

A Zirconium Hydrazide as a Synthone for a Metallanitrene Equivalent: Atom-by-Atom Assembly of $[\text{EN}_2]^{2-}$ Units ($\text{E} = \text{S}, \text{Se}$) by Chalcogen-Atom Transfer in the Coordination Sphere of a Transition Metal**

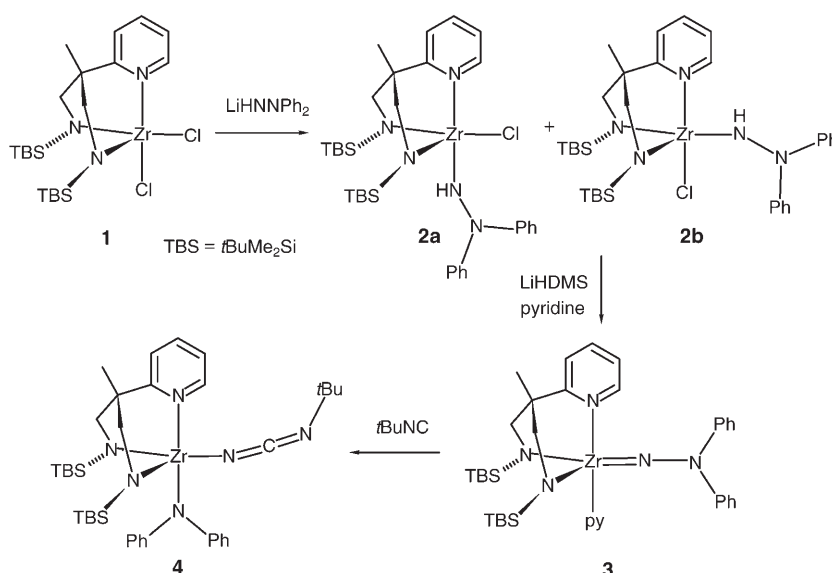
Heike Herrmann, Julio Lloret Fillol, Hubert Wadepohl, and Lutz H. Gade*

Interest in transition-metal hydrazides has been primarily due to the role they are thought to play in the stoichiometric and catalytic reduction of dinitrogen to ammonia.^[1] In this context, complexes of the transition metals in the middle of the d block have been most thoroughly studied.^[2,3] On the other hand, hydrazidotitanium complexes appear to be key intermediates in stoichiometric and catalytic hydrazinations of alkynes^[4] and in related reactions,^[5] which has recently directed attention to the Group 4 elements.^[6] For the heavier Group 4 metals, only one example, $[\text{Cp}_2\text{Zr}(\text{N}_2\text{Ph}_2)(\text{dmap})]$ ($\text{Cp} = \text{C}_5\text{H}_5$, $\text{dmap} = 4$ -dimethylaminopyridine), has been reported, by Bergman and co-workers. In a preliminary study into the reactivity of the compound, a tendency for N–N bond cleavage in reactions with alkynes and CO was observed.^[7] This contrasts with the known reactive behavior of the Ti complexes (e.g. in hydrazinations), in which coupling of substrates occurs with the N–N unit intact. Hydrazidozirconium compounds may therefore give rise to new patterns of reactivity in the coordination sphere of early-transition-metal elements.

We introduced a tridentate diamido-pyridyl ligand $[\text{N}_2^{\text{R}}\text{N}_{\text{py}}]^{2-}$ as a supporting ligand to stabilize early-transition-metal complexes containing reactive $\text{M}=\text{N}$ bonds and their derivatives,^[8] thus allowing, among other things, the isolation of key intermediates of the catalytic hydroamination of alkynes.^[8d] This ligand platform appeared particularly suited for the investigation of the reactivity of hydrazidozirconium complexes with respect to a potential cleavage of the N–N bond, which in turn would offer the opportunity to com-

bine the remaining metal-bonded N atom with other reactive fragments.

