Highlight Review

Recent Progress in the Chemistry of Quintuple Bonds

Yi-Chou Tsai* and Chih-Chieh Chang

(Received September 11, 2009; CL-098009)

Abstract

Recent developments in the new field of isolable quintuple bonded complexes of group 6 transition elements, Cr and Mo, are covered in this review. The geometrical preference of the metal–metal quintuple bonded complexes, quintuple bond lengths, bonding features, and preliminary reactivity of quintuple bonds are presented.

♦ Introduction

In main group chemistry, atomic orbitals in general can interact in a σ or π fashion, with the highest possible bond order of 3, a combination of one σ bond and two π bonds. When two transition-metal atoms interact, the most important interactions are between their outermost d orbitals. These d orbitals can combine to form not only σ and π orbitals, but also δ orbitals. The first isolable compound featuring a δ bond was the first quadruple bonded dirhenium compound, $[Re_2Cl_8]^{2-}$, discovered by Cotton et al. in 1964.[1,2] In the decades since, hundreds of compounds with formally quadruply bonded transition-metal atoms have been synthesized and fully characterized.[3] Notably, all these compounds exhibit a diagnostic *tetragonal* geometrical characteristic and 1σ, 2π, and 1δ bonding features.

During the past 40 years since the first quadruple metal–metal bond was recognized, the quest for complexes with even higher bond orders has continued. For example, the formally sextuply bonded diatomic Cr_2, Mo_2, and W_2 molecules, featuring 2σ, 2π, and 2δ bonds, have been probed from matrix isolation IR and UV–vis spectroscopic studies.[4–14] The interatomic separations in Cr_2 and Mo_2 are 1.68[4] and 1.93 Å,[7] respectively.

From the synthetic point of view, however, it is impractical to prepare these sextuple bonded diatomic molecules, mainly because they can only exist at low pressure and low temperature. As a result, it is very difficult to explore these simple molecules. On the contrary, the preparation of complexes featuring the metal–metal quintuple bonds seems feasible. On the theoretical side, Hoffmann et al. in 1979 first proposed that compounds M_2L_6 of D_{3h} symmetry could have metal–metal quintuple bonds.[15] Since then, there has been considerable theoretical work discussing the existence of the quintuple bonded dinuclear complexes and their possible geometry in the literature.[16–20] It is concluded that in order to achieve the synthesis of complexes featuring metal–metal quintuple bonds, the number of ligands must be minimized, since their binding reduces the number of valence orbitals available to form metal–metal bonds.

This review covers the chemistry of the metal–metal quintuple bonds, which has been centered on group 6 elements so far, mainly Cr and Mo. We also contribute to this field and report several quintuple bonded dichromium and dimolybdenum complexes supported by ligands with nitrogen donors and they all possess very short Cr–Cr bond lengths.

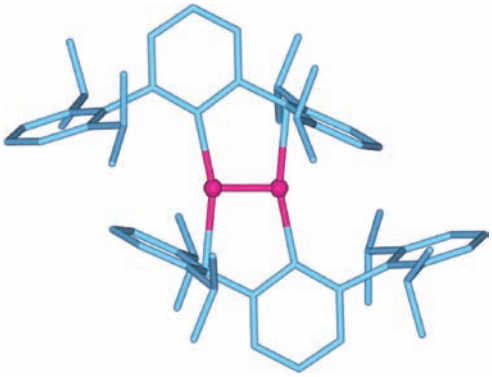


Figure 1. Molecular structure of complex **1**, where the Cr–Cr bond length is 1.8351(4) Å (color code: plum = Cr, turquoise = C).

♦ The Advent of Cr–Cr Quintuple Bonds

The landmark discovery for quintuple-bond chemistry was achieved by Power et al., who characterized the first isolable quintuple bonded dichromium complex, Ar′CrCrAr′ (**1**) (where Ar′ is the bulky 2,6-(2,6-*i*-Pr_2-C_6H_3)$_2$$C_6H_3$ ligand) depicted in Figure 1.[21] In addition to experimental data, the Cr–Cr quintuple bond in complex **1** was further corroborated by sophisticated computations.[22–26] It is however interesting to note that the Cr–Cr bond length of **1** is 1.8351(4) Å, which is slightly longer than the "supershort" Cr–Cr quadruple bond length (1.828(2) Å) in the paddlewheel complex $Cr_2(\mu$-η^2-2-MeO-5-$MeC_6H_3)_4$.[27] Though it is not clear as to the *long* Cr–Cr quintuple bond length, the close approach of one of the C_6H_3-2,6-*i*-Pr_2 substituents of each terphenyl ligand to a Cr atom.[21] The Cr–C(ipso) distance of the interacting flanking aryl rings is 2.294(1) Å. It is noteworthy that Frenking[22] has predicted theoretical controversies about the quintuple bond character in Ar′CrCrAr′ because of the trans-bent structure of the C–Cr–Cr–C entity, contrary to the trans-linear arrangement expected for a quintuple bond. According to Landis and Weinhold,[18] the origin of trans-bent geometries in quintuply bonded molecules is the preference of a strong σ bond from sd_{z^2} hybridization. Bending does not destroy the δ bond: the hybridization scheme proposed even leads to the creation of one more favorable δ bond via sd^4 hybridization besides a pure δd orbital. Moreover, on the basis of CASPT2 calculations on a model compound PhCrCrPh, a tiny energy difference between the trans-linear and the trans-bent structure has been ob-

Prof. Yi-Chou Tsai, Mr. Chih-Chieh Chang*
National Tsing Hua University, 101 Sec 2, Guang-Fu Road, Hsinchu 30013, Taiwan
E-mail: yictsai@mx.nthu.edu.tw

tained.[23] The preference for the latter in the experimental compound is ascribed to secondary interactions of Cr with the true ligand. A bond dissociation energy of 76 kcal mol^{-1} is computed, which is about twice as large as for Cr_2 molecule with a formal sixtuple bond. This counterintuitive result has been mainly ascribed to the destabilizing 4s–4s interactions in the dimer. From supplementary DFT calculations certain bond weakening interactions between Cr and the flanking aryl groups have been detected.[23] In summary, the Cr–Cr bond length found in Ar′CrCrAr′ is not the shortest possible for this type of system, which is an exciting perspective.

