Quintuply-Bonded Dichromium(I) Complexes Featuring Metal–Metal Bond Lengths of 1.74 Å**
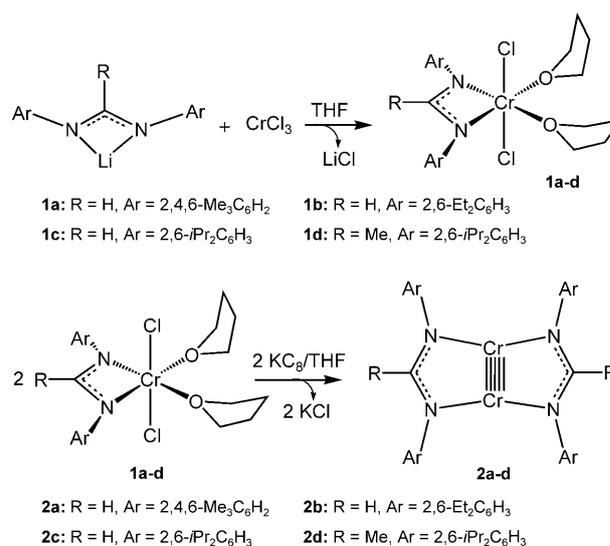
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The construction of a metal–metal quintuple bond has long been a challenge for chemists, since a large number of quadruple-bonded dinuclear complexes have been reported and their bonding and electronic structures extensively investigated and well understood.[1–4] On the basis of theoretical work,[5–10] many possible structures could be capable of accommodating a metal–metal quintuple bond, in contrast to the strict requirement of having two metal atoms embraced by eight ligands in a tetragonal geometry for a metal–metal quadruple bond.[1] Of particular interest is that all of these model structures display a common feature: a low-coordinate environment around metal centers. From a practical point of view, the first quintuple-bonded dichromium complex [Ar′Cr-CrAr′] (Ar′ = C_6H_3-2,6-(C_6H_3-2,6-iPr$_2$)$_2$, Cr—Cr = 1.8351(4) Å), which adopts a *trans*-bent geometry, was reported by Power and co-workers in 2005.[11–13] More recently, in 2007, Theopold and co-workers reported an interesting dichromium complex supported by α-diimines, [Cr_2(μ-η^2-{C(H)N(C_6H_3-2,6-iPr$_2$)}$_2$)$_2$], which was shown by computations to exhibit some degree of Cr—Cr quintuple-bond character.[14]

Since our first report on the characterization of an unconventional quadruple-bonded dimolybdenum complex [Mo_2(μ-η^2-(DippN)$_2$SiMe$_2$)$_2$], where each Mo atom is ligated by only two nitrogen donors,[15] we have been interested in the pursuit of low-coordinate and multiply-bonded dinuclear complexes. We recently characterized a mixed-valent dichromium complex stabilized by three amidinate ligands, [Cr_2-{Ar^{Xyl}NC(H)NAr^{Xyl}}$_3$] (Ar^{Xyl} = 2,6-C_6H_3(CH$_3$)$_2$), and its one-electron reduction partner [Cr_2{Ar^{Xyl}NC(H)NAr^{Xyl}}$_3$]$^-$, which

exhibited the shortest metal–metal bond length of 1.7397(9) Å.[16] Qualitatively, the latter is believed to incorporate a Cr—Cr quintuple bond. In view of Power's and Theopold's complexes, wherein both Cr^I centers were coordinated by two donor atoms, we set out to prepare dichromium bis(amidinato) complexes, from which metal–metal quintuple bonds are expected.[17] Herein we report a series of complexes of the form [Cr_2{μ-η^2-ArNC(R)NAr}$_2$], which all exhibit very short Cr—Cr quintuple-bond lengths of approximately 1.74 Å. Amidinate ligands, featuring substituents of different bulk, are used to stabilize these Cr—Cr quintuple bonds.