Reaction of the dichloro complex $[\text{Zr}(\text{N}_2^{\text{TBS}}\text{N}_{\text{py}})\text{Cl}_2]$ (**1**, Scheme 1) with one molar equivalent of LiHNNPh_2 gave a 75:25 mixture of the two stereoisomers **2a** and **2b** of the chloro hydrazido (1– charge) complex $[\text{Zr}(\text{N}_2^{\text{TBS}}\text{N}_{\text{py}})(\text{HNNPh}_2)\text{Cl}]$.^[9] The assignment given in Scheme 1 for the two isomers was confirmed by an X-ray diffraction study of the major component **2a**.^[10] This mixture of isomers could be cleanly converted to the deep green complex $[\text{Zr}(\text{N}_2^{\text{TBS}}\text{N}_{\text{py}})(\text{NNPh}_2)(\text{py})]$ (**3**) by dehydrohalogenation with lithium hexamethyldisilazide (LiHDMS) in the presence of one



Scheme 1. Synthesis of the hydrazindiido zirconium complex **3** and formal insertion of $t\text{BuNC}$ into the N–N bond to give the *tert*-butylcarbodiimido complex **4**.

[*] H. Herrmann, Dr. J. Lloret Fillol, Prof. Dr. H. Wadepohl, Prof. Dr. L. H. Gade
Anorganisch-Chemisches Institut
Universität Heidelberg
Im Neuenheimer Feld 270, 69120 Heidelberg (Germany)
Fax: (+49) 6221-545-609
E-mail: lutz.gade@uni-hd.de

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molar equivalent of pyridine (py). The linearly coordinated hydrazide in **3** is characterized by ^{15}N NMR spectroscopy resonances of $\delta = 287.8$ ppm for $\text{Zr}=\text{N}_\alpha$ and 178.2 for the $\text{N}_\beta\text{Ph}_2$ nuclei (NH_3 used as external reference). The molecular structure of **3** was established by X-ray diffraction and is depicted in Figure 1.^[11]

The overall molecular structure of **3** is best described as approximately trigonal bipyramidal with the pyridyl fragment of the polydentate ligand and the pyridine molecule occupying the axial positions ($\text{Zr}(1)-\text{N}(3)$ 2.256(2), $\text{Zr}(1)-\text{N}(4)$ 2.303(2) Å). The two amido functionalities and the almost

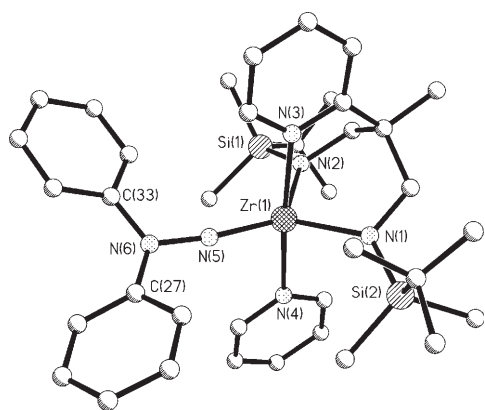


Figure 1. Molecular structure of complex **3**. Selected bond lengths [Å] and angles [°]: Zr(1)–N(1) 2.121(3), Zr(1)–N(2) 2.165(2), Zr(1)–N(3) 2.256(2), Zr(1)–N(4) 2.303(2), Zr(1)–N(5) 1.899(2), N(5)–N(6) 1.398(3); N(1)–Zr(1)–N(2) 104.18(9), N(1)–Zr(1)–N(3) 81.72(9), N(1)–Zr(1)–N(5) 126.00(11), N(2)–Zr(1)–N(3) 83.45(9), N(2)–Zr(1)–N(5) 128.17(10), N(3)–Zr(1)–N(4) 173.79(9), N(3)–Zr(1)–N(5) 91.05(9), N(4)–Zr(1)–N(5) 94.82(10), Zr(1)–N(5)–N(6) 172.7(2).

linearly coordinated hydrazindiido ligand are coordinated in the equatorial sites. The Zr(1)–N(5) bond length of 1.899(2) Å and the N(5)–N(6) bond length of 1.398(3) Å as well as the Zr(1)–N(5)–N(6) angle (172.7(2)°) are similar to the corresponding parameters in [Cp₂Zr(N₂Ph₂)(dmap)] (1.873(7), 1.364(10) Å, and 174.4(3)°, respectively).^[7] The observed N–N bond cleavage in reactions of the latter led us to investigate this aspect more closely.

