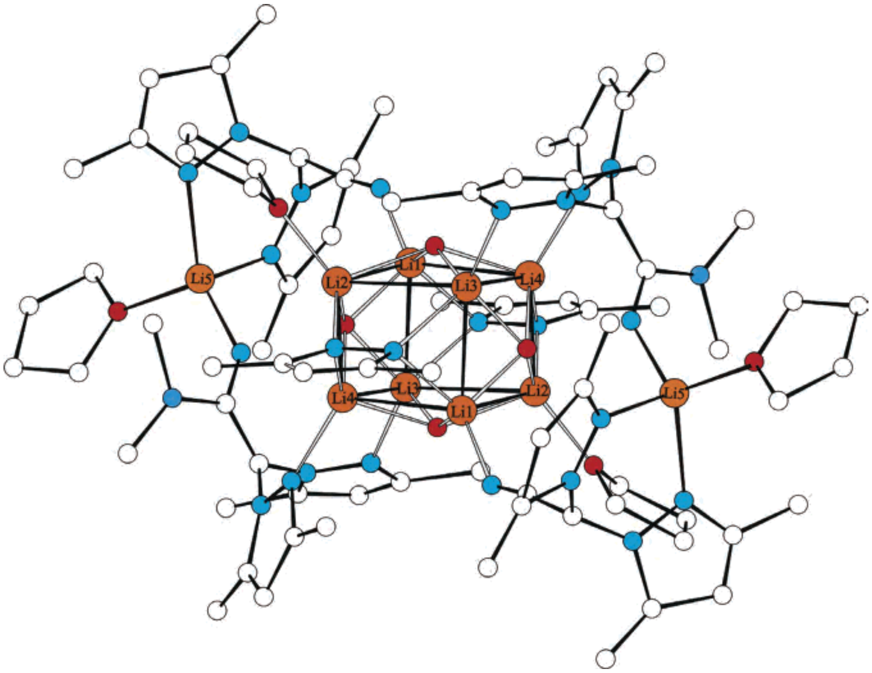


Figure 5. View of the molecular structure of $[Li_8(\mu_4\text{-}O)_2(\mu_4\text{-}OH)_2(\mu_4\text{-}pz)_2(\kappa^2\text{-}bpziLi)_2(bpzCN)_2(THF)_2]$ (**5**). Hydrogen atoms have been omitted for clarity.

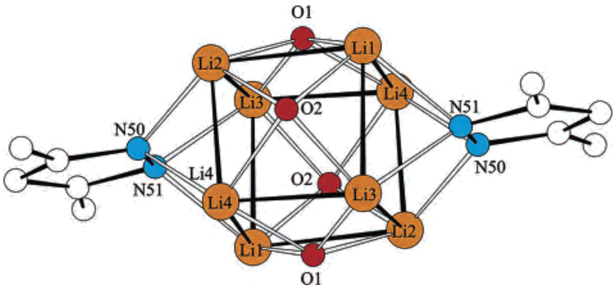


Figure 6. Cluster core of compound **5**.

these substituents. These data are indicative of monodentate binding of the amidinate moiety to the titanium and zirconium atoms similar to that in the lithium amidinate compounds. ^1H NOESY-1D experiments were also performed to confirm the assignment of the signals for the R^3, R^5, and H^4 groups. Futhermore, in compounds **9** and **10** (where $R_1 \neq R_2$), the response in the ^1H NOESY-1D experiment of the Me^5 protons of the pyrazolyl rings on irradiation of the ethyl group of the amidinate moiety suggests that this group is in the R_1 position whereas the *tert*-butyl group is in the R_2 position (see Scheme 6). $^1H-^{13}C$ heteronuclear correlation (g-HSQC) experiments were carried out and allowed us to assign the resonances corresponding to C^4, Me^3, and Me^5 of the pyrazole ring. These data confirm the octahedral disposition of the titanium or zirconium atom with κ^3-NNN-coordination for the heteroscorpionate ligand and the other three positions occupied with chloride ligands (see Scheme 6).