Prior to the synthesis of the target molecules, four green mononuclear complexes, **1a–d**, of the form [$CrCl_2$(thf)$_2${η^2-ArNC(R)NAr}] were prepared in good yields by treatment of [$CrCl_3$(thf)$_3$] or $CrCl_3$ with lithiated amidines (Scheme 1, see

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1a: R = H, Ar = 2,4,6-Me$_3$C$_6$H$_2$ **1b:** R = H, Ar = 2,6-Et$_2$C$_6$H$_3$
1c: R = H, Ar = 2,6-iPr$_2$C$_6$H$_3$ **1d:** R = Me, Ar = 2,6-iPr$_2$C$_6$H$_3$

2a: R = H, Ar = 2,4,6-Me$_3$C$_6$H$_2$ **2b:** R = H, Ar = 2,6-Et$_2$C$_6$H$_3$
2c: R = H, Ar = 2,6-iPr$_2$C$_6$H$_3$ **2d:** R = Me, Ar = 2,6-iPr$_2$C$_6$H$_3$

Scheme 1. Synthesis of complexes [$CrCl_2$(thf)$_2${η^2-ArNC(R)NAr}] (**1a–d**) and [Cr_2{μ-η^2-ArNC(R)NAr}$_2$] (**2a–d**).

the Supporting Information for experimental details). Complexes **1a–d** all display paramagnetism, and each of them has three unpaired electrons. The molecular structure of complex **1c** was determined by X-ray crystallography.[18] The Cr atom in **1c** adopts a distorted octahedral geometry with two chloride ligands arranged in a *trans* orientation (see the Supporting Information, Figure S1). Subsequent reduction of **1a–d** with two equivalents of KC_8 in THF elicited a quick color change to orange brown or reddish purple. After workup, two products were detected by ^{1}H NMR spectrosco-

py. One diamagnetic species (the major product) gave sharp resonance signals in the range $\delta = 0$–8 ppm and solid state SQUID measurements < 1.0 BM.[19] The minor product was a paramagnetic species, speculated to be the mononuclear complex [Cr{η^2-ArNC(R)NAr}$_2$]. The major product of each reduction was isolated by recrystallization of the mixture at −35°C or room temperature in appropriate hydrocarbon solvents, to give moderate yields of orange-brown crystals of quintuple-bonded compounds of the form [Cr$_2${μ-η^2-ArNC(R)NAr}$_2$] (**2a–d**, Scheme 1). The UV/Vis spectra of complexes **2a–d** display almost identical absorption profiles in which four absorption bands are detected in the visible region, indicating that complexes **2a–d** have similar molecular structures.

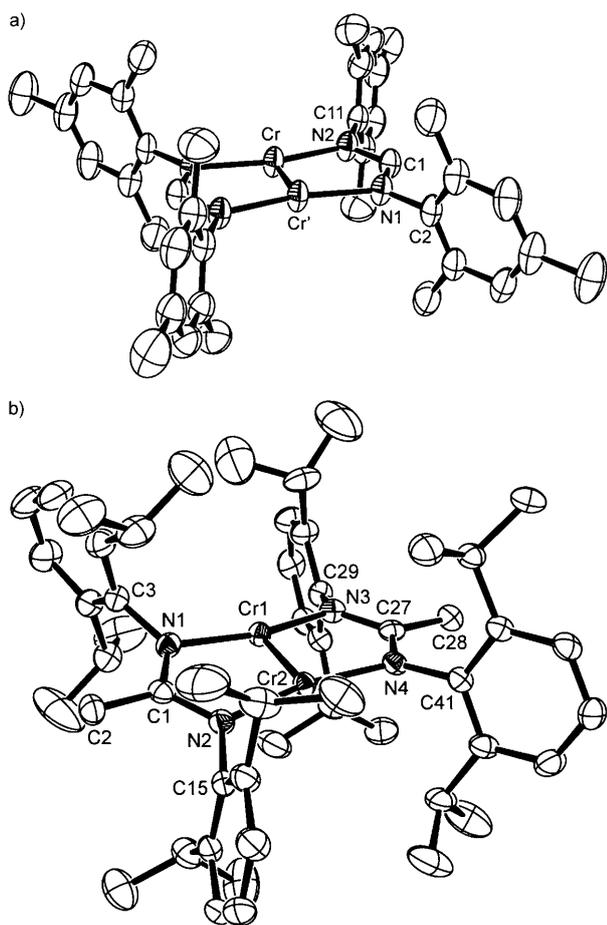The solid-state molecular structure of complex **2a** was deciphered by X-ray crystallography (Figure 1a).[18] Com-

coplanar, with N-Cr-Cr-N torsion angles of either 0° or 180°. In this bridging mode, metric parameters of the ligands are similar to those when the ligands chelate a metal center. Furthermore, the C1−N1 and C1−N2 bond lengths of the three-atom ligand backbone are 1.324(3) and 1.320(3) Å, respectively, indicating regular amidinato ligands. The Cr−N bond lengths of 2.000(2) and 1.999(2) Å are slightly shorter than those dichromium complexes bearing bridging amidinates.[1]