The axially bound pyridine molecule in **3** is very labile towards substitution, as established in the exchange with free pyridine by ¹H NMR spectroscopy line-shape analysis (*k* ≈ 20 s^{−1} at 295 K), and the reactive species in transformations of **3** is therefore thought to be the four-coordinate hydrazide **3a** (Figure 2). The latter was modeled using the DFT B3LYP-6-31G(d) computational tool combined with an ONIOM modeling of the ligand substituents in N₂^{TBS}N_{py}.^[12] Remarkably, the almost linear hydrazido ligand in **3a** possesses a very

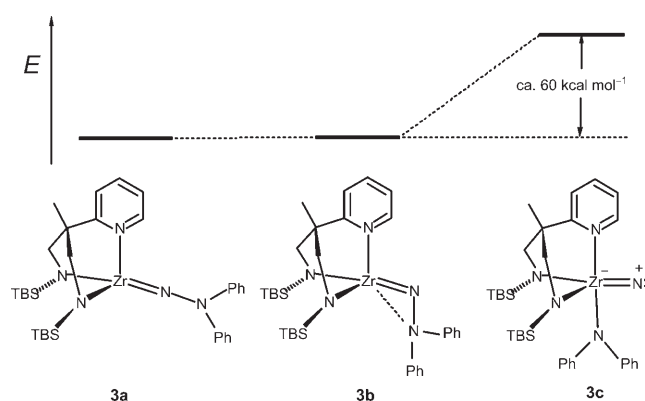


Figure 2. Energy profile of three local energy minima found for the four-coordinate hydrazido complex: the linear (**3a**) and the bent hydrazide (**3b**) as well as a potential amido nitride **3c**, which is destabilized by approximately 60 kcal mol^{−1} according to a DFT (B3LYP)/ONIOM study.

soft bending mode, leading to a second, almost isoenergetic local minimum structure **3b** in which the hydrazide moiety is bent (Figure 2). Such a bent hydrazide has been observed by NMR spectroscopy in [Cp*WMe₃(N₂H₂)] (Cp* = C₅Me₅), a model for an intermediate in the N₂ reduction cycle.^[13]

The bent hydrazide **3b** possesses low-lying acceptor orbitals primarily located on the N_α atom and a slightly elongated N–N bond. The constitutional isomer **3c**, the amidozirconium “nitride” complex, in which the N–N bond is broken, represents another local minimum, which is, however, approximately 60 kcal mol^{−1} higher in energy. Terminal Group 4 nitrides are unknown, and the Zr=N bonding is best described by the doubly bonded formally zwitterionic structure, with a very low lying acceptor orbital located on the nitride N atom.^[12] Such a species is expected to display the reactivity of a “metallanitrene”,^[14] that is, to engage in coupling reactions with suitable unsaturated nucleophiles.

In a first probe for this type of reaction pattern (emanating from **3b** or **3c**), **3** was treated with one molar equivalent of *t*BuNC (Scheme 1), which led instantaneously to N–N bond cleavage, thus giving the carbodiimido complex [Zr(N₂^{TBS}N_{py})(NPh₂)(NCN*t*Bu)] (**4**). Its molecular structure is depicted in Figure 3 and displays the metal-bonded diazacymulene NCN*t*Bu (N(4)–C(22) 1.194(3), N(5)–C(22) 1.233(3) Å, N(4)–C(22)–N(5) 174.6(2)°, which has resulted from a formal nitrene–isocyanide coupling similar to that observed in the thermal degradation of palladium azides.^[15]

