

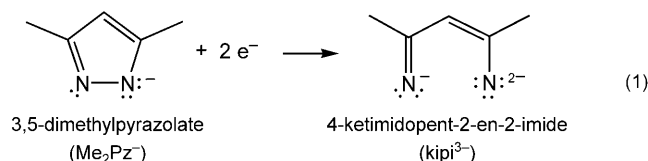
Tetranuclear Uranium Clusters by Reductive Cleavage of 3,5-Dimethylpyrazolate**

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Actinide metal centers are of fundamental interest as they have electronic structures that are distinct from those of transition metals and lanthanides. Indeed, the combination of increased spin–orbit coupling relative to transition metals and enhanced ligand field effects relative to lanthanides renders modeling the magnetic behavior of actinide-containing molecules particularly challenging.^[1] Such factors have a related impact on the chemical reactivity of actinide elements, which has prompted a revival of interest in the coordination chemistry and small-molecule reactivity of uranium. Among the intriguing reactivity patterns uncovered of late are transformations for which transition metal and lanthanide analogues had not previously been identified, as well as some transformations common for transition metal or lanthanide systems, but previously thought to be impossible for actinides.^[2]

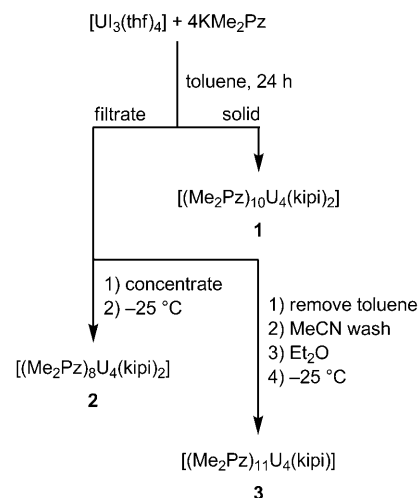
Our recent investigation of the reactivity of tetravalent uranium with 3,5-dimethylpyrazolate (Me_2Pz^-) led to formation of an unprecedented homoleptic dimer, $[\{\text{U}(\text{Me}_2\text{Pz})_4\}_2]$.^[3] Exposure of the dimer to traditional Lewis bases resulted in cleavage to afford mononuclear complexes, as observed for example in its reaction with THF to generate $[(\text{Me}_2\text{Pz})_4\text{U}(\text{thf})]$. Significantly, this reactivity was found to extend to the terminal chloride ligands of certain late transition metal complexes, enabling isolation of a series of linear chloride-bridged clusters of the formula $[(\text{cyclam})\text{M}(\mu\text{-Cl})\text{U}(\text{Me}_2\text{Pz})_4]_2$ (cyclam = 1,4,8,11-tetraazacyclotetradecane; $\text{M} = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$).^[3,4] Moreover, the isostructural nature of this series facilitated a partial deconvolution of the magnetic susceptibility data, thus revealing the presence of ferromagnetic exchange interactions in the Co^{II} - and Ni^{II} -centered clusters. In an effort to increase the strength of the exchange coupling within such species, we undertook investigations intended to produce analogues incorporating uranium(III) in place of uranium(IV). Herein, we report the unanticipated ability of uranium(III) to reductively cleave Me_2Pz^- , leading to a remarkable series of tetranuclear

clusters incorporating the new 4-ketimidopent-2-ene-2-imido (kpi^{3-}) ligand [Eq. (1)].



The kpi^{3-} ligand is an exotic latecomer to the acetylacetonato (acac^-) ligand family. Unlike the related and widely-utilized β -diketimido (nacnac^-) ligands,^[5] kpi^{3-} can be represented as containing both imido and ketimido functionalities. Therefore, it provides a true nitrogen-based, isoelectronic analogue of acac^- , a ligand that has played a long and vital role in coordination chemistry. The activation of Me_2Pz^- to form kpi^{3-} is unprecedented, both in f-element and transition metal chemistry, but is now found to provide the basis for the formation of three new tetranuclear uranium clusters: $[(\text{Me}_2\text{Pz})_{10}\text{U}_4(\text{kpi})_2]$ (**1**), $[(\text{Me}_2\text{Pz})_8\text{U}_4(\text{kpi})_2]$ (**2**), and $[(\text{Me}_2\text{Pz})_{11}\text{U}_4(\text{kpi})]$ (**3**). As outlined in Scheme 1, each cluster can be obtained from a reaction between $[\text{U}_3(\text{thf})_4]$ and KMe_2Pz , with the isolation of pure crystalline forms relying upon differences in solubilities and crystallization rates.^[6]