In conclusion, we have extended our previously developed synthetic route for heteroscorpionate ligands to other heterocumulenes, such as carbodiimides, and different results were found depending on the nature of the substituents in the carbodiimides. In fact, the use of sterically demanding isopropyl, cyclohexyl, *tert*-butyl, and ethyl-containing carbodiimides gave useful lithium compounds as a new class of tridentate ligands—the first amidinate scorpionates. These compounds were found to be excellent reagents for the introduction of the new class of scorpionate ligands into group 4 metal complexes, and a series of neutral titanium and zirconium complexes were prepared and characterized. However, the less sterically demanding methyl substituent gave a binuclear compound, the first type of diimino scorpionate ligand, through a process that probably involves the transformation of an initial unstable lithium acetamidinate by a sigmatropic [1,3]-shift followed by nucleophilic addition of the N atom of the resulting imino group to the other carbodiimide molecule. Furthermore, when the procedure with the *N*,*N′*-dimethylcarbodiimide was carried out in the presence of water, a selective hydrolytic process gave rise to a novel amidine−scorpionate ligand. However, it was possible to isolate alternative compounds from solutions exposed to air, in this case an unprecedented lithium cluster containing new types of scorpionates, namely, both imino and acetonitrile ligands.

Experimental Section

All reactions were performed using standard Schlenk-tube techniques under an atmosphere of dry nitrogen. Solvents were distilled from appropriate drying agents and degassed before use. Microanalyses were carried out with a Perkin-Elmer 2400 CHN analyzer. Mass spectra were recorded on a VG Autospec instrument using the FAB technique and nitrobenzyl alcohol as matrix. ^1H and ^{13}C NMR spectra were recorded on a Varian Inova FT-500 spectrometer and referenced to the residual deuterated solvent. The NOESY-1D spectra were recorded with the following acquisition parameters: irradiation time 2 s and number of scans 256, using standard VARIANT-FT software. Two-dimensional NMR spectra were acquired using standard VARIANT-FT software and processed using an IPC-Sun computer. The compounds *N*,*N′*-diisopropylcarbodiimide, *N*,*N′*-dicyclohexylcarbodiimide, *N*,*N′*-1-

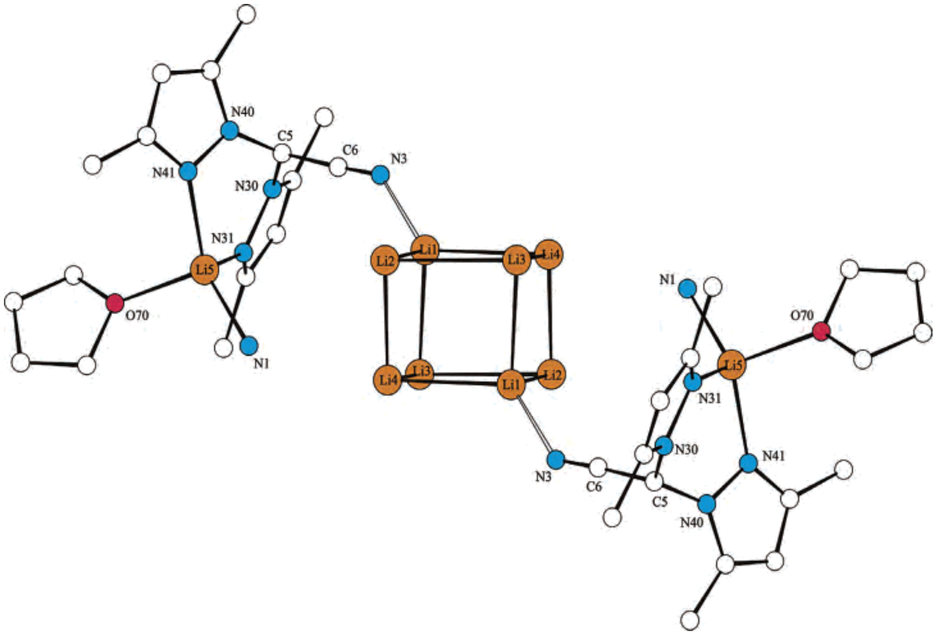


Figure 7. Coordination of the bpzCN entity in compound **5**.

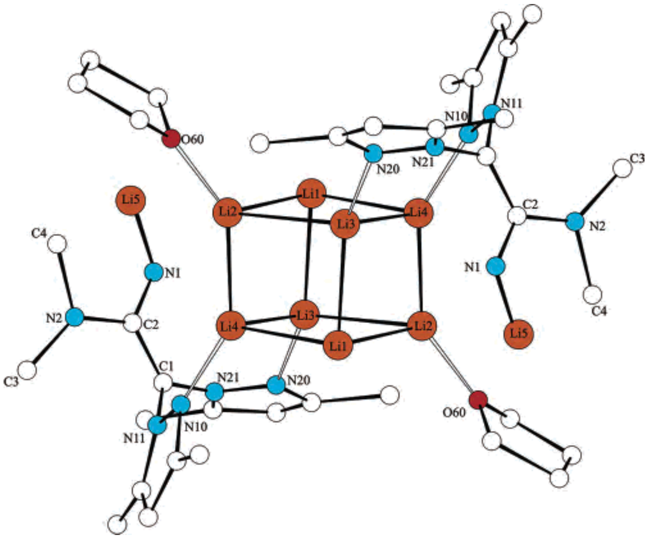
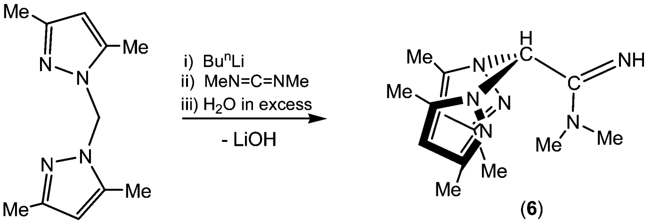