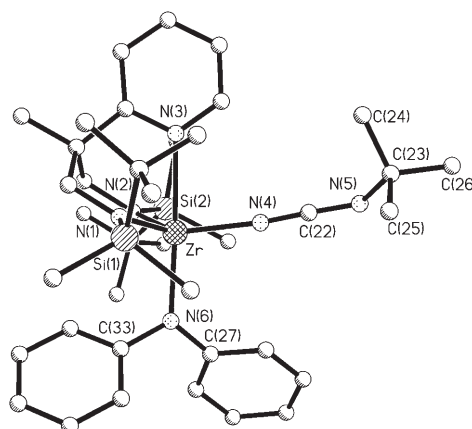


Figure 3. Molecular structure of complex **4**. Selected bond lengths [Å] and angles [°]: Zr–N(1) 2.010(2), Zr–N(2) 2.068(2), Zr–N(3) 2.408(2), Zr–N(4) 2.106(2), Zr–N(6) 2.161(2), N(4)–C(22) 1.194(3), C(22)–N(5) 1.233(3), N(5)–C(23) 1.478(4); N(3)–Zr(1)–N(6) 177.21(8), N(4)–Zr(1)–N(6) 99.53(7), Zr(1)–N(4)–C(22) 174.6(2), N(4)–C(22)–N(5) 175.2(3), C(22)–N(5)–C(23) 125.61(2).

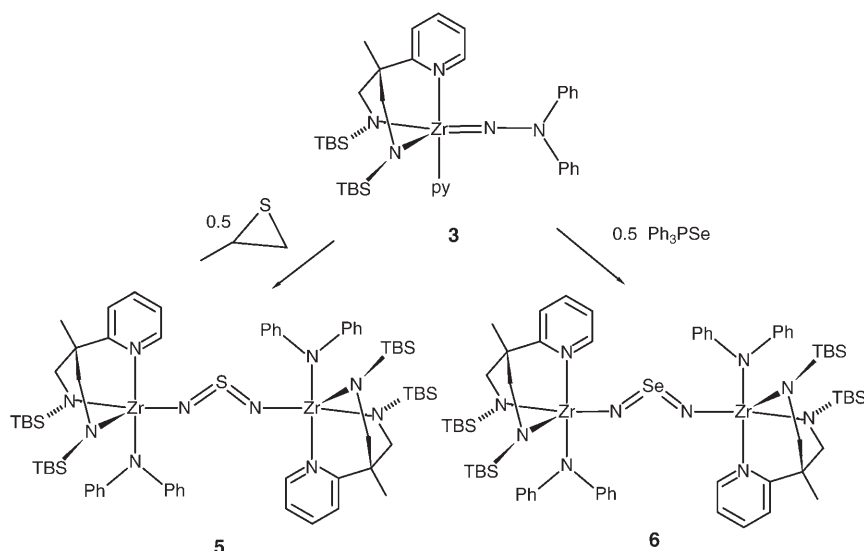
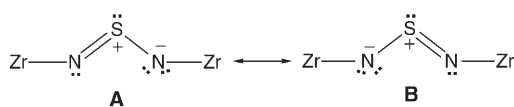
It has been shown that certain terminal nitrido ligands in late-transition-metal complexes may react with chalcogen-atom transfer reagents to give NO, NS, or NSe units,^[16] and this type of reaction was thought to provide a further indication of the reactive behavior of the activated hydrazido fragment in **3**. The reaction of **3** with 0.5 molar equivalents of the chalcogen-atom transfer reagents propylene sulfide^[17] or triphenylphosphine selenide^[18] gave the dinuclear complexes