The effects of different terphenyl ligand substituents on the quintuple Cr–Cr bonding in arylchromium(I) dimers stabilized by bulky terphenyl ligands (Ar) were also investigated.[28] A series of complexes, ArCrCrAr (**2**–**4**; Ar = C_6H_2-2,6-(C_6H_3-2,6-*i*-Pr_2)$_2$-4-R, where R = $SiMe_3$, OMe, and F), were synthesized and structurally characterized. Their X-ray crystal structures also display similar trans-bent C(ipso)–Cr–Cr–C(ipso) cores with short Cr–Cr distances that range from 1.8077(7) to 1.831(2) Å. The data show that the changes induced in the Cr–Cr bond length by the different substituents R in the para positions of the central aryl ring of the terphenyl ligand are probably a result of packing rather than electronic effects.

♦ *Ultra Short Cr–Cr Quintuple Bonds*

Since the Cr–Cr sextuple bond lengths of laser-evaporated Cr_2 and the Cr_2 generated via pulsed photolysis of $Cr(CO)_6$ are about 1.68 Å[4] and 1.71 Å,[29] reasonable Cr–Cr quintuple bond length should fall into the range of 1.84 Å (complex **1**) and 1.68 Å. Efforts were undertaken to find quintuple bonded complexes that have metal–metal bond lengths within this range. In this regard, the first and very stimulating report by Theopold and Landis et al. was the dichromium complex supported by 1,4-diazadiene (μ-η^2-$^{H}L^{iPr}$)$_2$$Cr_2$ [**5**, $^{H}L^{iPr}$ = *N*,*N*′-bis(2,6-diisopropylphenyl)-1,4-diazadiene] (Figure 2), in which the Cr–Cr bond length is 1.8028(9) Å.[30] Compound **5** was prepared by subsequent addition of an excess of sodium and a trivalent chromium(III) chloride to an encumbering α-diimine giving rise to a chromium monochloride which was then reduced by potassium graphite. The problem with the use of α-diimines as ligands is their redox ambiguity, making it difficult to conclude the oxidation state of the chromium atoms.[30] However, DFT calculations on model compound **5** indicate that one of the five occupied Cr–

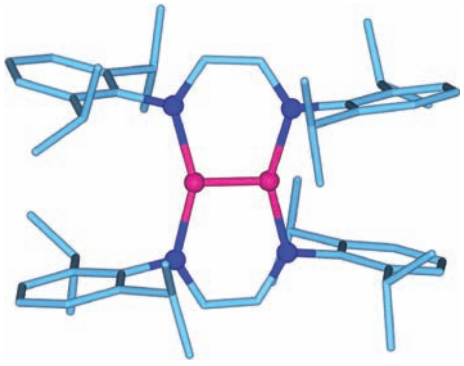


Figure 2. Molecular structure of **5**, where the Cr–Cr bond length is 1.8028(9) Å (color code: plum = Cr, blue = N, turquoise = C).

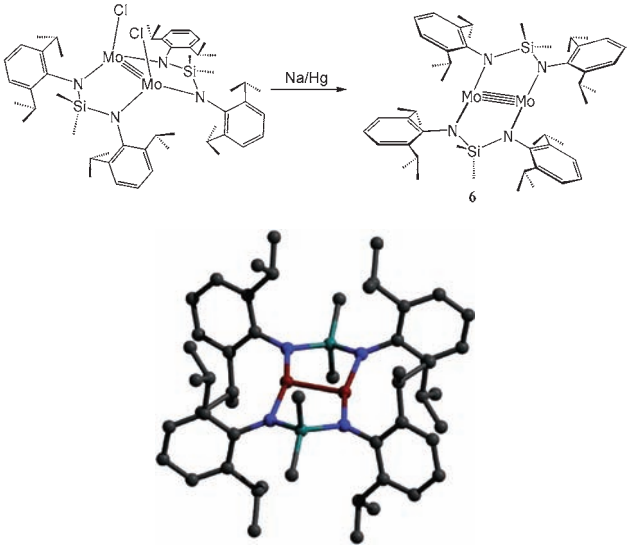


Figure 3. Synthesis and molecular structure of **6**, where Mo–Mo bond length is 2.1784(12) Å (color code: dark red = Mo, teal = Si, blue = N, gray = C).

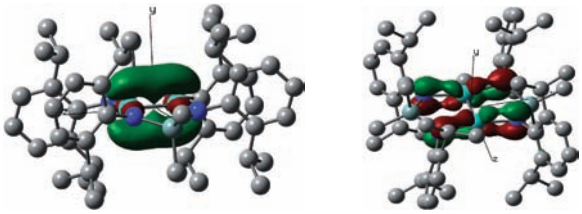


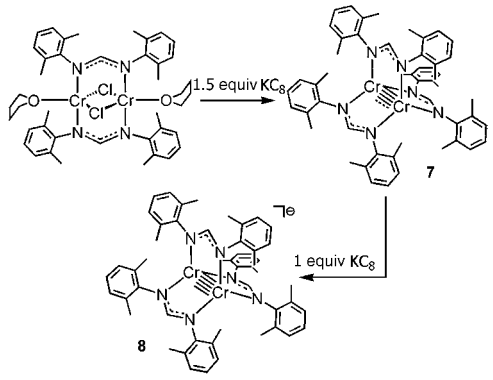
Figure 4. The contour plots of HOMO (left) and HOMO−11 (right) of compound **6**.

Cr bonding orbitals, the HOMO−2 dδ, is highly delocalized over the ligand. It should be noted that the metal–metal bond order of **5** is controversial. A bond order of 4.28 (a Cr–Cr quintuple bond) is obtained based on the DFT level including delocalization effects, whereas the Cr–Cr bond of **5** is considered a quadruple bond because a bond order of 3.43 is obtained at multiconfigurational level of theory.[31]

We recently reported a quadruply bonded dimolybdenum complex supported by only two diamido ligands, Mo_2[μ-η^2-Me_2Si(N-2,6-*i*-$Pr_2C_6H_3$)$_2$]$_2$ (**6**), which is obtained from reduction of the triply bonded *syn*-Mo_2Cl_2[μ-η^2-Me_2Si(N-2,6-*i*-$Pr_2C_6H_3$)$_2$]$_2$ (Figure 3).[32] The Mo–Mo quadruple bond of **6** is corroborated by DFT calculations. It is interesting to note that computations indicate presence of strong N–Mo(d_{xy}) π interactions (HOMO−11), which consequently results in no δ bonding between two d_{xy} orbitals (Figure 4). Accordingly, the group 6 metal–metal quintuple bonded complexes are expected if the said diamido ligands are replaced by the monoanionic amidinates. Moreover, inspired by complexes **5** and **6**, and the potential of three-atomic bridging amidinato ligands to accommodate short metal–metal bond lengths in amidinate-bridged paddlewheel compounds of M_2^{4+} units, we set out to synthesize quintuply bonded homobimetallic compounds stabilized by such three-atomic bridging ligands.