Figure 8. Coordination of the imino−lithium (bpziLi) entity in compound **5**.

Scheme 5. Synthesis of Compounds **6**



tert-butyl-3-ethylcarbodiimide, and *N*,*N*′-dimethylcarbodiimide were purchased from Aldrich. The compound bdmpzm (bdmpzm = bis(3,5-dimethylpyrazol-1-yl)methane) was prepared as reported previously.[15]

Preparation of Compounds 1−10. [Li(NNN)(THF)], (NNN) = (pbpamd) (**1**), (cbpamd) (**2**), (tbpamd) (**3**). In a 250 cm^3 Schlenk tube, bis(3,5-dimethylpyrazol-1-yl)methane (1.00 g, 4.89 mmol) was dissolved in dry THF (70 cm^3) and cooled to −70 °C. A 1.6 M solution of Bu^{n}Li (3.06 cm^3, 4.89 mmol) in hexane was added, and the suspension was stirred for 1 h. The reaction mixture was warmed to 0 °C, and the resulting yellow solution was treated with *N*,*N*′-diisopropylcarbodiimide (0.76 cm^3, 4.89 mmol) and stirred for 10 min. The solvent was removed, and the addition of hexane (70 cm^3) gave **1** as a white solid, which was crystallized from a mixture of THF/hexane. Compounds **2** and **3** were prepared using a similar experimental procedure.

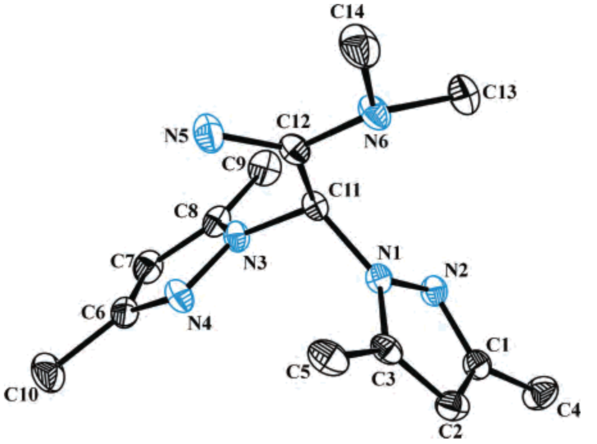
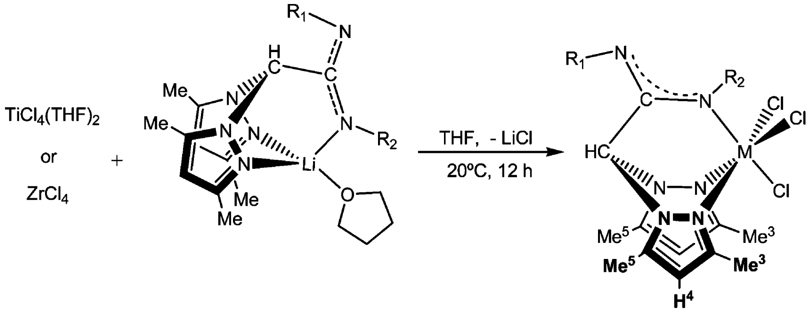


Figure 9. ORTEP view of bpzan (**6**). Ellipsoids are at the 30% probability level and hydrogen atoms have been omitted for clarity.