$[\{\text{Zr}(\text{N}_2^{\text{TBS}}\text{N}_{\text{py}})(\text{NPh}_2)\}_2(\mu\text{-N}_2\text{E})]$ ($\text{E} = \text{S}$: **5**, Se : **6**) in high yield (Scheme 2). The trigonal-bipyramidal zirconium complex fragments are linked by a central bridging $\{\text{EN}_2\}$ fragment. As in the formation of **4**, the N–N bond of the hydrazide moiety has been cleaved in both complexes, and the $\{\text{Ph}_2\text{N}\}$ unit has migrated to the Zr atom, to which it is bonded as an apical amido ligand. Formally, the N_α atom of the hydrazido unit has remained as a nitrene/nitride at the equatorial coordination site.^[14] Two of these units have assembled with the transferred chalcogen atom to generate the bridging dinitridosulfate(IV)^[19] and dinitridoselenate(IV) ligands in **5** and **6**, respectively. The ^{15}N NMR spectroscopy resonances in the $[\text{EN}_2]^{2-}$ units are observed at extremely low field (**5**: $\delta = 448.0$ ppm, **6**: 588.2, NH_3 used as external reference), the ^{15}N nuclei of complex **6** being among the most deshielded ever observed.^[20]

In order to establish the details of the molecular structures of **5** and **6**, X-ray diffraction studies of both compounds have been carried out. The two complexes are isomorphous and possess overall similar molecular structures displayed in Figure 4 for complex **6**.

The most interesting feature in the structure of complex **5** is the central SN_2 unit $[\text{SeN}_2]$ unit in **6**. The S–N bond lengths for S–N(5) (1.501(3) Å) and S–N(10) (1.506(3) Å) [Se–N(5) 1.671(1), Se–N(10) 1.670(1) Å] and the N(5)–S–N(10) angle of $118.45(15)^\circ$ [N(5)–Se–N(10) $112.28(8)^\circ$] are consistent with the formulation of the $[\text{EN}_2]^{2-}$ unit as a dianion (a dinitridosulfate (IV) or dinitridoselenate(IV)) with one lone pair at the sulfur [selenium] atom.^[21,22] The metal–ligand bonds to the two Zr centers of Zr(1)–N(5) 2.076(2) and Zr(2)–N(10) 2.066(2) Å [**6**: Zr(1)–N(5) 2.055(1), Zr(2)–N(10) 2.054(1) Å] are very similar to those of the Zr-bonded amido groups. A natural bond order (NBO) analysis of the molecular structure of complex **5**, based on a DFT (B3LYP)/ONIOM study, has revealed a formal N–S bond order for the NSN unit of approximately 1.5.^[12] This situation resembles the bonding in the organoelement analogues, the sulfur and selenium diimides,^[19b] which has been established in detail both experimentally and theoretically.^[23] The bonding is best described by the two resonance structures **A** and **B**.

As to the formation of both **5** and **6**, the high energy of a potential nitrido complex **3c** makes an attack of the chalcogen atom at the hydrazide **3b** prior to N–N bond cleavage the most likely process. A DFT study of a S adduct of **3b** at the N_α atom has established a local energy minimum out of which the subsequent transformation is expected to occur.^[12]



Scheme 2. Reaction of **3** with chalcogen-atom donors to give the dinuclear $[\mu\text{-EN}_2]^{2-}$ complexes ($\text{E} = \text{S}$, Se) **5** and **6**.