Reduction of the dichromium bis(amidinate) dichloride complex, (Cr[THF])$_2$(μ-Cl)$_2$[μ-η^2-(Ar^{Xyl}NC(H)NAr^{Xyl})]$_2$ [THF = tetrahydrofuran, Ar^{Xyl} = 2,6-$C_6H_3(CH_3)_2$],[33] in which

Published on the web (Advance View) October 31, 2009; doi:10.1246/cl.2009.1122



Scheme 1. Synthesis of compounds **7** and **8**.

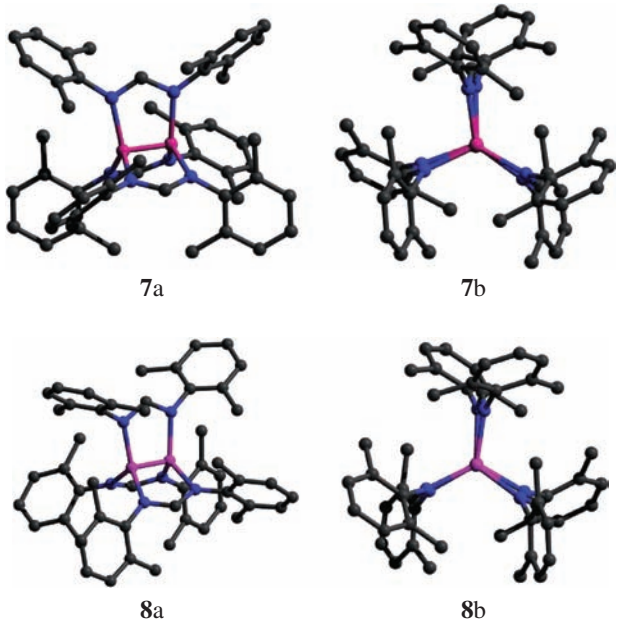


Figure 5. Molecular structures of **7** (top) and **8** (bottom) viewed (a) normal to and (b) along the Cr–Cr axis, where the Cr–Cr bond length is 1.8169(7) (**7**) and 1.7397(9) Å (**8**), respectively (color code: plum = Cr, blue = N, gray = C).

the Cr–Cr distance is 2.612(1) Å, with KC_8 interestingly engendered the formation of a mixed-valence dichromium tris(amidinate) compound **7** (Scheme 1).[34] Compound **7** is paramagnetic and possesses one unpaired electron. The X-ray structure of **7** (Figure 5) displays two Cr atoms surrounded by three amidinates, and it is interesting to note that its geometry significantly deviates from D_3 symmetry. Low-temperature EPR spectrum of **7** displays axial symmetry, suggesting that the unpaired electron resides in an orbital perpendicular to the z axis, namely, $d_{x^2-y^2}$ or d_{xy}. Moreover, DFT calculations indicate that SOMO has mostly metal $d_{x^2-y^2}$ character. Consequently, fivefold bonding between two Cr atoms, arising from a $\sigma^2\pi^4\delta^3$ configuration for the Cr_2 core is therefore implied. Although contributions from packing forces can not be completely ignored,[35] the structural distortion of **7** is essentially due to the rare Jahn–Teller effect in a dinuclear complex, a consequence of the nondegeneracy of SOMO and SOMO−1.[36,37] The formal bond order of the Cr–Cr bond is therefore 4.5, and the metal–metal bond length of 1.8169(7) Å for **7** is significantly shorter than the Cr–Cr quintuple bond length of **1**.

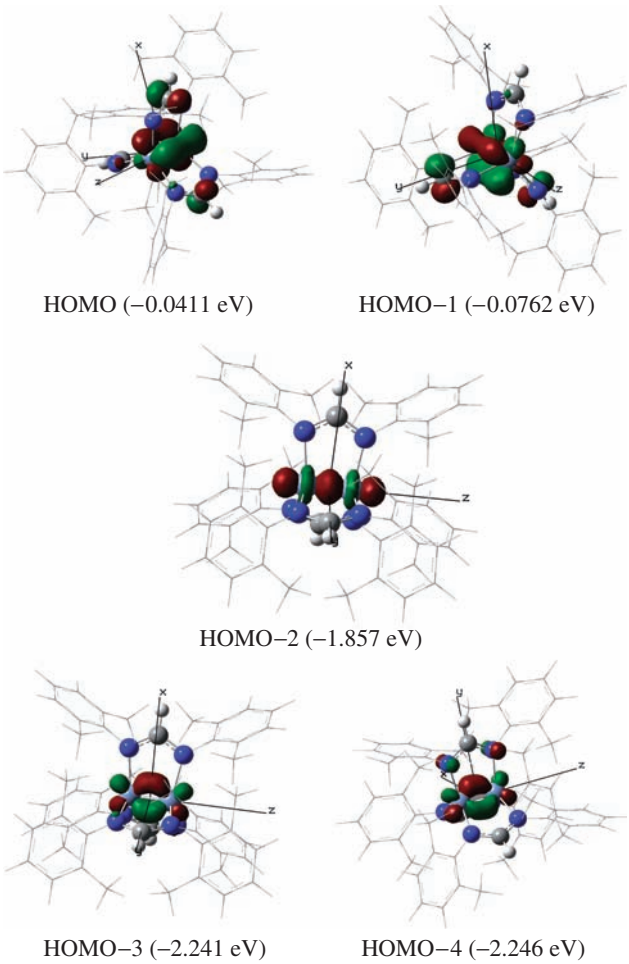


Figure 6. δ (top), σ (middle), and π (bottom) orbitals of **8**.

Subsequent reduction of **7** with KC_8 in the presence of 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (crypt[222]) gave the extremely air- and moisture-sensitive diamagnetic $\{K\text{-crypt-}[222]\}\{Cr_2(Ar^{Xyl}NC(H)NAr^{Xyl})_3\}$ (**8**).[34] In comparison with the distorted structure of **7**, diamagnetic complex **8** distinctly displays a more symmetrical D_3 symmetric lantern structure (Figure 5). The most remarkable feature of **8** is that the Cr–Cr separation contracts dramatically to an ultrashort distance of 1.7397(9) Å.

