DOI: 10.1002/anie.201208686

Heterometallic Complexes

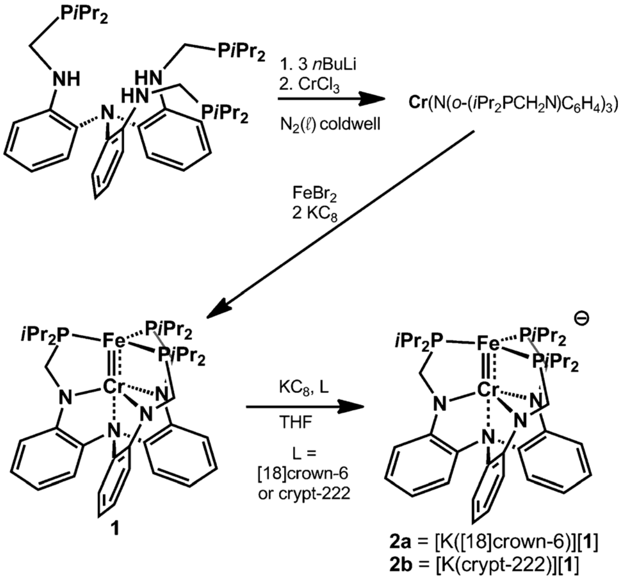
Multiple Metal–Metal Bonds in Iron–Chromium Complexes[**]

P. Alex Rudd, Shengsi Liu, Nora Planas, Eckhard Bill, Laura Gagliardi, and Connie C. Lu**

Dedicated to Professor Karl Wieghardt

Multiple metal–metal bonds are uncommon in heterobimetallic complexes.[1] Rare examples of heterobimetallics with short metal–metal bonds include [TiRh(OCMe$_2$CH$_2$PPh$_2$)$_3$],[2] [CoZr(MesNP*i*Pr$_2$)$_3$(thf)],[3] and [CrMo(O$_2$CCH$_3$)$_4$].[4] We report the first isolable examples of metal–metal multiple bonds between two different first-row transition metals, namely iron and chromium.[5] We have conducted spectroscopic and theoretical investigations of two Fe–Cr coordination complexes to understand the nature of these unprecedented metal–metal bonds.

We previously reported a dinucleating, double-decker ligand that was designed to enable the synthesis of heterobimetallic complexes in a modular manner.[6] To prepare the iron–chromium complexes herein, the ligand was first deprotonated and metalated with CrCl$_3$. The resulting monometallic species, [Cr(N(*o*-(*i*Pr$_2$PCH$_2$N)C$_6$H$_4$)$_3$)], which was confirmed by combustion analysis, acts as a metalloligand in a subsequent metalation (Scheme 1). For example, reaction of [Cr(N(*o*-(*i*Pr$_2$PCH$_2$N)C$_6$H$_4$)$_3$)] with FeBr$_2$ and two equiv KC$_8$ resulted in a color change from dark brown to green brown within minutes. The product, [FeCr(N(*o*-(*i*Pr$_2$PCH$_2$N)C$_6$H$_4$)$_3$)] (**1**), is paramagnetic, and its proposed structure has been confirmed by X-ray crystallography.



Scheme 1. Synthesis of iron–chromium complexes.

The redox properties of **1** were examined by electrochemical methods. The cyclic voltammogram (CV) of **1** (Supporting Information, Figure S3) reveals a rich redox profile, including: 1) a reversible reduction at −2.33 V; 2) a reversible oxidation at −1.32 V; and 3) a second, quasi-reversible oxidation at −0.62 V (versus FeCp$_2$/FeCp$_2^+$, 0.1 M N(*n*Bu)$_4$PF$_6$ in THF, 10 mV s^{-1}). In contrast, the redox profile of the related iron–alane adduct, [FeAl(N(*o*-(*i*Pr$_2$PCH$_2$N)C$_6$H$_4$)$_3$)], is much more limited.[6] It is characterized by a single reversible event, a reduction at −2.08 V (vs FeCp$_2$/FeCp$_2^+$).