[Li(pbpamd)(THF)] (1). Yield 86%. Anal. Calcd for $C_{22}H_{37}LiN_6O$: C, 64.70; H, 9.06; N, 20.58. Found: C, 64.72; H, 9.16; N, 20.62. ^{1}H NMR (DMSO, 297 K), δ 7.11 (s, 1 H, CH), 5.89 (s, 2 H, H^4), 3.76 (m, 1 H, *C*H(CH$_3$)$_2$), 3.61 (m, 4 H, THF), 3.45 (m, 1 H, *C*H(CH$_3$)$_2$), 2.30 (s, 6 H, Me^5), 2.08 (s, 6 H, Me^3), 1.75 (m, 4 H, THF), 1.02 (d, 6 H, $^3J_{H-H} = 6.2$ Hz, CH(*C*H$_3$)$_2$), 0.80 (d, 6 H, $^3J_{H-H} = 6.2$ Hz, CH(*C*H$_3$)$_2$). ^{13}C−{^{1}H} NMR (DMSO, 297 K), δ 146.2 (N═C−N), 148.1, 140.6 (C$^{3\text{ or }5}$), 106.4 (C^4), 66.9 (THF), 65.7 (CH), 47.1, 41.4 [*C*H(CH$_3$)$_2$], 25.1 (THF), 24.9, 21.8 [CH-(*C*H$_3$)$_2$], 13.3 (Me^3), 10.8 (Me^5). ^{7}Li NMR (DMSO, 297 K), δ 1.59 (s). IR (KBr, cm^{-1}) ν_a (CN$_2^-$) = 1615, ν_s(CN$_2^-$) = 1386, ν(C═N) = 1572. Mass spectrum (FAB) (*m*/*z* assignment, % intensity): 331 [M − THF − Li], 100.

[Li(cbpamd)(THF)] (2). White solid. Yield 82%. Anal. Calcd for $C_{28}H_{45}LiN_6O$: C, 68.85; H, 9.22; N, 17.21. Found: C, 68.88; H, 9.24; N, 17.16. ^{1}H NMR (DMSO, 297 K), δ 7.09 (s, 1 H, CH),

Scheme 6. Synthesis of Titanium and Zirconium Complexes **7**−**10**



$R_1 = R_2 = {}^iPr$; (pbpamd); M = Ti (**7**), Zr(**8**)
$R_1 = Et$, $R_2 = {}^tBu$; (tbpamd); M = Ti(**9**), Zr(**10**)

5.90 (s, 2 H, H^4), 3.62 (m, 4 H, THF), 2.31 (s, 6 H, Me^5), 2.07 (s, 6 H, Me^3), 1.98−1.10 (m, 22 H, Cy), 1.77 (m, 4 H, THF). $^{13}C-\{^1H\}$ NMR (DMSO, 297 K), δ 146.8 (N=C−N), 148.2, 141.2 ($C^{3 \text{ or } 5}$), 106.2 (C^4), 67.0 (CH), 66.9 (THF), 40.0−29.4 (Cy), 25.1 (THF), 13.3 (Me^3), 10.6 (Me^5). ^7Li NMR (DMSO, 297 K), δ 1.55 (s). IR (KBr, cm^{-1}) $\nu_a(CN_2^-) = 1614$, $\nu_s(CN_2^-) = 1382$, $\nu(C{=}N) = 1578$. Mass spectrum (FAB): (*m*/*z* assignment, % intensity): 409 [M − THF − Li], 100.

[Li(tbpamd)(THF)] (3). White solid. Yield 85%. Anal. Calcd for $C_{22}H_{37}LiN_6O$: C, 64.70; H, 9.06; N, 20.58. Found: C, 64.65; H, 9.02; N, 20.54. ^1H NMR (DMSO, 297 K), δ 7.09 (s, 1 H, CH), 5.88 (s, 2 H, H^4), 3.61 (m, 4 H, THF), 2.90 (q, 2 H, $^3J_{H-H} = 7.2$ Hz, CH_2-CH_3), 2.33 (s, 6 H, Me^5), 2.07 (s, 6 H, Me^3), 1.75 (m, 4 H, THF), 1.24 (s, 9 H, $C(CH_3)_3$), 0.93 (t, 3 H, $^3J_{H-H} = 7.2$ Hz, CH_2-CH_3). $^{13}C-\{^1H\}$ NMR (DMSO, 297 K), δ 147.2 (N=C−N), 148.1, 140.7 ($C^{3 \text{ or } 5}$), 106.2 (C^4), 66.9 (THF), 67.0 (CH), 41.4 (CH_2-CH_3), 27.9 ($C(CH_3)_3$), 25.14 (THF), 21.2 ($C(CH_3)_3$), 17.1 (CH_2-CH_3), 13.4 (Me^3), 10.9 (Me^5). ^7Li NMR (DMSO, 297 K), δ 1.59 (s). IR (KBr, cm^{-1}) $\nu_a(CN_2^-) = 1610$, $\nu_s(CN_2^-) = 1379$, $\nu(C{=}N) = 1573$. Mass spectrum (FAB) (*m*/*z* assignment, % intensity): 331 [M − THF − Li], 100.