The nature of the Cr–Cr bond in **8** is examined by DFT calculations (BP86). Considerable metal–metal bonding can be found from HOMO to HOMO−4 (Figure 6). Orbital HOMO−2 corresponds to the Cr–Cr σ bond ($d_{z^2} + d_{z^2}$), while the degenerate HOMO−3 and HOMO−4 display the Cr–Cr π bonding interactions ($d_{xz} + d_{xz}$ and $d_{yz} + d_{yz}$). Two almost degenerate Cr–Cr δ bonding character are apparently displayed by HOMO ($d_{x^2-y^2} + d_{x^2-y^2}$) and HOMO−1 ($d_{xy} + d_{xy}$). In contrast to the significant Cr–N π-bondings in **5**,[30] no π-bonding is observed between $d_{x^2-y^2}$ and d_{xy} orbitals of Cr atoms and N donors. These observations suggest two strong Cr–Cr δ-bonds and consequently support an extremely short Cr–Cr bond.

The origin of the ultrashort Cr–Cr bond length of **8** is still not clear in the context of formal quintuple bonding since the number of orbitals needed for metal–ligand bonding is considered to be minimized.[22] However, this is not due to the three-

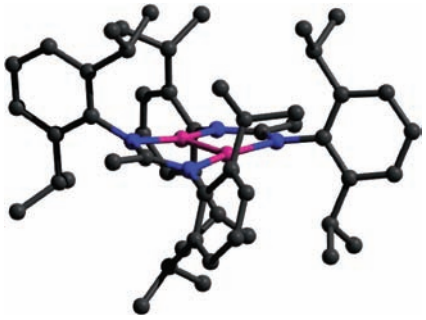
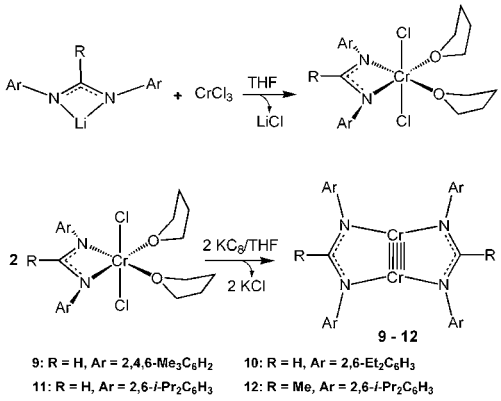


Figure 7. Molecular structure of **12**, where the Cr–Cr bond length is 1.7395(7) Å (color code: plum = Cr, blue = N, gray = C).



Scheme 2. Syntheses of compounds **9**–**12**.

atomic bridging amidinate ligands, because the Cr–Cr bond lengths in amidinate-bridged paddlewheel dichromium compounds range form 1.844(2) to 2.612(1) Å.[3] Moreover, it is interesting to note the characterization of **8** verifies Hoffmann's prediction that a metal–metal quintuple bond could exist in a trigonal eclipsing molecule M_2L_6.[15]

Interestingly, when more encumbering amidinato ligands are employed, a family of C_2 symmetric quintuply bonded dichromium complexes, $Cr_2[\mu\text{-}\eta^2\text{-ArNC(R)NAr}]_2$, (**9**: Ar = 2,4,6-$Me_3C_6H_2$, R = H; **10**: Ar = 2,6-$Et_2C_6H_3$, R = H; **11**: Ar = 2,6-*i*-$Pr_2C_6H_3$, R = H; **12**: Ar = 2,6-*i*-$Pr_2C_6H_3$, R = Me) are prepared.[38] The diamagnetic complexes **9**–**12** are obtained by reducing their respective mononuclear precursor structures of compounds **9**–**12** (**12** is shown in Figure 7) are $CrCl_2(THF)_2[\eta^2\text{-ArNC(R)NAr}]$ (Scheme 2).[38] The moleculardetermined by X-ray crystallography, and the Cr–Cr bond lengths are 1.7404(8) (**9**), 1.7454(1) (**10**), 1.7472(10) (**11**), and 1.7395(7) Å (**12**). These values suggest that the Cr–Cr bond lengths display weak correlation with the steric bulk of the auxiliary ligands. In principle, if the repulsion between substituents R and Ar increases, the amidinates tend to favor a chelating fashion.

The bonding schemes of **9**–**12** are corroborated by DFT calculations. Taking **10** as a representative example, the computations indicate that five metal–metal bonding orbitals can be found from HOMO to HOMO−3 and HOMO−7. HOMO−2 corresponds to the Cr–Cr σ bond ($d_{z^2} + d_{z^2}$), and HOMO−3 ($d_{xz} + d_{xz}$) and HOMO−7 ($d_{yz} + d_{yz}$) display the Cr–Cr dπ bonding interactions. Two Cr–Cr δ bonding characters are displayed by HOMO ($d_{xy} + d_{xy}$) and HOMO−1. It is noteworthy

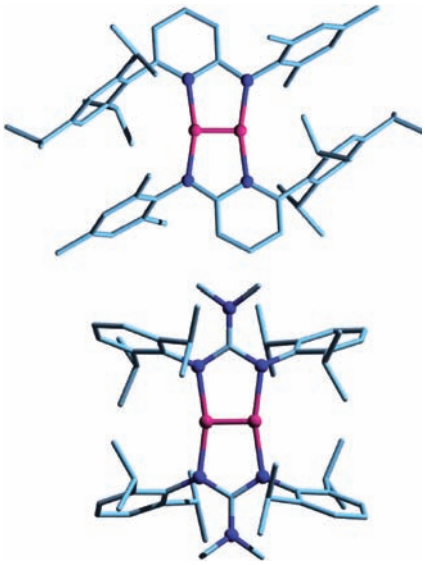


Figure 8. Molecular structures of **13** (top) and **14** (bottom), where the Cr–Cr bond length is 1.749(2) (**13**) and 1.7293(12) Å (**14**) (color code: plum = Cr, blue = N, turquoise = C).

that HOMO−1 is a side-on sd–$\pi\delta$ bond,[39] a hybridization of s (24.6%) and $d_{x^2-y^2}$ (75.4%), oriented such that the main hybrid orbital axes are parallel to one another.