Reduction of **1** with 1 equiv KC$_8$ generates a red-brown solution of paramagnetic [K(solv)$_n$][**1**] (**2**). Alternatively, **2** can be directly prepared by mixing [Cr(N(*o*-(*i*Pr$_2$PCH$_2$N)C$_6$H$_4$)$_3$)] with FeBr$_2$ and three equiv KC$_8$. Encapsulation of the potassium ion with either [18]crown-6 or crypt-222 enabled the isolation of crystalline [K([18]crown-6)][**1**] (**2a**) or [K(crypt-222)][**1**] (**2b**), respectively.

X-ray diffraction studies were conducted on single crystals of **1** and **2b** (Figure 1; Supporting Information, Table S1). The

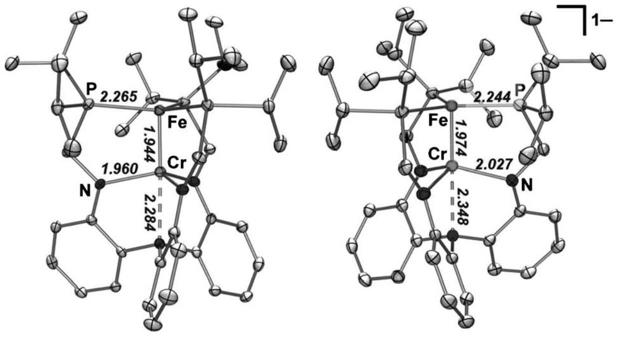


Figure 1. Solid-state structures of **1** (left) and **2b** (right). Ellipsoids set at 40% probability; H atoms and K(crypt-222) were omitted for clarity. For **1**, one of two independent molecules is shown with average bond distances [Å].

---

[*] P. A. Rudd, S. Liu, Dr. N. Planas, Prof. Dr. L. Gagliardi, Prof. Dr. C. C. Lu
Department of Chemistry and Supercomputing Institute
University of Minnesota
207 Pleasant St SE, Minneapolis, MN 55455 (USA)
E-mail: clu@umn.edu
Dr. E. Bill
Max Planck Institut für chemische Energiekonversion
Stiftstrasse 34–36, 45470 Mülheim an der Ruhr (Germany)

[**] Adam D. Miller (NSF-LANDO) gave synthetic assistance. We thank Andy Fielding for help with EPR spectra, and Prof. J. Ellis and Prof. D. Leopold for helpful discussions. We thank Dr. Victor G. Young, Jr. for sharing his crystallographic expertise. This work was funded by the University of Minnesota and the ACS PRF. The computational research (L.G., S.L., N.P.) was supported by the Office of Basic Energy Sciences, Heavy Element Chemistry program (USDOE/DE-SC002183).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201208686.

solid-state structures revealed surprisingly short Fe–Cr bond lengths of 1.94 Å in **1** and 1.97 Å in **2b**. Based on a CSD search,[7] the only shorter metal–metal bonds are found in the large family of dichromium compounds with quadruple and quintuple formal bond orders,[8] and in a handful of divanadium compounds.[9] A multiply bonded diiron complex with a short Fe–Fe distance of 2.13 Å is longer relative to **1** and **2b**.[10] Indeed, complexes **1** and **2b** have the shortest M–M bond length of all heterobimetallic species in terms of absolute distance. The previous record, 2.14 Å, was reported by Greenwood, Thomas, et al. for their Co–Zr complex.[3] Our finding is a consequence of the fact that compounds **1** and **2b** are the first reported heterometallics with multiple bonds between first-row transition metals.

A better measure for comparing M–M bonds is the covalent ratio r, the ratio of the M–M bond length to the sum of covalent radii of the metals, which reveals similar values for the Co–Zr complex ($r = 0.82$),[3] **1** ($r = 0.83$), and **2b** ($r = 0.84$).[11] For comparison, the expected r value for a single bond is unity. Together, these compounds join a small group of heterobimetallics containing ultra-short M–M bonds.