Crystals of **1** were isolated after washing the reaction mixture with toluene, following the removal of a gray precipitate by filtration. The preparation of **1** is less reliable than that of **2** or **3**, and consequently our characterization of it



Scheme 1. Synthesis of the tetranuclear clusters **1**, **2**, and **3**. $\text{Me}_2\text{Pz}^- = 3,5\text{-dimethylpyrazolate}$.

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is limited to a single crystal X-ray diffraction study. As shown in Figure 1, its solid-state structure consists of ten Me_2Pz^- ligands surrounding a core composed of four uranium(IV) centers and two kpi^{3-} ligands. The uranium(IV) centers are

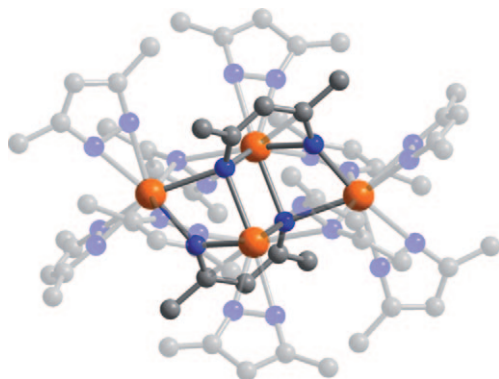


Figure 1. Structure of **1**, with the $[\text{U}_4(\text{kpi})_2]^{10+}$ core unit emphasized. U orange, N blue, C gray; H atoms are omitted for clarity. The cluster resides on an inversion center. A diagrammatic representation of **1** is available in the Supporting Information.

arranged in a rhombus with four edge-spanning pyrazolate ligands. The two metals at the acute corners of the rhombus each bear two terminal pyrazolates, while those at the obtuse corners are each ligated by just one terminal pyrazolate. The two $\mu_3:\mu_2$ bridging kpi^{3-} ligands lie above and below the U_4 plane and are related by inversion symmetry.

The geometry and highly-coordinating nature of the kpi^{3-} ligand in **1** are consistent with the changes expected for a formal two-electron reduction of Me_2Pz^- , resulting in cleavage of the N–N bond [Eq. (1)]. Although this is the first example of a structurally characterized kpi^{3-} unit, precedent for reductive cleavage of N–N bonds in molecules of the type $\text{RN}=\text{NR}$ by trivalent uranium is well-established.^[7] Nitrogen-based ligand reduction to form multinuclear uranium clusters has also been explored in compounds such as the azido/nitrido uranium(IV) chain, $[\{\text{Cs}(\text{MeCN})_3\}[\text{U}_4(\mu_4\text{-N})(\mu\text{-N}_3)_8(\text{MeCN})_8\text{I}_6]]_\infty$ ^[8] and the molecular ring species, $[(\text{C}_5\text{Me}_5)_2\text{U}(\mu\text{-N})\text{U}(\mu\text{-N}_3)(\text{C}_5\text{Me}_5)_2]_4$.^[9] In the new kpi^{3-} ligand, the pyrazolate backbone is bowed to a C–C–C angle of $127(2)^\circ$, while the N...N distance is increased to $2.99(2)$ Å, which is well beyond that of the intact Me_2Pz^- units in the structure (ca. 1.4 Å). Despite bridging multiple uranium centers, the U–N_{kpi} distances in **1** (see Table 1) are only slightly longer than the terminal U–N_{ketimido} distances of $2.179(6)$ Å and $2.185(5)$ Å reported for $[(\text{C}_5\text{Me}_5)_2\text{U}\{\text{-N}=\text{CPh}_2\}_2]$ ^[10] and the terminal U=N_{imido} distance of 1.952 Å reported for $[(\text{C}_5\text{Me}_5)_2\text{U}=\text{N}(\text{C}_6\text{H}_2\text{fBu}_3)]$.^[11] Note that the core of **1** may garner additional stabilization from the short U...C_{kpi} distances, which are comparable to the mean U–C separation in sterically saturated uranium cyclopentadienyl compounds.^[12]