Meanwhile, the pyridylamide is also employed to stabilize the Cr–Cr quintuple bond by Kempe et al.[40] The quintuply bonded dichromium complex $Cr_2[\mu\text{-}\eta^2\text{-TippPyNMes}]_2$ [**13**, DippPyNMes = 6-(2,4,6-triisopropylphenyl)pyridine-2-yl(2,4,6-trimethylphenyl)amide] (Figure 8). Compound **13** is prepared by reducing its mononuclear $CrCl_2(THF)_2(\eta^2\text{-TippPyNMes})$ or dinuclear $[Cr(THF)(\mu\text{-Cl})(\eta^2\text{-TippPyNMes})]_2$ precursor. The X-ray crystal structure of **13** indicates that the Cr–Cr bond length is 1.749(2) Å, slightly longer than that of **9**–**12**. Just recently, the same group reports a sterically encumbering guanidinate-supported dichromium complex, $Cr_2[\mu\text{-}\eta^2\text{-DippNC(NMe}_2\text{)NDipp}]_2$ (**14**, Dipp = 2,6-*i*-$Pr_2C_6H_3$, Figure 8),[41] where the Cr–Cr bond length is determined by X-ray crystallography to be 1.7293(12) Å, which represents the shortest metal–metal bond yet. The Cr–Cr distance of compound **14** is 0.1 Å shorter than the distances observed for the complexes that had been holding the record of the shortest metal–metal distance in a stable molecule for nearly 30 years.

It is noteworthy that the said C_2-symmetric complexes **9**–**14** are essentially reminiscent of complexes **1**–**4** in structure, but their Cr–Cr quintuple bond lengths are much shorter than those of **1**–**4**. The striking difference in these two groups of complexes is the supporting ligands. It seems that the auxiliary ligands play a crucial role in the lengths of the Cr–Cr quintuple bonds. Accordingly, a shorter Cr–Cr quintuple bond is thus expected via variation of the ligand environment.

Alvarez et al. analyzed structural data for more than 350 dinuclear compounds of the types M_2X_8, M_2X_8L, and $M_2X_8L_2$ with a multiple bond, mainly quadruple bonds, between the transition-metal atoms M, and found the existence of a clear correlation between the average pyramidality angle (M–M–X, or α) and the metal–metal bond distance.[42] They explained the pyramidality effect in terms of major change in hybridization affecting the metal–metal σ- and π-bonding. As a matter of fact, this

correlation works not only well with quadruply bonded complexes, but also with the aforementioned quintuply bonded dichromium complexes,[34,38] except for those ultrashort Cr–Cr quintuple bonds in complexes **12** and **14**. Given the weak δ-bonding, it seems sensible to assume that quadruple and quintuple bonds have essentially the same behavior.

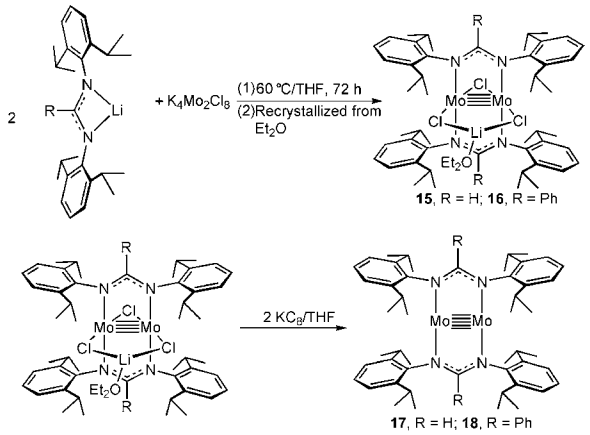
Besides the construction of metal–metal quintuple bonds, another focus here is on ultrashort metal–metal quintuple bonds. What is a short bond then? A way of comparing the shortness of bonds across the periodic table is the formal shortness ratio (FSR) coined by Cotton.[3] FSR is a dimensionless number calculated by the ratio of the atom–atom distance d of a bond (A–B), and the sum of the radii of the two atoms involved, $r_A + r_B$; FSR $= d/(r_A + r_B)$. The advantage of this formalism is its inter-element applicability. For example, complex **14** has a FSR of 0.729, whereas the FSR of the "supershort" Cr–Cr quadruple bond[27] and dinitrogen is 0.771 and 0.786, respectively.

♦ Beyond Chromium

It may be due to the issue of starting precursors, so the quintuply bonded complexes are dominated by homobichromium so far. However, it has been well known that group 6 elements, due to their electron configuration, are able to form metal–metal bonds of high formal bond orders. Among them, molybdenum is notable for its ability to form strong Mo–Mo multiple bonds. For example, molybdenum forms the most quadruply bonded compounds and consequently accumulates a wealth of structural and spectroscopic data.[3] Furthermore, it must be noted that the singlet state diatomic Mo_2 molecule containing a true sextuple bond has been observed in the gas phase at low temperatures,[43] and the Mo–Mo bond length was determined to be 1.93 Å.[44] Overall, owing to the success in the recognition of its homologous Cr–Cr quintuple bonded complexes and being sandwiched between Mo–Mo quadruple and sextuple bonded compounds, Mo–Mo quintuple bonded complexes have thus been proposed to be synthesized.

Just recently, we reported the first two Mo–Mo quintuply bonded complexes, $Mo_2[\mu\text{-}\eta^2\text{-RC(N-2,6-}i\text{-Pr}_2C_6H_3)_2]_2$ (**17**, R = H; **18**, R = Ph).[45] In analogy to the access of the aforementioned quadruply bonded complex, $Mo_2[\mu\text{-}\eta^2\text{-Me}_2\text{Si(N-2,6-}i\text{-Pr}_2C_6H_3)_2]_2$, where molybdenum is two-coordinated with respect to the diamido ligands.[32] Two quadruply bonded complexes $Mo_2(\mu\text{-Cl})[Cl_2Li(OEt_2)][\mu\text{-}\eta^2\text{-RC(N-2,6-}i\text{-Pr}_2C_6H_3)_2]_2$ (**15**, R = H; **16**, R = Ph) are thus prepared, and the Mo–Mo bond length is 2.0875(4) and 2.0756(8) Å, respectively.[45] Complexes **17** and **18** are then obtained by reducing **15** and **16** with KC_8 (Scheme 3). Their X-ray crystal structures (Figure 9) are essentially similar to those of the aforementioned dichromium complexes, except for **7** and **8**. The Mo–Mo quintuple bond lengths of **17** and **18** are 2.0187(9) and 2.0157(4) Å, respectively, dramatically shorter than those in **15** and **16**. Although the X-ray determined shortest Mo–Mo quadruple bond is 2.037(3) Å in the tetragonal dimolybdenum complex, $Mo_2[\mu\text{-}\eta^2\text{-pyNC(O)-CH}_3]_4$, reported by Cotton et al.,[46] this unusually short quadruple bond was later suggested unreliable by the same group.