[Li(bpzii)(THF)]$_2$ (4). In a 250 cm^3 Schlenk tube, bis(3,5-dimethylpyrazol-1-yl)methane (1.00 g, 4.89 mmol) was dissolved in dry THF (70 cm^3) and cooled to −70 °C. A 1.6 M solution of Bu^nLi (3.06 cm^3, 4.89 mmol) in hexane was added, and the suspension was stirred for 1 h. The reaction mixture was warmed to 0 °C, and the resulting yellow solution was treated with *N*,*N*′-dimethylcarbodiimide (0.79 cm^3, 9.78 mmol) and was stirred for 10 min. The solvent was removed, and the addition of hexane (70 cm^3) gave a orange solid, which was crystallized from a mixture of THF/hexane. Yield 80%. Anal. Calcd for $C_{42}H_{70}Li_2N_{16}O_2$: C, 59.71; H, 8.29; N, 26.54. Found: C, 59.75; H, 8.32; N, 26.51. ^1H NMR (DMSO, 297 K), δ 5.91 (s, 2 H, CH), 5.67, (s, 2 H, H^4), 5.60 (s, 2 H, H^4), 3.60 (m, 8 H, THF), 2.75 (s, 6 H, NMe_2), 2.67 (s, 6 H, NMe_2), 2.37 (s, 6 H, Me^3), 2.24 (s, 6 H, NMe_2), 2.20 (s, 6 H, Me^5), 2.10 (s, 6 H, Me^5), 2.02 (s, 6 H, NMe_2), 1.99 (s, 6 H, Me^3), 1.76 (m, 8 H, THF). $^{13}C-\{^1H\}$ NMR (DMSO, 297 K), δ 157.3, 148.2 ($Me_2N-C{=}N$), 147.2, 141.8, 146.9, 140.2 ($C^{3 \text{ or } 5}$), 107.1, 106.3 (C^4), 67.9 (THF), 68.0 (CH), 37.4, 35.0, 33.3, 31.6 ($Me_2N-C{=}N$), 25.1 (THF), 13.4, 12.8, 10.7, 10.2 ($Me^{3 \text{ or } 5}$).

Synthesis of [$Li_8(\mu_4\text{-}O)_2(\mu_4\text{-}OH)_2(\mu_4\text{-}pz)_2(\kappa^2\text{-}bpziLi)_2(bpzCN)_2(THF)_4$] (5). In a 250 cm^3 Schlenk tube, bdmpzm (1.00 g, 4.89 mmol) was dissolved in dry THF (70 cm^3) and was cooled to −70 °C. A 1.6 M solution of Bu^nLi (3.06 cm^3, 4.89 mmol) in hexane was added, and the solution was stirred for 1 h. The reaction mixture was warmed to 0 °C, and the resulting yellow solution was treated with *N*,*N*′-dimethylcarbodiimide (0.39 cm^3, 4.89 mmol) and was stirred for 10 min. The solution was slowly evaporated in an air atmosphere, and after 72 h, white crystals suitable for X-ray analysis were deposited from the solution. Yield 35%. Anal. Calcd for $C_{78}H_{120}Li_{10}N_{26}O_8$: C, 57.84; H, 7.41; N, 22.49. Found: C, 57.69; H, 7.22; N, 22.38. ^1H NMR (DMSO, 297 K), δ 5.90, 566, 5.69, 5.58, 5.37 (CH and H^4-pz), 2.77, 2.74, 2.66, 2.50, 2.40, 2.35, 2.18, 2.10, 2.00, 2.40, 1.99, (Me signals of pz and imino groups), 3.60 (THF), 1.74 (THF).