Further concentration of solutions from which **1** had been isolated led to crystallization of $[(\text{Me}_2\text{Pz})_8\text{U}_4(\text{kpi})_2]$ (**2**; Figure 2). A more compact cubane-type cluster core is observed that consists of a tetrahedron of uranium atoms with each face capped by a nitrogen atom from one of two

Table 1: Selected interatomic distances [Å] in **1**, **2**, and **3**.

	U–N _{kpi}	C–N _{kpi}	U...C _{kpi}
$[(\text{Me}_2\text{Pz})_{10}\text{U}_4(\text{kpi})_2]$ (1)	2.2182(9) 2.298(1) 2.347(1) 2.556(1) 2.558(1)	1.3141(7) 1.3286(6)	2.852(1) 2.965(1) 3.05(1)
$[(\text{Me}_2\text{Pz})_8\text{U}_4(\text{kpi})_2]$ (2)	2.4089(3) 2.4251(3)	1.3560(4)	2.6704(3) 2.7092(3) 2.7851(4) 2.7851(4)
$[(\text{Me}_2\text{Pz})_{11}\text{U}_4(\text{kpi})]$ (3)	2.2171(5) 2.2368(4) 2.2456(4) 2.2473(5) 2.3311(5) 2.3348(4) 2.3376(5) 2.3550(4) 2.3557(4) 2.3588(4) 2.3679(6) 2.3896(6)	1.4035(3) 1.4056(3) 1.4203(3) 1.4449(3)	2.5859(5) 2.6082(6) 2.6153(4) 2.6209(6) 2.6285(4) 2.6542(5) 2.6751(4) 2.6804(5) 2.6903(5) 2.6983(5) 2.6993(5) 2.7048(4)

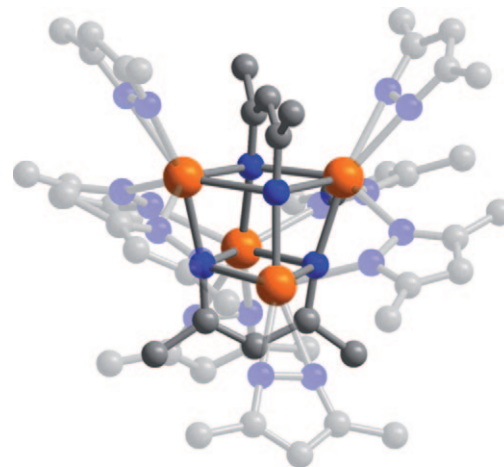


Figure 2. Structure of **2**, with the $[\text{U}_4(\text{kpi})_2]^{8+}$ core unit emphasized. U orange, N blue, C gray; H atoms are omitted for clarity. The cluster resides on a $\bar{4}$ site in the crystal, imparting it with rigorous D_{2d} symmetry. A diagrammatic representation of **2** is available in the Supporting Information.

opposing kpi^{3-} ligands. Four bridging Me_2Pz^- ligands span the equatorial faces of the cubane unit, whilst the other four Me_2Pz^- ligands provide a terminal ligand for each uranium center. The U...C_{kpi} distances are significantly shorter than in **1** owing to the co-planarity of the nitrogen atoms of the kpi^{3-} ligand and two of the uranium centers. As opposed to the structure of **1**, in which the carbon backbone of each kpi^{3-} ligand is tilted toward a single uranium atom, the carbon atoms of the kpi^{3-} ligands in **2** are equidistant from two uranium atoms. Furthermore, the N–C_{kpi} bonds of **2** are longer than in **1**, which suggests more extensive delocalization

of the ligand charge within the more compact structure of the cubane cluster core.