As is the case for most multiply-bonded metal–metal dimers, the most interesting metric parameter is the metal–metal bond length. The value of 1.7404(8) Å for **2a** is close to the shortest reported metal–metal bond length (1.7397(9) Å) of the complex [Cr$_2${Ar^{Xyl}NC(H)NAr^{Xyl}}$_3$]$^-$ (Ar^{Xyl} = 2,6-C$_6$H$_3$-(CH$_3$)$_2$).[16] In terms of Cotton's "formal shortness ratio" (FSR), complex **2a** has a FSR of 0.733, whereas the FSR of dinitrogen is 0.786.[1]

We then investigated whether the extremely short Cr−Cr distance of **2a** is a consequence of the bridging fashion of the amidinato ligands, which push two chromium atoms inward and close together. Interestingly, a survey of the literature reveals that the Cr−Cr distances in paddlewheel complexes supported by amidinates are greater than 1.84 Å.[1, 20–25] Cr−Cr separations would be expected to shorten as the steric repulsion between R and Ar substituents of the ligands increases (Figure 2). To further examine the relationship
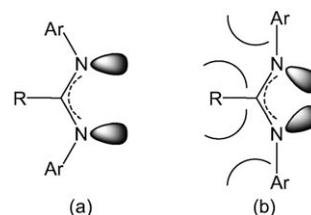

Figure 2. a) bridging and b) chelating modes of amidinates.

between Cr−Cr bond lengths and steric hindrance of the bridging amidinates, three complexes **2b–d** with increasing bulk of ligands were prepared and their molecular structures were elucidated by X-ray crystallography. Interestingly, complexes **2a–c** (Figure 1a and Figures S2 and S3 in the Supporting Information) feature a planar skeleton, whereas the core structure of **2d** (Figure 1b) is nonplanar, with torsion angles of 171.12° (N2-Cr2-Cr1-N3) and 156.05° (C29-N3-Cr1-Cr2), as a result of interligand steric repulsion between adjacent 2,6-*i*Pr$_2$C$_6$H$_3$ substituents. The Cr−N bond lengths of complexes **2a–d** were all roughly equal (approximately 2 Å). Surprisingly, Cr−Cr separations in compounds **2b–d** and **2a** are also roughly equal, at 1.7454(1), 1.7472(10), and 1.7395(7) Å, respectively. These measurements suggest that the Cr−Cr bond lengths of dichromium bis(amidinato) complexes are independent of the steric constraints imposed by the three-atom N−C−N bridges.

The geometries of the theoretically optimized structures were found to be in good agreement with those of the crystal structures of **2a–d**. Notably, the calculated Cr−Cr bond lengths, 1.7216 Å (**2a**), 1.7230 Å (**2b**), 1.7250 Å (**2c**), and

Figure 1. Molecular structures of **2a** (a) and **2d** (b) with thermal ellipsoids set at 30% probability. Hydrogen atoms have been omitted for clarity.