The solid-state structures of **1** and **2b** revealed significant perturbations upon the addition/removal of an electron (Table 1). While **2b** is C_3-symmetric, **1** deviates slightly from three-fold symmetry, especially about the Cr center (max. $\Delta_{\text{Cr-Neq}} = 0.065$ Å, max. $\Delta_{\text{Neq-Cr-Neq}} = 6.4°$). The $\{\text{FeCr}\}^{11}$ electronic configuration of **1** should promote Jahn–Teller distortion, which is most evident in the significant splitting of the Cr d_{xy} and $d_{x^2-y^2}$ orbitals (see below). In reducing **1** to **2b**, several bonds elongate, including the Fe–Cr bond by 0.03 Å. The greatest elongations occur in the Cr–L bond distances: Cr–N_{ax} and Cr–N_{eq} increase by 0.06 and 0.07 Å, respectively. The Fe–P bond contracts by 0.02 Å from **1** to **2b**, which is consistent with a more reduced metal center in **2b** that can better backbond.

Table 1: Geometric parameters, including bond lengths [Å] and angles [°], for **1** and **2b**.

	1[a]	**2b**
Fe–Cr [Å]	1.943(1) 1.944(1)	1.974(1)
Fe–P [Å]	2.256(2), 2.265(1), 2.265(1) 2.266(2), 2.266(1), 2.270(2)	2.2444(8)
Cr–N_{eq} [Å]	1.925(3), 1.964(3), 1.990(3) 1.948(3), 1.962(3), 1.969(3)	2.027(2)
Cr–N_{axial} [Å]	2.275(3) 2.292(3)	2.348(4)
P-Fe-P [°]	118.06, 118.78, 121.37(6) 118.08, 118.34, 121.05(6)	119.838(4)
N_{eq}-Cr-N_{eq} [°]	112.2, 116.4, 118.6(1) 113.5, 114.2, 119.3(1)	113.68(5)
Fe-Cr-N_{axial} [°]	176.36(7) 178.71(7)	180

[a] Two sets of values are given for the two unique molecules in the asymmetric unit.

Based on these structural changes, the one-electron reduction of **1** is localized primarily at chromium. Therefore, we tentatively propose the formal oxidation states of Fe^0/Cr^{III} for **1** and Fe^0/Cr^{II} for **2b**. Unfortunately, there are few existing coordination complexes that can corroborate our assignment of oxidation states. The most relevant complexes we could find for comparison are a pair of low-spin iron complexes, $[\text{Fe}(\text{N}_2)(\text{Si}(o\text{-}(\text{P}i\text{Pr}_2)\text{C}_6\text{H}_4)_3]$ and $[\text{Na}([12]\text{crown-4})_2][\text{Fe}(\text{N}_2)(\text{Si}(o\text{-}(\text{P}i\text{Pr}_2)\text{C}_6\text{H}_4)_3]$, with formal oxidation states of Fe^I and Fe^0, respectively.[12] The average Fe–P bond lengths in **1** and **2b** are between those reported for this Fe^I (2.29 Å) and Fe^0 (2.20 Å) pair. Based on these values, the Fe oxidation states in **1** and **2b** would be consistent with Fe^0, but also Fe^I. Likewise, the anionic chromium triamidoamine complex, $[\text{Cr}(\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)_3)]^-$, possesses similar Cr^{II}-N_{eq} (2.04 Å) bond lengths to **2b**, although the neutral analogue has admittedly shorter Cr^{III}–N_{eq} (1.88 Å) bonds than **1**.[13]