In contrast to **1**, which contains four uranium(IV) ions, the highly symmetric cubane cluster $[(\text{Me}_2\text{Pz})_8\text{U}_4(\text{kpi})_2]$ (**2**) is mixed-valent. With eight Me_2Pz^- and three kpi^{3-} anions, it formally contains two uranium(III) centers and two uranium(IV) centers. Such mixed valency has been observed in a growing number of examples in molecular uranium cluster chemistry.^[13] Compound **2** is unusual in that the majority of these mixed-valent uranium clusters exhibit structures with a different coordination geometry associated with the differing uranium oxidation states, whereas the $\bar{4}$ crystallographic symmetry of the cubane cluster enforces equivalent coordination environments about each of its four uranium atoms. Such equivalent ligand fields with mixed oxidation states suggest the possibility of electron delocalization. The ^1H NMR spectrum at 298 K offers evidence for the solution equivalence of the four uranium sites on the NMR timescale, because the signals that are due to the Me_2Pz^- methyl groups correspond to the same symmetry observed in the solid-state structure. Thus, the possibility of magnetic double exchange between the uranium(III) and uranium(IV) centers in **2** exists, although the small quantities of the compound available to date has thwarted our attempts at probing this by magnetic susceptibility measurements.

Removal of the toluene solvent enabled isolation of an additional cluster from the solution that provided compound **2**. The resulting black residue was washed with cold acetonitrile to afford $[(\text{Me}_2\text{Pz})_{11}\text{U}_4(\text{kpi})]$ (**3**) as a brown solid. As depicted in Figure 3, this cluster is similar to **1** and **2** in that it

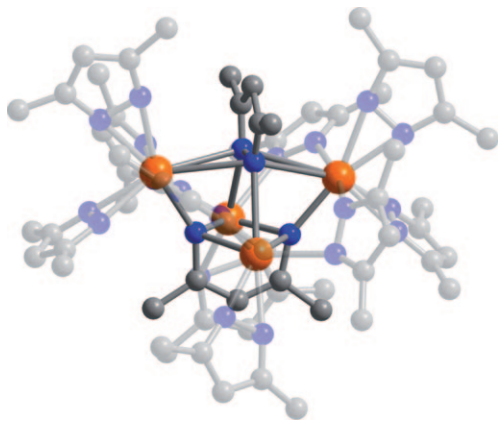


Figure 3. Structure of **3**, with the $[\text{U}_4(\text{kpi})(\text{Me}_2\text{Pz})]^{10+}$ core unit emphasized. U orange, N blue, C gray; H atoms are omitted for clarity. The cluster has no crystallographically imposed symmetry. A diagrammatic representation of **3** is available in the Supporting Information.

too features a kpi^{3-} ligand formed by reductive cleavage of an N–N bond of a Me_2Pz^- ligand. However, the structure of **3** is unique in that one core kpi^{3-} ligand has been replaced by a bridging $\mu^3\text{:}\mu^3\text{-Me}_2\text{Pz}^-$ ligand, which to the best of our knowledge represents a new bonding mode for pyrazolates.^[14] Intriguingly, the $[\text{U}_4(\text{kpi})(\text{Me}_2\text{Pz})]^{10+}$ cluster core of **3**, which also formally contains two uranium(III) and two uranium(IV) centers, is related to the $[\text{U}_4(\text{kpi})_2]^{8+}$ core of **2** through a two-

electron reduction of the $\mu^3\text{:}\mu^3\text{-Me}_2\text{Pz}^-$ ligand to give a second kpi^{3-} ligand. In the structure of **3**, the uranium atoms that make two bonds to the kpi^{3-} ligand each have one terminal pyrazolate ligand, whilst the uranium atoms with only one bond to the kpi^{3-} ligand each coordinate two terminal pyrazolates. This coordination is probably a steric effect owing to the larger space requirements of kpi^{3-} compared to the Me_2Pz^- ligand, but it most likely also reflects the two different oxidation states of uranium. Thus, unlike **2**, the structure of **3** is not consistent with the possibility of electron delocalization.