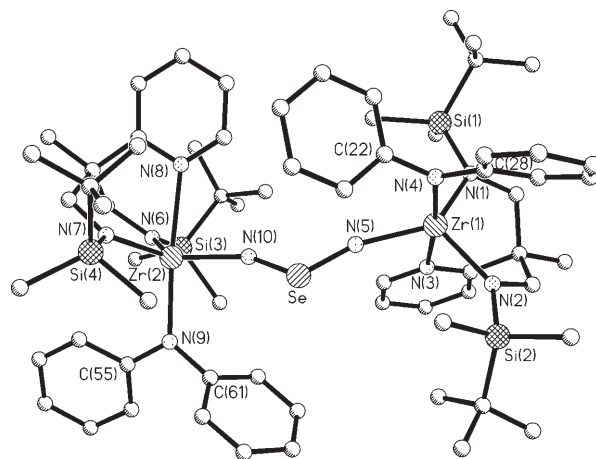


Figure 4. Molecular structure of complex **6**. Selected bond lengths [Å] and angles $^\circ$: Zr(1)–N(1) 2.077(1), Zr(1)–N(2) 2.036(1), Zr(1)–N(3) 2.409(1), Zr(1)–N(4) 2.178(1), Zr(1)–N(5) 2.055(1), N(5)–Se 1.671(1), N(10)–Se 1.670(1), Zr(2)–N(6) 2.048(1), Zr(2)–N(7) 2.064(1), Zr(2)–N(8) 2.398(1), Zr(2)–N(9) 2.178(1), Zr(2)–N(10) 2.054(1); Zr(1)–N(5)–Se 158.83(10), N(5)–Se–N(10) $112.28(8)^\circ$, Zr(2)–N(10)–Se 150.69(9). Selected bond lengths [Å] and angles $^\circ$ of the isostructural compound **5**: Zr(1)–N(1) 2.072(2), Zr(1)–N(2) 2.029(2), Zr(1)–N(3) 2.405(2), Zr(1)–N(4) 2.175(2), Zr(1)–N(5) 2.076(2), N(1)–Si(1) 1.726(3), N(5)–S 1.501(3), N(10)–S 1.506(3), Zr(2)–N(6) 2.043(2), Zr(2)–N(7) 2.058(2), Zr(2)–N(8) 2.400(2), Zr(2)–N(9) 2.168(2), Zr(2)–N(10) 2.066(2); Zr(1)–N(5)–S 160.86(17), N(5)–S–N(10) $118.45(15)^\circ$, Zr(2)–N(10)–S 155.66(17).

Terminal nitride complexes of the Group 4 elements have so far been elusive and, given their reactive nature, are unlikely to be isolated with highly charged supporting ligands such as the diamido donor system employed herein. However, hydrazido complexes may serve as readily accessible synthons for $\{\text{M}=\text{N}\}$ units ($\text{M} = \text{Group 4 metal}$), which are expected to

have a rich synthetic and catalytic^[4,5] potential that remains to be tapped.^[24]