The electronic structures of the Fe–Cr complexes have been elucidated by spectroscopic methods. Compound **1** has an $S = \frac{1}{2}$ ground state based on the observation of a broad, axial signal in the EPR spectrum with $g = (1.944, 1.935$, and $1.759)$ and $g_{\text{ave}} = 1.88$ (Supporting Information, Figure S5; 80 % based on spin quantification). The magnetic moment of **2a** is 2.65 μ_B and is temperature-independent from 20 to 290 K (Supporting Information, Figure S7). Thus, complex **2a** has an $S = 1$ ground state that is energetically well-isolated with $g_{\text{ave}} = 1.91$. The g_{ave} values less than 2.0 are more consistent with unpaired spin density residing at chromium opposed to iron (see below).[14]

Complexes **1**, **2a**, and **2b** have been further investigated by Mössbauer spectroscopy (Figure 2). The isomer shifts measured for **1**, **2a**, and **2b** are all quite similar with values of 0.25, 0.26, and 0.29 mm s^{-1}, respectively (Supporting Information, Figures S8–S10), which seems to indicate that the iron oxidation state remains relatively constant in **1** and **2**. The actual isomer shift values are consistent with Fe^0,[5a,12,15] but a definitive assignment is problematic because of: 1) the dearth of non-carbonyl Fe^0 species suitable for comparison and the consequent lack of appropriate Mössbauer parameters; and 2) the general loss of isomer shift correlation for low oxidation states of iron that result from the strong compensatory effects of Fe–L π-back-bonding.[16]

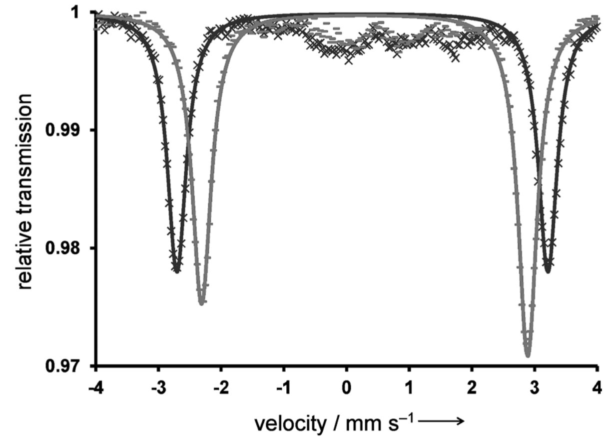


Figure 2. Mössbauer spectra overlay of **1** (dark gray) and **2b** (light gray) at 80 K. The major species were fitted with $\delta = 0.25$ and $\Delta E_Q = 5.92$ mm s^{-1} for **1**, and $\delta = 0.29$ and $\Delta E_Q = 5.20$ mm s^{-1} for **2b**.

Most remarkably, these complexes exhibit unusually large quadrupole splittings $|\Delta E_Q|$ of 5.92, 5.04, and 5.20 mm s^{-1} for **1**, **2a**, and **2b**, respectively. Quadrupole splittings of this magnitude have only been previously observed for high-valent iron nitrides, that is, Fe≡N, in pseudotetrahedral ligand fields.[17] The large $|\Delta E_Q|$ value was attributed to the strong axial electric field gradient (EFG) created by the placement of a hard nitride near the low-spin iron center.[17a] Using a ligand field rationale, the main contributor to the EFG is the high charge density in the *xy*-plane that arises from the localization of iron d-electrons in the d_{xy} and $d_{x^2-y^2}$ orbitals.[17,18] The localization of d-electrons along a Cartesian axis or plane is difficult to visualize for **1** and **2** because their d-electrons are highly delocalized between the two metal centers (see below). A strong covalent contribution to the EFG is clearly present in **1** and **2**, wherein the nitride is substituted by a hard chromium atom in a highly covalent Fe≡X linkage. The formal oxidation states within the Fe≡X linkages are practically opposite in nature: $Fe^{4+}{\equiv}N^{3-}$ versus $Fe^0{\equiv}Cr^{3+}$. To our knowledge, this is the first report of exceedingly large quadrupole splittings (> 5 mm s^{-1}) for any low-valent iron species.