pound **2a** incorporates two amidinato ligands spanning the metal–metal bond. The solid-state structure exhibits approximate C_{2h} symmetry, which is consistent with the single set of alkyl resonances in the ^{1}H NMR spectrum. Interestingly, the two Cr centers, the two three-atom N−C−N backbones, and the four *ipso* carbon atoms of the phenyl rings are completely
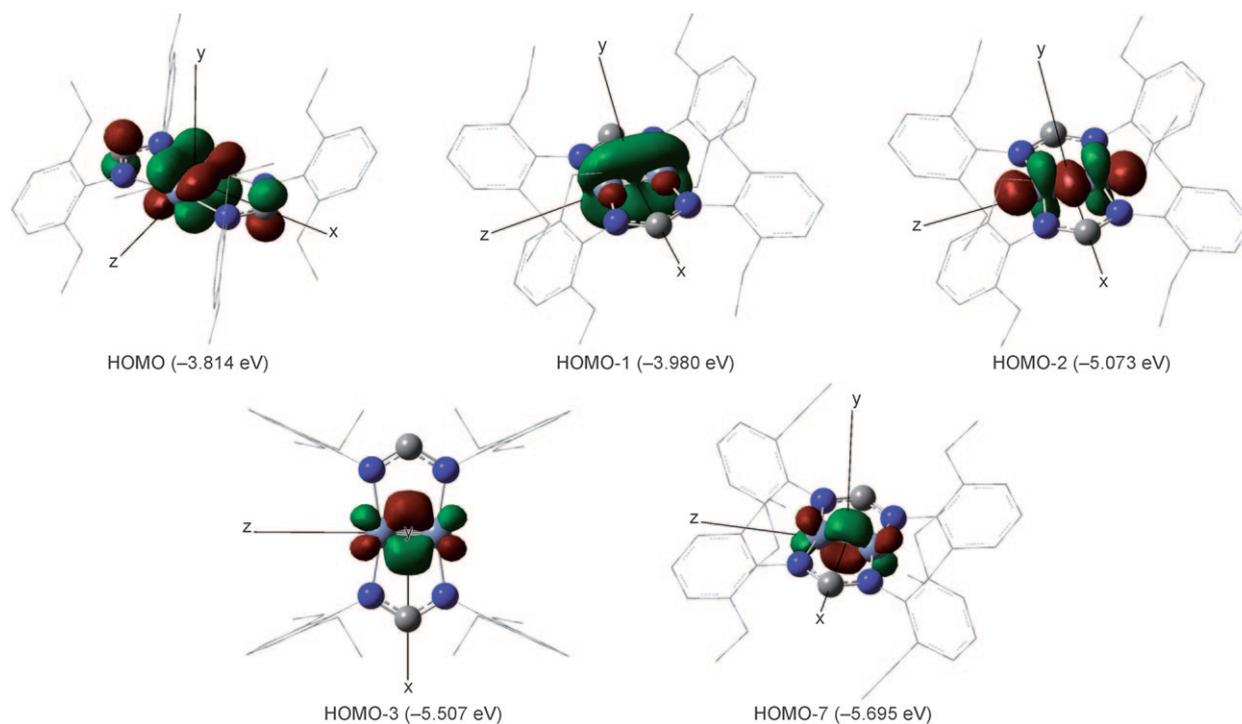
Figure 3. Frontier orbitals displaying Cr−Cr bonding in **2b**.

1.7188 Å (**2d**), are very close to the experimental values. The bonding schemes of **2a–d** were further corroborated by unrestricted density functional (DFT) calculations (UBP86).[26] Taking **2b** as a representative example, the calculations showed that considerable metal–metal bonding character can be found through HOMO to HOMO−3, and HOMO−7 (Figure 3), whereas metal–metal antibonding orbitals (δ*) are displayed by LUMO and LUMO+1 (see the Supporting Information), and ligand-based orbitals can be found from HOMO−4 to HOMO−6. 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. HOMO−1 is a side-on sd δ bond,[14,15,27] which results from 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. In contrast to the significant Cr−N π bonding (HOMO−2) in Theopold's complex [$Cr_2(\mu$-η^2-{C(H)N(C_6H_3-2,6-iPr$_2$)}$_2$)$_2$],[14] there is no π bonding between Cr atoms and N donors. As a result, complexes **2a–d** have stronger δ bonding and, consequently, shorter Cr−Cr bond lengths.

Accordingly, we conclude that the extremely short Cr−Cr distances in **2a–d** are a consequence of strong interactions between two d^5 Cr^I centers, rather than the constraint of the ligands. Thus, the five bonding orbitals of **2a–d** (1 σ, 2 π, and 2 δ orbitals) are filled with five pairs of electrons.

Mota et al.[28] proposed that, in quadruply bonded dinuclear complexes, the metal–metal distance is correlated to the average metal–metal–ligand pyramidality angle, which has been termed pyramidality effect. We have recently demonstrated that the pyramidality effect also works very well in the quintuple-bonded dichromium complexes [Cr$_2$-{Ar^{Xyl}NC(H)NAr^{Xyl}}$_3$] and [Cr$_2${Ar^{Xyl}NC(H)NAr^{Xyl}}$_3$]$^-$,[16] presumably as a result of the weak δ-bonding. For complexes **2a–d**, the Cr−Cr bond lengths are thus predicted to be 1.7409, 1.7486, 1.7451, and 1.7735 Å, respectively, amazingly close to the experimental values. Notably, the pyramidality effect suggests that **2d** has the longest metal–metal separation among complexes **2a–d**. This discrepancy is presumably ascribed to the nonplanar core structure of **2d**. The above results substantiate the fact that quadruple and quintuple bonds have essentially the same behavior.