Remarkably, the clusters in **1** and **3** are structural isomers. Transformation of **3** into **1** would entail transfer of two electrons, one from each uranium(III) center, to the $\mu^3\text{:}\mu^3\text{-Me}_2\text{Pz}^-$ ligand, leading to cleavage of its N–N bond, and a rearrangement of the core structure involving loss of two U-N_{kpi} bonds and planarization of the four uranium atoms. Attempts to use heat or redissolution in toluene to convert **3** into **1** were unsuccessful, which indicates that **3** is the more stable isomer under the conditions tested, even though structurally, it seems a very reasonable intermediate in the reaction between UI_3 and KMe_2Pz to form **1**.

Of the three cluster compounds, **3** could be obtained most reliably and in the highest yields. A number of characterization methods were therefore used to probe this species (see the Supporting Information). The complicated nature of its ^1H NMR spectrum suggests that the C_1 symmetry of the cluster in the solid state is maintained in solution, although the peaks could not be accurately integrated in this case. Cyclic voltammetry was performed on **3** to probe whether the mixed-valence cluster could be readily reduced or oxidized. In acetonitrile solution with 0.1M $\text{Bu}_4\text{N}(\text{PF}_6)$ as the supporting electrolyte, an irreversible reduction wave was observed at about -2 V versus $\text{Cp}_2\text{Fe}^{0/+}$. However, this wave cannot be unambiguously assigned to a $\text{U}^{\text{IV/III}}$ conversion owing to the possibility of Me_2Pz^- ligand reduction. Furthermore, an irreversible oxidation occurs at approximately 0.06 V versus $\text{Cp}_2\text{Fe}^{0/+}$. In this case it is also unclear whether the redox change involves a $\text{U}^{\text{III/IV}}$ process or oxidation of the kpi^{3-} ligand. Unfortunately, efforts to isolate a clean product from chemical oxidations were unsuccessful.

Variable-temperature magnetic susceptibility data were collected for **3** from 5 to 300 K under a direct-current field of 0.5 T. The data show an almost linear decrease in $\chi_M T$ with decreasing temperature down to circa 150 K, at which point the drop becomes more severe, and eventually reaches $0.30 \text{ cm}^3 \text{ K mol}^{-1}$ at 5 K. With the convoluting effects of temperature-independent magnetism, crystal field splitting, and spin–orbit coupling, it is difficult to draw any conclusions about the presence of magnetic coupling in this system.^[1] As the moment falls well below the level expected for a ground state featuring two independent uranium(III) centers, anti-ferromagnetic coupling may be present between these two atoms of the mixed-valence cluster. However, confidence in this assessment would require a more complete understanding of how the crystal field splits the spin–orbit-coupled ground state of each uranium ion and the extent of orbital angular momentum quenching owing to covalency between uranium and the kpi^{3-} ligand.

The above results demonstrate the use of uranium(III) in the reductive cleavage of the N–N bond in Me_2Pz^- to form an unprecedented 4-ketimidopent-2-ene-2-imido (kpi^{3-}) ligand, which is found integrated within three related tetranuclear uranium clusters. It is possible that such chemistry can extend to other actinides, as well as to highly reducing lanthanide and transition metal systems, thus potentially providing access to a broad family of kpi^{3-} -based cluster molecules. Of particular interest for the present uranium system are efforts to improve upon the synthesis of the mixed-valence cubane cluster **2**, and experiments aimed at probing electron delocalization within its highly symmetric core structure.