To gain more insights into the electronic structure of compounds **1** and **2**, we turned to theoretical calculations using both density functional theory (DFT) and multi-configurational quantum chemical methods (CASSCF/CASPT2). Geometry optimizations were performed at the DFT level for several possible spin states of each complex. The DFT and CASPT2 energies confirm the doublet and triplet ground states of **1** and **2**, respectively; the optimized structures of the ground states are reasonably close to the experimental structures (Supporting Information, Tables S2–S4). A qualitative MO diagram of the d-orbital manifold is shown in Figure 3 with the dominating electronic configurations of **1** (58%) and **2** (60%) (CASSCF). The d-orbital manifold is comprised of delocalized σ/σ* and π/π* MOs as well as localized $d_{x^2-y^2}/d_{xy}$ orbitals. No δ-bonding is evident. Though **1** and **2** each have a formal Fe–Cr bond order of 3.0 (from occupation of 1σ + 2π MOs), the effective bond order,[19] which takes into account the partial occupation of the σ* and π* orbitals, is lower at 2.21 for **1** and 2.30 for **2** (Supporting Information, Figures S14 and S15).

The calculated spin densities corroborate that the reduction is chromium-based in that the spin density at Cr increases by exactly one electron from **1** to **2** (Supporting Information, Table S6). For **1** and **2**, the spin-density values affirm the proposed oxidation states of Fe^0/Cr^{III} and Fe^0/Cr^{II}, respectively, with the overall spin density residing at Cr. The calculations also show that the MOs are asymmetrically delocalized over the Fe–Cr unit, as might be expected given the disparity in d-electron count between these two metals. A decomposition analysis of the MOs reveals that the d-electron count in **2** is Fe d^8 and Cr d^4, which supports the proposed oxidation states of Fe^0 and Cr^{II}, respectively (Supporting Information, Table S8). The situation for **1** is more complicated, with the resulting electron count favoring non-integer oxidation states, namely Fe(0.5)–Cr(2.5), which may be a more accurate electronic picture for **1** (Supporting Information, Table S9).

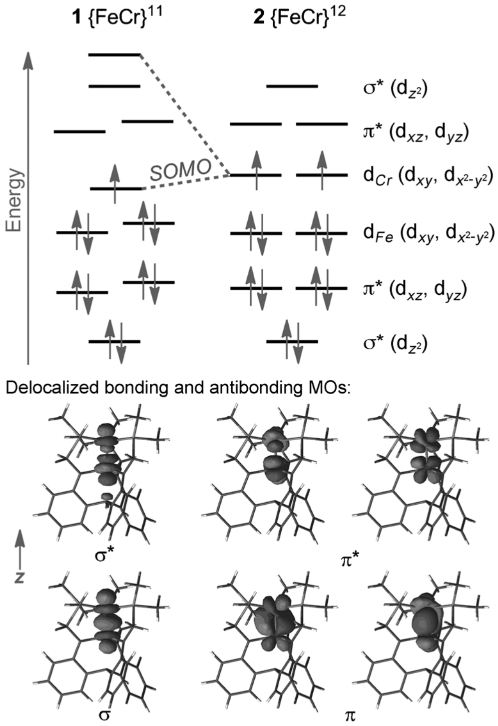


Figure 3. Qualitative MO diagram of the d-orbital manifold for **1** and **2**, shown with the dominant electronic configurations (CASSCF).