In summary, we have demonstrated a systematic preparation and characterizations of four dichromium complexes stabilized by two amidinate ligands incorporating various bulky substituents, and from which Cr−Cr quintuple bonds with extremely short metal–metal separations of approximately 1.74 Å are identified. Measurements for these remarkably short metal–metal bonds also show good agreement with computed Cr−Cr quintuple bond lengths. We anticipate that this stimulating report may trigger extensive exploration of metal–metal multiple bonds with higher bond order. Extensive reactivity studies of complexes **2a–d** are currently underway in this laboratory.

Communications

[1] F. A. Cotton, C. A. Murillo, R. A. Walton, *Multiple Bonds Between Metal Atoms*, 3rd ed., Springer, Berlin, **2005**.

[2] V. M. Miskowski, M. D. Hopkins, J. R. Winkler, H. B. Gray, *Inorganic Electronic Structure and Spectroscopy* (Eds.: E. I. Solomon, A. B. P. Lever), Wiley, New York, **1999**.

[3] F. A. Cotton, D. G. Nocera, *Acc. Chem. Res.* **2000**, *33*, 483.

[4] M. D. Hopkins, H. B. Gray, V. M. Miskowski, *Polyhedron* **1987**, *6*, 705.

[5] F. Weinhold, C. R. Landis, *Chem. Educ. Res. Pract.* **2001**, *2*, 91.

[6] F. Weinhold, C. R. Landis, *Valency and Bonding: A Natural Bond Orbital Donor–Acceptor Perspective*, Cambridge University Press, Cambridge, **2005**, pp. 555–559.

[7] L. Gagliardi, B. O. Roos, *Nature* **2005**, *433*, 848.

[8] C. R. Landis, F. Weinhold, *J. Am. Chem. Soc.* **2006**, *128*, 7335.

[9] F. Weinhold, C. R. Landis, *Science* **2007**, *316*, 61.

[10] G. Merino, K. J. Donald, J. S. D'Acchioli, R. Hoffmann, *J. Am. Chem. Soc.* **2007**, *129*, 15295.

[11] T. Nguyen, A. D. Sutton, S. Brynda, J. C. Fettinger, G. J. Long, P. P. Power, *Science* **2005**, *310*, 844.

[12] G. Frenking, *Science* **2005**, *310*, 796.

[13] M. Brynda, L. Gagliardi, P. O. Widmark, P. P. Power, B. O. Roos, *Angew. Chem.* **2006**, *118*, 3888; *Angew. Chem. Int. Ed.* **2006**, *45*, 3804.

[14] K. A. Kreisel, G. P. A. Yap, O. Dmitrenko, C. R. Landis, K. H. Theopold, *J. Am. Chem. Soc.* **2007**, *129*, 14162.

[15] Y.-C. Tsai, Y.-M. Lin, J.-S. K. Yu, J.-K. Hwang, *J. Am. Chem. Soc.* **2006**, *128*, 13980.

[16] Y.-C. Tsai, C.-W. Hsu, J.-S. K. Yu, G.-H. Lee, Y. Wang, T.-S. Kuo, *Angew. Chem.* **2008**, *120*, 7360; *Angew. Chem. Int. Ed.* **2008**, *47*, 7250.

[17] A similar quintuple-bonded dichromium complex, supported by two sterically encumbered amidopyridines, was reported online by Kempe et al. seven days after we submitted this manuscript for publication. A. Noor, F. R. Wagner, R. Kempe, *Angew. Chem.* **2008**, *120*, 7356; *Angew. Chem. Int. Ed.* **2008**, *47*, 7246.