Experimental Section

The syntheses and manipulations of the extremely air- and moisture-sensitive compounds were conducted under nitrogen with rigorous exclusion of air and water using Schlenk and glovebox techniques. The glovebox used was a Vacuum Atmospheres Nexus One employing an Engelhard Corp. Q-5 catalyst. Tetrahydrofuran was distilled over sodium and benzophenone. Toluene and diethyl ether were saturated with N_2 , passed through an activated alumina column, degassed by three freeze-pump-thaw cycles, and stored under N_2 over 3 Å molecular sieves. The solvent C_6D_6 (Cambridge Isotope Laboratories) was distilled over NaK alloy and benzophenone and degassed by three freeze-pump-thaw cycles. The compounds UI_3 ^[15] and KMe_2Pz ^[3] were synthesized as previously described. NMR experiments were conducted with Bruker 300, 400, and 500 MHz spectrometers. Elemental analyses were performed by the analytical laboratories at the University of California, Berkeley on a Perkin–Elmer 2400 Series II combustion analyzer. Experimental details of the magnetic measurements and electrochemistry can be found in the Supporting Information.

$[(\text{Me}_2\text{Pz})_{10}\text{U}_4(\text{kpi})_2]$ (**1**) and $[(\text{Me}_2\text{Pz})_8\text{U}_4(\text{kpi})_2]$ (**2**): Tetrahydrofuran (10 mL) was added to a vial charged with UI_3 (0.682 g, 1.10 mmol). After stirring for 2 h, residual solvent was removed under reduced pressure (10^{-3} Torr) to give $[\text{UI}_3(\text{thf})_4]$. Toluene (10 mL) was added to the deep blue solid, and solid KMe_2Pz (0.583 g, 4.34 mmol) was subsequently added with vigorous stirring. Stirring was continued for 24 h, and a gray, slightly radioactive precipitate was removed from the brown solution by filtration. Attempts to solubilize and characterize any uranium-containing products from this solid were unsuccessful. The solution was concentrated under reduced pressure for 3 h, affording a brown tar. Toluene was added, and filtration of the resulting solution infrequently yielded sub-milligram quantities of crystalline **1**, which was analyzed by single-crystal X-ray diffraction. Solvent was removed from the filtrate under reduced pressure until the solution reached saturation. Cooling of the saturated solution to -25°C resulted in the formation of purple hexagonal crystals identified as **2** by single-crystal X-ray analysis (30 mg, 5%). ^1H NMR (400 MHz, C_6D_6 , 298 K): $\delta = -21.8$ (s, 12H, $(\text{N}=\text{C})_2\text{CHMe}_2$, $\Delta\nu_{\text{f}} = 7.5$ Hz), -6.3 (s, 4H, $\text{Me}_2\text{HC}_3\text{N}_2$, $\Delta\nu_{\text{f}} = 1.9$ Hz), -6.2 (s, 24H, $\text{Me}_2\text{HC}_3\text{N}_2$, $\Delta\nu_{\text{f}} = 5.6$ Hz), 8.2 (s, 24H, $\text{Me}_2\text{HC}_3\text{N}_2$, $\Delta\nu_{\text{f}} = 3.1$ Hz), 29.3 ppm (s, 4H, $\text{Me}_2\text{HC}_3\text{N}_2$, $\Delta\nu_{\text{f}} = 2.5$ Hz). Anal. calcd. (%) for $\text{C}_{50}\text{H}_{70}\text{N}_{20}\text{U}_4$: C 31.55, H 3.71, N 14.72; found: C 31.82, H 3.70, N 14.67.

$[(\text{Me}_2\text{Pz})_{11}\text{U}_4(\text{kpi})]$ (**3**): Tetrahydrofuran (10 mL) was added to a vial charged with UI_3 (0.682 g, 1.10 mmol). After stirring for 2 h, residual solvent was removed under reduced pressure (10^{-3} Torr) to give $[\text{UI}_3(\text{thf})_4]$. Toluene (10 mL) was added to the deep blue solid, and solid KMe_2Pz (0.583 g, 4.34 mmol) was subsequently added with vigorous stirring. Stirring was continued for 24 h, and a gray, slightly radioactive precipitate was removed from the brown solution by filtration. Attempts to solubilize and characterize any uranium-containing products from this solid were unsuccessful. The solvent