As for the electronic structures, the calculations at BP86/def2-TZVP[47,48] on **17** showed that there is no N–Mo π bonding interactions, and metal–metal bonding characters can be found from HOMO to HOMO−2, HOMO−10, and HOMO−12 (Figure 10). Those orbitals between HOMO−3 and HOMO−9



Scheme 3. Syntheses of compounds **15**–**18**.

Figure 9. Molecular structures of **17** (top) and **18** (bottom), where the Mo–Mo bond length is 2.0187(9) (**17**) and 2.0157(4) Å (**18**) (color code: dark red = Mo, blue = N, gray = C).

are primarily contributed from ligands. Of these five Mo–Mo bonding orbitals, HOMO−10 ($d_{xz} + d_{xz}$) and HOMO−12 ($d_{yz} + d_{yz}$) represent two Mo–Mo π bonds, while the Mo–Mo σ character is found at HOMO−2 ($d_{z^2} + d_{z^2}$). HOMO ($d_{xy} + d_{xy}$) and HOMO−1 ($d_{x^2-y^2} + d_{x^2-y^2}$) clearly indicate a pair of Mo–Mo δ bonds. Noteworthy is that HOMO−1, the side-on sd δ bond, results from hybridization of s (36.7%) and d (63.3%) orbitals, oriented such that the main hybrid orbital axes are parallel to one another. As a result, computations unambiguously support that each of **17** and **18** possesses a Mo–Mo quintuple bond, and these two extremely short Mo–Mo bonds are a consequence of strong interactions between two d^5 Mo(I) centers.

♦ Outlook

In principle, the 4f and 5f metals could potentially form higher bond orders as transition metals. However, due to their

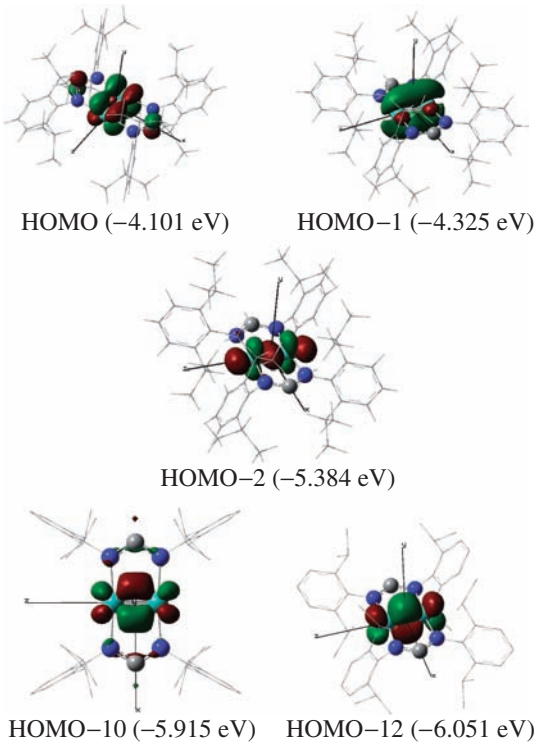


Figure 10. δ (top), σ (middle), and π (bottom) orbitals of **17**.

atomic-like localized 4f states, lanthanides are not considered candidates in this regard, but the dimers of the 5f actinides are more attractive. In fact, some actinide dimers are experimentally observed from matrix isolation and gas-phase detection (U_2).[49]

To understand the electronic structures of such species, Gagliardi and Roos[50] performed calculations on U_2 at the CASPT2 level of theory. They indicated that ten of the twelve valence electrons are chemically active exhibiting an exotic bonding scheme with a classical bonding part consisting of one σ ($7s\sigma_g$) and two π ($6d\pi_u$) doubly occupied bonding orbitals, and a ferromagnetic bonding part[51] with four singly occupied bonding orbitals ($6d\sigma_g$, $6d\delta_g$, and $5f\pi_u$, $5f\delta_g$). The remaining two electrons are found to be situated in localized 5f orbitals on each U atom. In total, a formal bond order of 5 is thus obtained. The calculations show all six electrons are ferromagnetically coupled.

In a broader and more refined study[52] of Ac_2, Th_2, Pa_2, and U_2, the concept of the effective bond order (EBO) has been additionally applied to characterize the chemical bonding. EBO values of 1.7, 3.7, 4.5, and 4.2 have thus been obtained for Ac_2, Th_2, Pa_2, and U_2, respectively. It is noteworthy that Pa_2 molecule displays the highest EBO value, the highest computed bond energy (4.0 eV) and the shortest bond length (2.37 Å). Despite the rather close EBO value, U_2 has a much lower bond energy (1.2 eV), while Th_2 with a lower EBO is found to have much higher bond energy (3.3 eV). It should be noted that there is no direct relation between the EBO and the bond energy, because the latter is a complicated energy difference which depends on variable electronic properties of the actual molecule and the isolated atoms. The study has not been extended to heavier homologues, because their bond orders are expected to be generally smaller than those for the early actinides, due to increasing 7s promotion energies and the increasing localization of the 5f electrons bond energies.

Accordingly, the highest possible bond order of a covalent bond should be in homobimetallic transition elements. Roos, Borin, and Gagliardi,[26] based on CASPT2 calculations, have argued that the maximum bond order between two transition-metal atoms can be six, with 2σ, 2π, and 2δ bonds. In contrast to the main group elements, high effective bond orders have been found to be more favorable for the heavier homologues. Scalar relativistic effects give rise to more itinerant $(n-1)$d orbitals leading to higher effective EBO contributions from the δ bonds and to more contracted ns orbitals yielding more optimal σ bonding contributions. Thus, while for Cr_2, an EBO of 3.5 and a dissociation energy of only 1.65 eV (calcd) has been obtained, EBO values of 5.2 are computed for both Mo_2 and W_2 molecules with dissociation energies of 4.41 eV (calcd) and 5.37 eV (calcd), respectively.

Likewise, in order to achieve high EBOs for formal quintuple bonds, the Mo and W homologues of univalent Cr compounds have been proposed to be synthesized, and the quintuply bonded dimolybdenum complexes, **17** and **18**,[45] have just been characterized and their bond orders are currently under investigation. Another candidate for a strong quintuple bond has been predicted to be Nb_2, because the Nb atom is already fully polarized ($4d^45s^1$ configuration) in its ground state. However, the heavier homologue Ta_2, is less favorable due to the higher promotion energy of the Ta atom (d^3s^2 configuration) to a valence state with 5 unpaired electrons.