Synthesis of [bpzan] (6). In a 250 cm^3 Schlenk tube, bis(3,5-dimethylpyrazol-1-yl)methane (1.00 g, 4.89 mmol) was dissolved in dry THF (70 cm^3) and was cooled to −70 °C. A 1.6 M solution of Bu^nLi (3.06 cm^3, 4.89 mmol) in hexane was added, and the suspension was stirred for 1 h. The reaction mixture was warmed to 0 °C, the resulting yellow solution was treated with *N*,*N*′-dimethylcarbodiimide (0.39 cm^3, 4.89 mmol) and stirred for 10 min, and finally, an excess of water (0.18 cm^3, 10 mmol) was added. The solvents were removed to afford a white solid, which was crystallized from THF. Yield 82%. Anal. Calcd for $C_{14}H_{22}N_6$: C, 61.31; H, 8.02; N, 30.65. Found: C, 61.32; H, 8.09; N, 30.62. ^1H NMR (DMSO, 297 K), δ 5.95 (s, 1 H, CH), 5.50 (s, 2 H, H^4), 2.45 (s, 6 H, $N-Me_2$), 2.26 (s, 6 H, Me^3), 2.11 (s, 6 H, Me^5). $^{13}C-\{^1H\}$ NMR (DMSO, 297 K), δ 153.3 ($N-C{=}N$), 147.8, 141.3 ($C^{3 \text{ or } 5}$), 104.1 (C^4), 69.2 (CH), 35.2 ($N-Me_2$), 12.2 (Me^3), 10.2 (Me^5). IR (KBr, cm^{-1}) $\nu(N-H) = 3410$, $\nu(C{=}N) = 1625$, 1580, 1550.

[$MCl_3(\kappa^3\text{-}pbpamd)$] M = Ti (7), Zr (8); [$MCl_3(\kappa^3\text{-}tbpamd)$] M = Ti (9), Zr (10). In a 250 cm^3 Schlenk tube, $TiCl_4(THF)_2$ (1.00 g, 2.99 mmol) and [Li(pbpamd)(THF)] (**1**) (1.22 g, 2.99 mmol) were suspended in cool THF (80 cm^3). The resulting suspension was stirred for 12 h at −70 °C. The solvent was removed under vacuum, and the solid was extracted with CH_2Cl_2. After removal of the volatiles, the resulting yellow solid (**7**) was crystallized from a mixture of THF/hexane. Complexes **8**, **9**, and **10** were prepared by using a similar procedure.

[$TiCl_3(\kappa^3\text{-}pbpamd)$] (7). Yield 89%. Anal. Calcd for $C_{18}H_{29}Cl_3N_6Ti$: C, 44.69; H, 6.00; N, 17.38. Found: C, 44.72; H, 5.98; N, 17.35. ^1H NMR ($CDCl_3$, 297 K), δ 7.36 (s, 1 H, CH), 5.95 (s, 2 H, H^4), 5.21 (m, 1 H, $CH(CH_3)_2$), 4.08 (m, 1 H, $CH(CH_3)_2$), 2.49 (s, 6 H, Me^3), 2.11 (s, 6 H, Me^5), 1.35 (d, 6 H, $^3J_{H-H} = 6.2$ Hz, $CH(CH_3)_2$), 1.22 (d, 6 H, $^3J_{H-H} = 6.2$ Hz, $CH(CH_3)_2$). $^{13}C-\{^1H\}$ NMR ($CDCl_3$, 297 K), δ 154.0 ($N{=}C-N$), 149.6, 144.7 ($C^{3 \text{ or } 5}$), 108.3 (C^4), 62.7 (CH), 41.6, 40.4 ($CH(CH_3)_2$), 15.3, 13.9 ($CH(CH_3)_2$), 13.9 (Me^5), 11.8 (Me^3). IR (KBr, cm^{-1}) $\nu_a(CN_2^-) = 1619$, $\nu_s(CN_2^-) = 1388$, $\nu(C{=}N) = 1579$, $\nu(M-Cl) = 422$, 359. Mass spectrum (FAB) (*m*/*z* assignment, % intensity): 447 [M − Cl], 100.

[$ZrCl_3(\kappa^3\text{-}pbpamd)$] (8). White solid. Yield 83%. Anal. Calcd for $C_{18}H_{29}Cl_3N_6Zr$: C, 41.01; H, 5.50; N, 15.95. Found: C, 41.09; H, 5.59; N, 15.88. ^1H NMR ($CDCl_3$, 297 K), δ 7.11 (s, 1 H, CH), 5.89 (s, 2 H, H^4), 5.09 (m, 1 H, $CH(CH_3)_2$), 3.99 (m, 1 H, $CH(CH_3)_2$), 2.52 (s, 6 H, Me^3), 2.18 (s, 6 H, Me^5), 1.40 (d, 6 H, $^3J_{H-H} = 6.2$ Hz, $CH(CH_3)_2$), 1.30 (d, 6 H, $^3J_{H-H} = 6.2$ Hz, $CH(CH_3)_2$). $^{13}C-\{^1H\}$ NMR ($CDCl_3$, 297 K), δ 157.9 ($N{=}C-N$),

Table 2. Crystal Data and Structure Refinement for **1**, **3**, **4**·$2C_4H_8O$, **5**, and **6**·H_2O