[18] Crystallographic data for **1c**: $C_{33}H_{51}Cl_2N_2O_2Cr$, $M_r = 630.66$; $T = 200(2)$ K; monoclinic; space group $C2/c$, $a = 17.6101(4)$, $b = 8.9222(2)$, $c = 22.4384(6)$ Å; $\beta = 108.3720(10)°$; $V = 3345.84(14)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.252$ Mg m^{-3}; $\mu = 0.532$ mm^{-1}; reflections measured: 13450 ; independent reflections: 3037 ($R_{int} = 0.0992$); final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0672$, $wR_2 = 0.1806$; R indices (all data): $R_1 = 0.0858$, $wR_2 = 0.1987$. **2a**·0.5 *n*-hexane: $C_{41}H_{53}N_4Cr_2$, $M_r = 705.87$; $T = 150(2)$ K; trigonal; space group $R\bar{3}c$, $a = 33.8181(5)$, $b = 33.8181(5)$, $c = 19.1232(2)$ Å; $V = 18940.4(4)$ Å^3; $Z = 18$; $\rho_{calcd} = 1.114$ Mg m^{-3}; $\mu = 0.546$ mm^{-1}; reflections collected: 30207; independent reflections: 4836 ($R_{int} = 0.0411$); final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0484$, $wR_2 = 0.1515$; R indices (all data): $R_1 = 0.0766$, $wR_2 = 0.1686$. **2b**: $C_{42}H_{54}N_4Cr_2$: $M_r = 718.89$; $T = 200(2)$ K; triclinic; space group $P\bar{1}$, $a = 9.6922(4)$, $b = 10.0189(4)$, $c = 10.8279(4)$ Å; $\alpha = 73.440(2)$, $\beta = 83.428(2)$, $\gamma = 73.584(2)°$; $V = 966.09(7)$ Å^3; $Z = 1$; $\rho_{calcd} = 1.236$ Mg m^{-3}; $\mu = 0.596$ mm^{-1}; reflections collected: 10851; independent reflections: 3384 ($R_{int} = 0.0531$); final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0568$, $wR_2 = 0.1556$; R indices (all data): $R_1 = 0.0727$, $wR_2 = 0.1658$. **2c**: $C_{50}H_{70}N_4Cr_2$: $M_r = 831.10$; $T = 150(2)$ K; monoclinic; space group $C2/c$, $a = 46.9512(4)$, $b = 10.3920(1)$, $c = 21.5457(2)$ Å; $\beta = 115.7385(5)°$; $V = 9469.51(15)$ Å^3; $Z = 8$; $\rho_{calcd} = 1.166$ Mg m^{-3}; $\mu = 0.495$ mm^{-1}; reflections collected: 29262; independent reflections: 10817 ($R_{int} = 0.0371$); final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0464$, $wR_2 = 0.1266$; R indices (all data): $R_1 = 0.0729$, $wR_2 = 0.1379$. **2d**: $C_{52}H_{74}N_4Cr_2$: Crystals of **2d** contained a minor component of mononuclear species [$Cr(\eta^2\text{-}\{C(CH_3)N(C_6H_3\text{-}2,6\text{-}i Pr_2)\}_2)_2$], so a disordered model of two molecules was made. The percentage of the two molecules is 95% and 5%, respectively; site occupancy factors (sof) of the Cr1, Cr2, and Cr3 atoms are, accordingly, 0.95, 0.95, and 0.1, respectively. $M_r = 853.95$; $T = 150(2)$ K; monoclinic; space group $P2_1/c$, $a = 14.4343(8)$, $b = 17.6732(10)$, $c = 20.4374(12)$ Å; $\beta = 106.330(1)°$; $V = 5003.3(5)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.134$ Mg m^{-3}; $\mu = 0.450$ mm^{-1}; reflections collected: 30132; independent reflections: 8808 ($R_{int} = 0.0553$); final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0587$, $wR_2 = 0.1338$; R indices (all data): $R_1 = 0.0780$, $wR_2 = 0.1461$. CCDC 694478 (**1c**), 694479 (**2a**), 695882 (**2b**), 694480 (**2c**), and 694481 (**2d**) 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.

[19] These deviations from diamagnetism are due to the presence of a trace amount of [$Cr\{\eta^2\text{-}ArNC(R)NAr\}_2$], which is difficult to completely remove from [$Cr_2\{\eta^2\text{-}ArNC(R)NAr\}_2$].

[20] F. A. Cotton, L. M. Daniels, C. A. Murillo, P. Schooler, *J. Chem. Soc. Dalton Trans.* **2008**, 2007.

[21] F. A. Cotton, T. Ren, *J. Am. Chem. Soc.* **1992**, *114*, 2237.

[22] F. A. Cotton, C. A. Murillo, I. Pascual, *Inorg. Chem.* **1999**, *38*, 2182.

[23] S. Hao, S. Gambarotta, C. Bensimon, J. J. H. Edema, *Inorg. Chim. Acta* **1999**, *213*, 65.

[24] F. A. Cotton, C. A. Murillo, I. Pascual, *Inorg. Chem. Commun.* **1999**, *2*, 101.

[25] F. A. Cotton, L. M. Daniels, C. A. Murillo, P. Schooler, *J. Chem. Soc. Dalton Trans.* **1999**, 2001.

[26] See the Supporting Information.

[27] C. R. Landis, F. Weinhold, *J. Am. Chem. Soc.* **2006**, *128*, 7335.

[28] F. Mota, J. J. Novoa, J. Losada, S. Alvarez, R. Hoffmann, J. Silvestre, *J. Am. Chem. Soc.* **1993**, *115*, 6216.