The search for the shortest metal–metal bond in a stable compound has been of interest to chemists for decades. In this regard, chromium features the smallest ion radius, so is the best candidate in group 6, which are well known to form metal–metal bonds of high formal bond orders.[24] As of now, ultrashort Cr–Cr quintuple bonds were found in those N-based ligands supported complexes. One very important and successful reason using N-based ligands to support Cr–Cr quintuple bonds is their steric pressure, which can be easily tuned. The steric congestion of auxiliary ligands ensures low-coordinate complexes, and this has been proposed a critical role in stabilizing Cr–Cr quintuple bonds, except for compound **8**. In this regard, the N,O-based ligands might have a chance to preserve the shortest Cr–Cr quintuple bond.

Since stable quintuply bonded species could be isolated and characterized, thus, the question arises: besides fundamental interest from the bonding perspective, what they are good for or what can be done with them? The best answer for these questions would be the investigation of their reactivity. In contrast to most of the reactions of the quadruple bonded M_2^{4+} complexes involving ligand replacement with preservation of the M_2^{4+} unit, the aforementioned thermodynamically stable C_2 symmetric quintuple bonded M_2 complexes feature low-coordinate (two-coordinated with respect to the ligand) and low-valent metal centers, which render them kinetically reactive. For example, Power et al. have demonstrated that the Cr–Cr quintuple bond of compound **1** is frangible when it was treated with N_2O and organic azides and resulted in the formation of compounds which have no metal–metal bonding.[53] However, on the other hand, Kempe et al. show that the chromium–chromium quintuple bond of **19** undergoes carboalumination reaction and gives a product **20** where a Cr–Cr quadruple bond is formed instead (Figure 11).[54] It has been well known that carbometallation and especially carboalumination reactions of C–C double and triple bonds are a

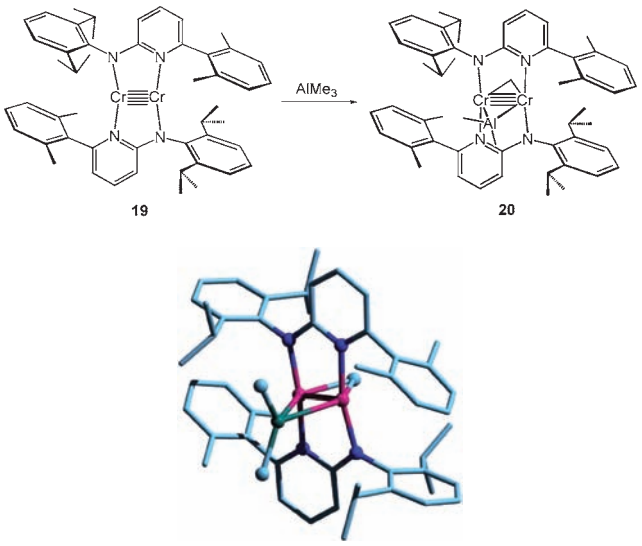


Figure 11. Carboalumination of a Cr–Cr quintuple bond **19** and the molecular structure of the product **20**, where the Cr–Cr bond length is 1.8365(8) Å (color code: plum = Cr, teal = Al, blue = N, turquoise = C).

well established synthetic protocol in organometallic chemistry and organic synthesis. These studies reveal rich chemistry of quintuple bonds and open a door to find potential applications of such bonds.

This work was supported by the National Science Council, Taiwan under Grant NSC 96-2113-M-007-019-MY3.