	1	**3**	**4**·$2C_4H_8O$	**5**	**6**·H_2O
formula	$C_{22}H_{37}LiN_6O$	$C_{22}H_{37}LiN_6O$	$C_{42}H_{68}Li_2N_{16}O_2\cdot 2C_4H_8O$	$C_{78}H_{118}Li_{10}N_{26}O_8$	$C_{14}H_{22}N_6\cdot H_2O$
fw (g/mol)	408.52	408.52	987.21	1617.38	292.39
T (K)	250(2)	150(2)	160(2)	250(2)	180(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	triclinic	triclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P2_1/c$	$P\bar{1}$
a (Å)	10.386(5)	10.073(4)	22.883(6)	13.739(3)	8.970(1)
b (Å)	10.996(5)	10.445(4)	11.983(3)	18.195(8)	9.628(1)
c (Å)	13.197(6)	13.078(6)	21.052(5)	22.337(9)	10.646(1)
α (deg)	65.725(9)	79.548(9)			91.898(3)
β (deg)	85.059(8)	68.950(8)	102.064(7)	95.14(3)	99.040(3)
γ (deg)	63.990(8)	68.878(8)			117.182(2)
V (Å^3)	12 267(1)	1195.8(9)	5645(2)	5561(4)	802.0(2)
Z	2	2	4	2	2
ρ_{calcd} (g/cm^3)	1.106	1.135	1.162	0.966	1.211
μ (cm^{-1})	0.070	0.72	0.76	0.63	0.81
F (000)	444	444	2136	1724	316
cryst size (mm^3)	0.35 × 0.29 × 0.05	0.47 × 0.29 × 0.14	0.39 × 0.27 × 0.07	0.43 × 0.34 × 0.33	0.40 × 0.25 × 0.17
index ranges	$-8 \le h \le 8$	$-12 \le h \le 12$	$-27 \le h \le 26$	$-16 \le h \le 16$	$-10 \le h \le 10$
	$-9 \le k \le 9$	$-13 \le k \le 12$	$-14 \le k \le 14$	$0 \le k \le 21$	$-10 \le k \le 11$
	$-11 \le l \le 10$	$-16 \le l \le 15$	$-23 \le l \le 24$	$0 \le l \le 26$	$-12 \le l \le 11$
reflns collected	3529	9493	13 916	10 070	5336
independent reflns, [R(int)]	1570, 0.0558	5263, 0.1578	4877, 0.0791	9797, 0.1058	2778, 0.0415
data/restraints/parameters	1570/0/280	5263/0/290	4877/54/380	9797/234/452	2778/0/200
GOF	1.054	0.874	0.946	0.739	1.019
final R indices [$I > 2\sigma(I)$]	R1 = 0.0754	R1 = 0.0981	R1 = 0.0710	R1 = 0.1401	R1 = 0.0633
wR2	0.1975	0.1883	wR2 = 0.1775	0.3053	0.1511
largest diff peak and hole (e·Å^{-3})	0.258, −0.265	0.218, −0.253	0.423, −0.212	0.361, −0.390	0.211, −0.243

149.5, 144.6 ($C^{3\text{ or }5}$), 108.2 (C^4), 64.9 (CH), 42.6, 40.1 ($CH(CH_3)_2$), 14.8, 14.3 ($CH(CH_3)_2$), 11.7 (Me^3), 10.8 (Me^5). IR (KBr, cm^{-1}) ν_a (CN_2^-) = 1605, ν_s (CN_2^-) = 1376, ν (C═N) = 1565, ν (M−Cl) = 412, 298. Mass spectrum (FAB) (*m*/*z* assignment, % intensity): 491 [M − Cl], 100.

[TiCl$_3$(κ^3-tbpamd)] (9). Yellow solid. Yield 83%. Anal. Calcd for $C_{18}H_{29}Cl_3N_6Ti$: C, 44.69; H, 6.00; N, 17.38. Found: C, 44.65; H, 6.09; N, 17.41. ^{1}H NMR (CDCl$_3$, 297 K), δ 7.29 (s, 1 H, CH), 5.99 (s, 2 H, H^4), 3.72 (q, 2 H, $^3J_{H-H}$ = 7.2 Hz, CH_2-CH_3), 2.39 (s, 6 H, Me^3), 2.17 (s, 6 H, Me^5), 1.49 (s, 9 H, $C(CH_3)_3$), 1.09 (t, 3 H, $^3J_{H-H}$ = 7.2 Hz, CH_2-CH_3). ^{13}C−{^{1}H} NMR (CDCl$_3$, 297 K), δ 155.1 (*N*═*C*—N), 152.6, 143.7 ($C^{3\text{ or }5}$), 107.9 (C^4), 63.8 (CH), 55.5 ($C(CH_3)_3$), 41.9 (CH_2-CH_3), 27.5 ($C(CH_3)_3$), 14.1 (CH_2-CH_3), 13.5 (Me^5), 11.1 (Me^3). IR (KBr, cm^{-1}) ν_a(CN_2^-) = 1607, ν_s(CN_2^-) = 1379, ν(C═N) = 1573, ν(M−Cl) = 419, 365. Mass spectrum (FAB) (*m*/*z* assignment, % intensity): 447 [M − Cl], 100.