Compounds **1** and **2** belong to a rare class of formally zero-valent iron complexes with a ligand scaffold comprising three equatorial phosphine donors and a variable axial donor that has included B,[20] Al,[6] P,[21] and Si^-[12,22] and is now extended to Cr. The $Fe^0/Fe(-1)$ redox potential is nearly identical for the Lewis pairs Fe→B and Fe→Al, but is not observed for $Fe{-}Si^-$ or Fe≡Cr. Instead, $Fe{-}Si^-$ and Fe≡Cr each have two reversible oxidations, which are not observed in the Lewis pairs. Current efforts are directed at completing the four-member Fe–Cr redox family and evaluating their competence in multi-electron reactivity.[23]

Received: October 30, 2012

Keywords: chromium · heterometallic complexes · iron · metal–metal bonds · multiple bonds

[1] a) F. A. Cotton, C. A. Murillo, R. A. Walton, *Multiple Bonds Between Metal Atoms*, Springer Science, New York, **2005**; b) J. P. Collman, R. Boulatov, *Angew. Chem.* **2002**, *114*, 4120–4134; *Angew. Chem. Int. Ed.* **2002**, *41*, 3948–3961.
[2] L. M. Slaughter, P. T. Wolczanski, *Chem. Commun.* **1997**, 2109–2110.
[3] B. P. Greenwood, G. T. Rowe, C.-H. Chen, B. M. Foxman, C. M. Thomas, *J. Am. Chem. Soc.* **2010**, *132*, 44–45.
[4] C. D. Garner, R. G. Senior, T. J. King, *J. Am. Chem. Soc.* **1976**, *98*, 3526–3529.
[5] a) H. M. Nagarathna, P. A. Montano, V. M. Naik, *J. Am. Chem. Soc.* **1983**, *105*, 2938–2943; b) H. Lu, B. Zhao, J. R. Lombardi, *Chem. Phys. Lett.* **2003**, *376*, 49–54.

[6] P. A. Rudd, S. Liu, L. Gagliardi, V. G. Young, C. C. Lu, *J. Am. Chem. Soc.* **2011**, *133*, 20724 – 20727.

[7] F. Allen, *Acta Crystallogr. Sect. B* **2002**, *58*, 380 – 388.

[8] a) C.-W. Hsu, J.-S. K. Yu, C.-H. Yen, G.-H. Lee, Y. Wang, Y.-C. Tsai, *Angew. Chem.* **2008**, *120*, 10081 – 10084; *Angew. Chem. Int. Ed.* **2008**, *47*, 9933 – 9936; b) K. A. Kreisel, G. P. A. Yap, O. Dmitrenko, C. R. Landis, K. H. Theopold, *J. Am. Chem. Soc.* **2007**, *129*, 14162 – 14163; c) Y.-C. Tsai, C.-W. Hsu, J.-S. K. Yu, G.-H. Lee, Y. Wang, T.-S. Kuo, *Angew. Chem.* **2008**, *120*, 7360 – 7363; *Angew. Chem. Int. Ed.* **2008**, *47*, 7250 – 7253; d) A. Noor, G. Glatz, R. Müller, M. Kaupp, S. Demeshko, R. Kempe, *Nat. Chem.* **2009**, *1*, 322 – 325; e) T. Nguyen, A. D. Sutton, M. Brynda, J. C. Fettinger, G. J. Long, P. P. Power, *Science* **2005**, *310*, 844 – 847; f) G. La Macchia, G. Li Manni, T. K. Todorova, M. Brynda, F. Aquilante, B. O. Roos, L. Gagliardi, *Inorg. Chem.* **2010**, *49*, 5216 – 5222; g) G. La Macchia, F. Aquilante, V. Veryazov, B. O. Roos, L. Gagliardi, *Inorg. Chem.* **2008**, *47*, 11455 – 11457; h) M. Brynda, L. Gagliardi, P.-O. Widmark, P. P. Power, B. O. Roos, *Angew. Chem.* **2006**, *118*, 3888 – 3891; *Angew. Chem. Int. Ed.* **2006**, *45*, 3804 – 3807.

[9] a) F. A. Cotton, E. A. Hillard, C. A. Murillo, X. Wang, *Inorg. Chem.* **2003**, *42*, 6063 – 6070; b) F. A. Cotton, E. A. Hillard, C. A. Murillo, *J. Am. Chem. Soc.* **2003**, *125*, 2026 – 2027.