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- [10] To be published. Crystal data of **2a**: C₃₃H₅₂ClN₅Si₂Zr, orthorhombic, space group *Pna2*₁, *a* = 10.2241(15), *b* = 35.855(5), *c* = 9.8844(15) Å, *V* = 3623.5(9) Å³, *Z* = 4, μ = 0.472 mm^{–1}, *F*₀₀₀ = 1480.
- [11] Crystal data of **3**: C₃₈H₅₆N₆Si₂Zr, monoclinic, space group *P2*₁/*c*, *a* = 10.2312(9), *b* = 12.4990(11), *c* = 30.880(3) Å, β = 97.632(2)°, *V* = 3913.9(6) Å³, *Z* = 4, μ = 0.376 mm^{–1}, *F*₀₀₀ = 1576. Reflections measured: 75 589, independent: 8979 [*R*_{int} = 0.098], index ranges –13 ≤ *h* ≤ 13, –16 ≤ *k* ≤ 0, –40 ≤ *l* ≤ 12, θ range 1.8 to 28.5°. Final *R* values [*I* > 2 σ (*I*)]: *R*₁ = 0.0486, *wR*₂ = 0.1142, *Goof* = 1.033. **4**: C₃₈H₆₀N₆Si₂Zr, monoclinic, space group *Cc*, racemically twinned (refined fractions of the two crystallites 0.945 and 0.055), *a* = 11.7568(8), *b* = 18.3226(12), *c* = 18.9636(13) Å, β = 91.6860(10)°, *V* = 4083.3(5) Å³, *Z* = 4, μ = 0.361 mm^{–1}, *F*₀₀₀ = 1592. Reflections measured: 100 972, independent: 13 059 [*R*_{int} = 0.0379], index ranges –17 ≤ *h* ≤ 17, –27 ≤ *k* ≤ 27, –26 ≤ *l* ≤ 28, θ range 2.1 to 32.0°. Final *R* values [*I* > 2 σ (*I*)]: *R*₁ = 0.0350, *wR*₂ = 0.0825, *Goof* = 1.183. **5**: C₆₆H₁₀₂N₁₀SSi₄Zr₂·0.5 C₇H₈, triclinic, space group *P* $\bar{1}$, *a* = 13.6391(3), *b* = 16.3628(3), *c* = 18.3324(3) Å, α = 77.4440(11), β = 89.7670(12), γ = 67.5910(11)°, *V* = 3677.80(12) Å³, *Z* = 2, μ = 0.423 mm^{–1}, *F*₀₀₀ = 1490. Reflections measured: 69 600, independent: 15 625 [*R*_{int} = 0.0850], index ranges –17 ≤ *h* ≤ 17, –20 ≤ *k* ≤ 20, 0 ≤ *l* ≤ 23, θ range 1.6 to 26.7°. Final *R* values [*I* > 2 σ (*I*)]: *R*₁ = 0.0439, *wR*₂ = 0.0948, *Goof* = 1.019. **6**: C₆₆H₁₀₂N₁₀SeSi₄Zr₂·0.5 C₇H₈, triclinic, space group *P* $\bar{1}$, *a* = 13.6511(6), *b* = 16.4735(7), *c* = 18.3587(8) Å, α = 77.1450(10), β = 89.3640(10), γ = 67.4010(10)°, *V* = 3703.3(3) Å³, *Z* = 2, μ = 0.883 mm^{–1}, *F*₀₀₀ = 1526. Reflections measured: 93 395, independent: 24 353 [*R*_{int} = 0.0424], index ranges –20 ≤ *h* ≤ 20, –23 ≤ *k* ≤ 24, 0 ≤ *l* ≤ 27, θ range 1.9 to 32.2°. Final *R* values [*I* > 2 σ (*I*)]: *R*₁ = 0.0342, *wR*₂ = 0.0806, *Goof* = 1.059. Intensity data were collected at low temperature (**3**: 150 K; **4–6**: 100 K; Bruker AXS Smart 1000 CCD diffractometer, MoK α radiation, graphite monochromator, λ = 0.71073 Å) and corrected for Lorentz, polarization, and absorption effects (semiempirical, SADABS).^[11a] Structure solution: heavy-atom method combined with structure expansion by direct methods (DIRDIF).^[11b] Refinement: full-matrix least-squares methods based on *F*².^[11c] all non-hydrogen atoms anisotropic, hydrogen atoms at calculated positions (refined riding). CCDC-658106 (**3**), -658494 (**4**), -658107 (**5**), and -658108 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. a) G. M. Sheldrick, *SADABS-2004/1*, Bruker AXS, **2004**; b) P. T. Beurskens, G. Beurskens, R. de Gelder, S. Garcia-Granda, R. O. Gould, R. Israel, J. M. M. Smits, *DIRDIF-99*, University of Nijmegen, The Netherlands, **1999**; c) G. M. Sheldrick, *SHELXL-97*, University of Göttingen, **1997**.
- [12] All of the molecular systems were optimized using X-ray diffraction data as input structures. Hybrid quantum mechanical:molecular mechanical (QM:MM, B3LYP:UFF) computational tools were used to model the complexes. The inner segment (QM: B3LYP; (C, N: 6-31g(d); H: 6-31g; Zr: LANL2DZ)) was defined by only the essential elements of the first coordination sphere. Stationary points were characterized by frequency analysis. Compound **3a** was used as reference, which is ca. 20 kcal mol^{–1} higher in energy (in the gas phase) than compound **3**. All the calculations, including orbital analysis (NBO 3.0), have been carried out using Gaussian 03 program package.^[12a] A detailed description of the methods is provided in the supporting info. a) Gaussian 03, Revision B.03, M. J. Frisch, et al., see the Supporting Information.
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