References and Notes

1 F. A. Cotton, N. F. Curtis, C. B. Harris, B. F. G. Johnson, S. J. Lippard, J. T. Mague, W. R. Robinson, J. S. Wood, *Science* **1964**, *145*, 1305.
2 F. A. Cotton, C. B. Harris, *Inorg. Chem.* **1965**, *4*, 330.
3 F. A. Cotton, C. A. Murillo, R. A. Walton, in *Multiple Bonds Between Metal Atoms*, 3rd ed., Springer Science and Business Media Inc., New York, **2005**.
4 E. P. Kundig, M. Moskovits, G. A. Ozin, *Nature* **1975**, *254*, 503.
5 W. Klotzbucher, G. A. Ozin, *Inorg. Chem.* **1977**, *16*, 984.
6 S. K. Gupta, R. M. Atkins, K. A. Gingerich, *Inorg. Chem.* **1978**, *17*, 3211.
7 Y. M. Efremov, A. N. Samoilova, V. B. Kozhukhovsky, L. V. Gurvich, *J. Mol. Spectrosc.* **1978**, *73*, 430.
8 W. Weltner, Jr., R. J. Van Zee, *Annu. Rev. Phys. Chem.* **1984**, *35*, 291, and references therein.
9 M. D. Morse, *Chem. Rev.* **1986**, *86*, 1049.
10 Z. L. Xiao, R. H. Hauge, J. L. Margrave, *J. Phys. Chem.* **1992**, *96*, 636.
11 a) S. M. Casey, P. W. Villalta, A. A. Bengali, C. L. Cheng, J. P. Dick, P. T. Fenn, D. G. Leopold, *J. Am. Chem. Soc.* **1991**, *113*, 6688. b) S. M. Casey, D. G. Leopold, *J. Phys. Chem.* **1993**, *97*, 816. c) S. M. Casey, D. G. Leopold, *Chem. Phys. Lett.* **1993**, *201*, 205.
12 M. H. Chisholm, A. M. Macintosh, *Chem. Rev.* **2005**, *105*, 2949.
13 A. Kant, B. Strauss, *J. Chem. Phys.* **1966**, *45*, 3161.
14 D. Kraus, M. Lorenz, V. E. Bondybey, *PhysChemComm* **2001**, *4*, 44.
15 A. Dedieu, T. A. Albright, R. Hoffmann, *J. Am. Chem. Soc.* **1979**, *101*, 3141.
16 F. Weinhold, C. R. Landis, *Valency and Bonding: A Natural Bond Orbital Donor-Acceptor Perspective*, Cambridge University Press, Cambridge, UK/New York, **2005**.
17 L. Gagliardi, B. O. Roos, *Nature* **2005**, *433*, 848.
18 C. R. Landis, F. Weinhold, *J. Am. Chem. Soc.* **2006**, *128*, 7335.
19 F. Weinhold, C. R. Landis, *Science* **2007**, *316*, 61.
20 G. Merino, K. J. Donald, J. S. D'Acchioli, R. Hoffmann, *J. Am. Chem. Soc.* **2007**, *129*, 15295.
21 T. Nguyen, A. D. Sutton, M. Brynda, J. C. Fettinger, G. J. Long, P. P. Power, *Science* **2005**, *310*, 844.
22 G. Frenking, *Science* **2005**, *310*, 796.
23 M. Brynda, L. Gagliardi, P. O. Widmark, P. P. Power, B. O. Roos, *Angew. Chem., Int. Ed.* **2006**, *45*, 3804.
24 G. Frenking, R. Tonner, *Nature* **2007**, *446*, 276.
25 G. La Macchia, L. Gagliardi, P. P. Power, M. Brynda, *J. Am. Chem. Soc.* **2008**, *130*, 5104.
26 B. O. Roos, A. C. Borin, L. Gagliardi, *Angew. Chem., Int. Ed.* **2007**, *46*, 1469.
27 F. A. Cotton, S. A. Koch, M. Millar, *Inorg. Chem.* **1978**, *17*, 2084.
28 R. Wolf, C. Ni, T. Nguyen, M. Brynda, G. J. Long, A. D. Sutton, R. C. Fischer, J. C. Fettinger, M. Hellman, L. Pu, P. P. Power, *Inorg. Chem.* **2007**, *46*, 11277.
29 Y. M. Efremov, A. N. Samoilova, L. V. Gurvich, *Opt. Spectrosc.* **1974**, *36*, 654.
30 K. A. Kreisel, G. P. A. Yap, O. Dmitrenko, C. R. Landis, K. H. Theopold, *J. Am. Chem. Soc.* **2007**, *129*, 14162.
31 G. La Macchia, F. Aquilante, V. Veryazov, B. O. Roos, L. Gagliardi, *Inorg. Chem.* **2008**, *47*, 11455.
32 Y.-C. Tsai, Y.-M. Lin, J.-S. K. Yu, J.-K. Hwang, *J. Am. Chem. Soc.* **2006**, *128*, 13980.
33 F. A. Cotton, L. M. Daniels, C. A. Murillo, P. Schooler, *J. Chem. Soc., Dalton Trans.* **2000**, 2007.
34 Y.-C. Tsai, C.-W. Hsu, J.-S. K. Yu, G.-H. Lee, Y. Wang, T.-S. Kuo, *Angew. Chem., Int. Ed.* **2008**, *47*, 7250.
35 The core of complex $Fe_2(DPhF)_3$ also displays C_{2v} symmetry, but the structural distortion is due to the packing of the molecules in the crystals: a) F. A. Cotton, L. M. Daniels, L. R. Falvello, J. H. Matonic, C. A. Murillo, *Inorg. Chim. Acta* **1997**, *256*, 269. b) F. A. Cotton, X. Feng, C. A. Murillo, *Inorg. Chim. Acta* **1997**, *256*, 303.
36 a) R. Englman, *The Jahn–Teller Effect in Molecules and Crystals*, Wiley-Interscience, London, **1972**. b) R. G. Pearson, *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 2104. c) I. B. Bersuker, *Electronic Structure and Properties of Transition Metal Compounds*, Wiley-Interscience, New York, **1996**. d) T. A. Barckholtz, *Int. Rev. Phys. Chem.* **1998**, *17*, 435.
37 The difficulty in observing expected Jahn–Teller distortions in multiply bonded dinuclear complexes has been encountered earlier. An example is the series of face-sharing bioctahedral anions of the type $W_2X_9^{3-}$. These typically have nondistorted D_{3h} symmetry. Only once a slight canting of two planes that lowered the symmetry to C_{2v} was measured in the $W_2Br_9^{3-}$ anion. See: J. L. Templeton, R. A. Jacobson,

R. E. McCarley, *Inorg. Chem.* **1977**, *16*, 3320.
38 C. W. Hsu, J.-S. K. Yu, C.-H. Yen, G.-H. Lee, Y. Wang, T.-S. Kuo, *Angew. Chem., Int. Ed.* **2008**, *47*, 9933.
39 C. R. Landis, F. Weinhold, *J. Am. Chem. Soc.* **2006**, *128*, 7335.
40 A. Noor, F. R. Wagner, R. Kempe, *Angew. Chem., Int. Ed.* **2008**, *47*, 7246.
41 A. Noor, G. Glatz, R. Müller, M. Kaupp, S. Demeshko, R. Kempe, *Z. Anorg. Allg. Chem.* **2009**, *635*, 1149.
42 F. Mota, J. J. Novoa, J. Losoda, S. Alvarez, R. Hoffmann, J. Silvestre, *J. Am. Chem. Soc.* **1993**, *115*, 6216.
43 a) D. Kraus, M. Lorenz, V. E. Bondybey, *PhysChemComm* **2001**, *4*, 44. b) M. J. Pellin, T. Foosnaes, D. M. Gruen, *J. Chem. Phys.* **1981**, *74*, 5547. c) B. E. Bursten, F. A. Cotton, M. B. Hall, *J. Am. Chem. Soc.* **1980**, *102*, 6348. d) P. M. Atha, I. H. Hillier, M. F. Guest, *Chem. Phys. Lett.* **1980**, *75*, 84.
44 Y. M. Efremov, A. N. Samoilova, V. B. Kozhukhovsky, L. V. Gurvich, *J. Mol. Spectrosc.* **1978**, *73*, 430.
45 Y.-C. Tsai, H.-Z. Chen, C.-C. Chang, J.-S. K. Yu, G.-H. Lee, Y. Wang, T.-S. Kuo, *J. Am. Chem. Soc.* **2009**, *131*, 12534.
46 F. A. Cotton, L. M. Daniels, E. A. Hillard, C. A. Murillo, *Inorg. Chem.* **2002**, *41*, 2466.
47 a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098. b) J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822.
48 F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.
49 L. N. Gorokhov, A. M. Emelyanov, Y. S. Khodeev, *High Temp.* **1974**, *12*, 1156.
50 L. Gagliardi, B. O. Roos, *Nature* **2005**, *433*, 848.
51 M. N. Glukhovtsev, P. v. R. Schleyer, *Isr. J. Chem.* **1993**, *33*, 455.
52 B. O. Roos, P.-A. Malmqvist, L. Gagliardi, *J. Am. Chem. Soc.* **2006**, *128*, 17000.
53 C. Ni, B. D. Ellis, G. J. Long, P. P. Power, *Chem. Commun.* **2009**, 2332.
54 A. Noor, G. Glatz, R. Müller, M. Kaupp, S. Demeshko, R. Kempe, *Nat. Chem.* **2009**, *1*, 322.