was removed under reduced pressure (10^{-3} Torr) and toluene was added to the brown tar-like product. The solution was filtered and solvent was completely removed from the filtrate to form another dark brown tar. The tar was washed with cold acetonitrile (10 mL), and the product was collected on MAGNA nylon-supported filter paper with 0.22 μm pores. After drying on the filter paper, the resulting brown powder was washed with cold acetonitrile (3×2 mL) to give **3** (110 mg, 19%). Although the acetonitrile washes lower the yield significantly owing to the moderate solubility of **3** in acetonitrile, the washes are necessary to obtain pure product. Single crystals of **3** suitable for X-ray analysis were obtained by dissolving the brown powder in a minimal amount of diethyl ether and cooling the saturated solution to -25°C for two days. ^1H NMR (400 MHz, CDCl_3 , 294 K): $\delta = 56.8, 51.4, 38.0, 34.1, 30.8, 30.7, 16.3, 14.9, 14.1, 13.9, 11.0, 9.9, 3.4, 1.1, -13.2, -14.2, -16.3, -17.2, -22.8, -31.4, -32.0, -119.2, -123.8, -123.9$ ppm. Anal. calcd. (%) for $\text{C}_{60}\text{H}_{84}\text{N}_{24}\text{U}_4$: C 34.42, H 4.04, N 16.06; found: C 33.87, H 3.92, N 15.40.

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- [1] J. D. Rinehart, T. D. Harris, S. A. Kozimor, B. M. Bartlett, J. R. Long, *Inorg. Chem.* **2009**, *48*, 3382.
- [2] a) A. L. Odom, P. L. Arnold, C. C. Cummins, *J. Am. Chem. Soc.* **1998**, *120*, 5836; b) W. J. Evans, G. W. Nye, J. W. Ziller, *Angew. Chem.* **2000**, *112*, 246; *Angew. Chem. Int. Ed.* **2000**, *39*, 240; c) J. L. Kiplinger, D. E. Morris, B. L. Scott, C. J. Burns, *Organometallics* **2002**, *21*, 3073; d) I. Castro-Rodriguez, H. Nakai, L. N. Zakharov, A. L. Rheingold, K. Meyer, *Science* **2004**, *305*, 1757; e) T. W. Hayton, J. M. Boncella, B. L. Scott, P. D. Palmer, E. R. Batista, P. J. Hay, *Science* **2005**, *310*, 1941; f) O. T. Summerscales, F. G. N. Cloke, P. B. Hitchcock, J. C. Green, N. Hazari, *Science* **2006**, *311*, 829; g) A. R. Fox, S. C. Bart, K. Meyer, C. C. Cummins, *Nature* **2008**, *455*, 341; h) S. G. Minasian, J. L. Krinsky, V. A. Williams, J. Arnold, *J. Am. Chem. Soc.* **2008**, *130*, 10086.
- [3] S. A. Kozimor, B. M. Bartlett, J. D. Rinehart, J. R. Long, *J. Am. Chem. Soc.* **2007**, *129*, 10672.
- [4] J. D. Rinehart, B. M. Bartlett, S. A. Kozimor, J. R. Long, *Inorg. Chim. Acta* **2008**, *361*, 3534.
- [5] a) R. H. Holm, M. J. O'Connor, *Prog. Inorg. Chem.* **1971**, *14*, 241; b) D. J. Emslie, W. E. Piers, *Coord. Chem. Rev.* **2002**, *233–234*, 131; c) L. Bourget-Merle, M. F. Lappert, J. S. Severn, *Chem. Rev.* **2002**, *102*, 3031; d) H. W. Roesky, S. Singh, V. Jancik, V. Chandrasekhar, *Acc. Chem. Res.* **2004**, *37*, 969; e) D. J. Mindiola, *Acc. Chem. Res.* **2006**, *39*, 813; f) P. L. Holland, *Acc. Chem. Res.* **2007**, *40*, 601.
- [6] Full crystallographic parameters are included in the Supporting Information.
- [7] W. J. Evans, S. A. Kozimor, *Coord. Chem. Rev.* **2006**, *250*, 911.
- [8] G. Nocton, J. Pécaut, M. Mazzanti, *Angew. Chem.* **2008**, *120*, 3082; *Angew. Chem. Int. Ed.* **2008**, *47*, 3040.
- [9] W. J. Evans, S. A. Kozimor, J. W. Ziller, *Science* **2005**, *309*, 1835.
- [10] R. E. Da Re, K. C. Jantunen, J. T. Golden, J. L. Kiplinger, D. E. Morris, *J. Am. Chem. Soc.* **2005**, *127*, 682.
- [11] D. S. J. Arney, C. J. Burns, *J. Am. Chem. Soc.* **1995**, *117*, 9448.
- [12] a) H. J. Wasserman, A. J. Zozulin, D. C. Moody, R. R. Ryan, *J. Organomet. Chem.* **1983**, *254*, 305; b) W. J. Evans, K. J. Forrestal, J. W. Ziller, *Angew. Chem.* **1997**, *109*, 798; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 774; M. Conejo, J. S. Parry, E. Carmona, M. Schultz, J. G. Brennann, S. M. Beshouri, R. A.