[10] L. Fohlmeister, S. Liu, C. Schulten, B. Moubaraki, A. Stasch, J. D. Cashion, K. S. Murray, L. Gagliardi, C. Jones, *Angew. Chem.* **2012**, *124*, 8419 – 8423; *Angew. Chem. Int. Ed.* **2012**, *51*, 8294 – 8298.

[11] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, NY, **1960**.

[12] Y. Lee, N. P. Mankad, J. C. Peters, *Nat. Chem.* **2010**, *2*, 558 – 565.

[13] A. C. Filippou, S. Schneider, G. Schnakenburg, *Inorg. Chem.* **2003**, *42*, 6974 – 6976.

[14] A. T. Casey, S. Mitra in *Theory and Applications of Molecular Paramagnetism* (Eds.: E. A. Boudreaux, L. N. Mulay), Wiley, New York, **1976**, pp. 135 – 255.

[15] a) R. Greatrex, N. N. Greenwood, *Discuss. Faraday Soc.* **1969**, *47*, 126 – 135; b) R. H. Havlin, N. Godbout, R. Salzmann, M. Wojdelski, W. Arnold, C. E. Schulz, E. Oldfield, *J. Am. Chem. Soc.* **1998**, *120*, 3144 – 3151.

[16] P. Gütlich, E. Bill, A. X. Trautwein, *Mössbauer Spectroscopy and Transition Metal Chemistry: Fundamentals and Applications*, Springer, Berlin, **2011**.

[17] a) M. P. Hendrich, W. Gunderson, R. K. Behan, M. T. Green, M. P. Mehn, T. A. Betley, C. C. Lu, J. C. Peters, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 17107 – 17112; b) C. Vogel, F. W. Heinemann, J. Sutter, C. Anthon, K. Meyer, *Angew. Chem.* **2008**, *120*, 2721 – 2724; *Angew. Chem. Int. Ed.* **2008**, *47*, 2681 – 2684; c) J. J. Scepaniak, C. S. Vogel, M. M. Khusniyarov, F. W. Heinemann, K. Meyer, J. M. Smith, *Science* **2011**, *331*, 1049 – 1052.

[18] J. M. Smith, D. Subedi, *Dalton Trans.* **2012**, *41*, 1423 – 1429.

[19] a) M. Brynda, L. Gagliardi, B. O. Roos, *Chem. Phys. Lett.* **2009**, *471*, 1 – 10; b) B. O. Roos, A. C. Borin, L. Gagliardi, *Angew. Chem.* **2007**, *119*, 1491 – 1494; *Angew. Chem. Int. Ed.* **2007**, *46*, 1469 – 1472.

[20] M.-E. Moret, J. C. Peters, *Angew. Chem.* **2011**, *123*, 2111 – 2115; *Angew. Chem. Int. Ed.* **2011**, *50*, 2063 – 2067.

[21] a) L. D. Field, R. W. Guest, K. Q. Vuong, S. J. Dalgarno, P. Jensen, *Inorg. Chem.* **2009**, *48*, 2246 – 2253; b) L. D. Field, R. W. Guest, P. Turner, *Inorg. Chem.* **2010**, *49*, 9086 – 9093.

[22] a) Y. Lee, J. C. Peters, *J. Am. Chem. Soc.* **2011**, *133*, 4438 – 4446; b) N. P. Mankad, M. T. Whited, J. C. Peters, *Angew. Chem.* **2007**, *119*, 5870 – 5873; *Angew. Chem. Int. Ed.* **2007**, *46*, 5768 – 5771.

[23] a) C. M. Thomas, *Comments Inorg. Chem.* **2011**, *32*, 14 – 38; b) D. W. Stephan, *Coord. Chem. Rev.* **1989**, *95*, 41 – 107; c) N. Wheatley, P. Kalck, *Chem. Rev.* **1999**, *99*, 3379 – 3420; d) R. M. Bullock, C. P. Casey, *Acc. Chem. Res.* **1987**, *20*, 167 – 173.