[ZrCl$_3$(κ^3-tbpamd)] (10). White solid. Yield 88%. Anal. Calcd for $C_{18}H_{29}Cl_3N_6Zr$: C, 41.01; H, 5.50; N, 15.95. Found: C, 40.88; H, 5.54; N, 16.05. ^{1}H NMR (CDCl$_3$, 297 K), δ 7.18 (s, 1 H, CH), 5.87 (s, 2 H, H^4), 3.68 (q, 2 H, $^3J_{H-H}$ = 7.2 Hz, CH_2-CH_3), 2.45 (s, 6 H, Me^3), 2.16 (s, 6 H, Me^5), 1.55 (s, 9 H, $C(CH_3)_3$), 1.03 (t, 3 H, $^3J_{H-H}$ = 7.2 Hz, CH_2-CH_3). ^{13}C−{^{1}H} NMR (CDCl$_3$, 297 K), δ 157.3 (*N*═*C*—N), 151.3, 142.2 ($C^{3\text{ or }5}$), 108.2 (C^4), 64.6 (CH), 54.5 ($C(CH_3)_3$), 41.4 (CH_2-CH_3), 28.6 ($C(CH_3)_3$), 14.9 (CH_2-CH_3), 13.9 (Me^5), 11.8 (Me^3). IR (KBr, cm^{-1}) ν_a(CN_2^-) = 1607, ν_s (CN_2^-) = 1379, ν(C═N) = 1573, ν(M−Cl) = 415, 295. Mass spectrum (FAB) (*m*/*z* assignment, % intensity): 491 [M − Cl], 100.

X-ray Crystallographic Structure Determination for Complexes 1, 3, 4·$2C_4H_8O$, 5, and 6·H_2O. A summary of crystal data collection and refinement parameters for all compounds is given in Tables 1 and 2.

Single crystals of **1**, **3**, **4**·$2C_4H_8O$, and **6**·H_2O were mounted on a glass fiber and transferred to a Bruker X8 APPEX II CCD-based diffractometer equipped with a graphite-monochromated Mo Kα radiation source (λ = 0.71073 Å). Data were integrated using SAINT,[27] and an absorption correction was performed with the program SADABS.[28] The software package SHELXTL version 6.12[29] was used for space group determination, structure solution, and refinement by full-matrix least-squares methods based on F^2. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed using a "riding model" and included in the refinement at calculated positions.

For **5**, single crystals of low quality were obtained and were placed in a NONIUS-MACH3 diffractometer equipped with a graphite-monochromated Mo Kα radiation source (λ = 0.71073 Å). Intensity data were collected using an $\omega/2\theta$ scan technique. The structure was solved by direct methods using the SHELXS[30] computer program, completed by subsequent difference-Fourier syntheses, and refined by full-matrix least-squares procedures (SHELXL97)[31] on F^2. Because of the poor quality of crystals, not all non-hydrogen atoms could be refined anisotropically. The hydrogen atoms were placed using a "riding model" and included in the refinement at calculated positions. Unfortunately, due to the poor quality of the isolated crystals and the poor reflection properties of such a light atom cluster compound, the structure of **5** was only refined to an R value of 14.01%. Despite these poor results from the crystallographic point of view, the results obtained are sufficient for the description of geometry for this compound.

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(27) *SAINT+*, v7.12a; Area-Detector Integration Program; Bruker-Nonius AXS: Madison, WI, 2004.

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(29) *SHELXTL-NT*, version 6.12; Structure Determination Package; Bruker-Nonius AXS: Madison, WI, 2001.

(30) Sheldrick, G. M. *SHELXS-97*; Program for Structure Solution; *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

(31) Sheldrick, G. M. *SHELXL-97*; Program for Crystal Structure Refinement; University of Göttingen: Göttingen, Germany, 1997.

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Supporting Information Available: Details of data collection, refinement, atom coordinates, anisotropic displacement parameters, and bond lengths and angles for complexes **1**, **3**, **4**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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