- Andersen, R. D. Rogers, S. Coles, M. Hursthouse, *Chem. Eur. J.* **1999**, *5*, 3000.
- [13] a) A. J. Zozulin, D. C. Moody, R. R. Ryan, *Inorg. Chem.* **1982**, *21*, 3083; b) F. A. Cotton, D. O. Marler, W. Schwotzer, *Inorg. Chem.* **1984**, *23*, 4211; c) P. B. Hitchcock, M. F. Lappert, D.-S. Liu, *J. Organomet. Chem.* **1995**, *488*, 241; d) P. Roussel, P. B. Hitchcock, N. Tinker, P. Scott, *Chem. Commun.* **1996**, 2053; e) P. Roussel, P. Scott, N. D. Tinker, *J. Alloys Compd.* **1998**, *271–273*, 150; f) P. B. Duval, C. J. Burns, W. E. Buschmann, D. L. Clark, D. E. Morris, B. L. Scott, *Inorg. Chem.* **2001**, *40*, 5491; g) I. Korobkov, S. Gambarotta, G. P. A. Yap, L. Thompson, P. J. Hay, *Organometallics* **2001**, *20*, 5440; h) L. Salmon, P. Thuéry, S. Miyamoto, T. Yamato, M. Ephritikhine, *Polyhedron* **2006**, *25*, 2439; i) J. Maynadié, J.-C. Berthet, P. Thuéry, M. Ephritikhine, *Organometallics* **2007**, *26*, 2623; j) G. Nocton, F. Burdet, J. Pécaut, M. Mazzanti, *Angew. Chem.* **2007**, *119*, 7718; *Angew. Chem. Int. Ed.* **2007**, *46*, 7574; k) C. P. Larch, F. G. N. Cloke, P. B. Hitchcock, *Chem. Commun.* **2008**, 82; l) E. J. Schelter, R. Wu, B. L. Scott, J. D. Thompson, D. E. Morris, J. L. Kiplinger, *Angew. Chem.* **2008**, *120*, 3035; *Angew. Chem. Int. Ed.* **2008**, *47*, 2993.
- [14] a) C. W. Eigenbrot, Jr., K. N. Raymond, *Inorg. Chem.* **1981**, *20*, 1553; b) I. A. Guzei, A. G. Baboul, G. P. A. Yap, A. L. Rheingold, H. B. Schlegel, C. H. Winter, *J. Am. Chem. Soc.* **1997**, *119*, 3387; c) J. E. Cosgriff, G. B. Deacon, *Angew. Chem.* **1998**, *110*, 298; *Angew. Chem. Int. Ed.* **1998**, *37*, 286; d) G. B. Deacon, C. M. Forsyth, A. Gitlits, R. Harika, P. C. Junk, B. W. Skelton, A. H. White, *Angew. Chem.* **2002**, *114*, 3383; *Angew. Chem. Int. Ed.* **2002**, *41*, 3249; e) O. M. El-Kadri, M. J. Heeg, C. H. Winter, *J. Organomet. Chem.* **2009**, *694*, 3902.
- [15] F. G. N. Cloke, P. B. Hitchcock, *J. Am. Chem. Soc.* **2002**, *124*, 9352.