must be taken to ensure that the activation enthalpy attributed to solvent dissociation refers to a true, rather than an apparent, rate constant. Bond strengths determined from time-resolved photoacoustic calorimetry also should be viewed with caution, since they depend upon the experimentally-determined bond strength for CO dissociation from $Cr(CO)_6$ in the gas phase[19] and upon quantum yields for CO dissociation upon photolysis.[15] The latter recently have been found to be sensitive to the identity of weakly-interacting solvents such as perfluoroalkanes.[20]

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Supplementary Material Available: Tables I and II, listing pseudo-first-order rate constants for $Cr(CO)_6$/PhX/L and $Cr(CO)_6$/PhX/hex/pip reactions (5 pages). Ordering information is given on any current masthead page.

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Dimeric and Monomeric Chromium(II) and Monomeric Chromium(III) Aryls. Crystal Structure of Pyramidal $Mz_2Cr(py)$ (Mz = o-$Me_2NCH_2C_6H_4$, py = Pyridine), Dimeric $[(Me_2NC_6H_4)_2Cr]_2$, and Octahedral $(Me_2NC_6H_4)_3Cr$

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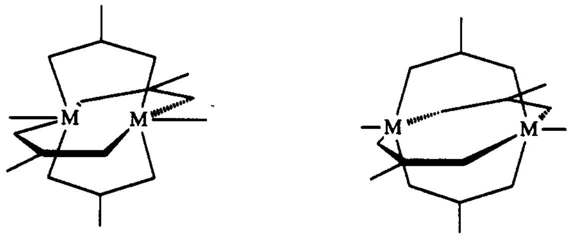
Reaction of $CrCl_2(THF)_2$ with 2 equiv of [o-$Me_2NCH_2C_6H_4$]Li and [o-$Me_2NC_6H_4$]Li led to formation of the monomeric pyramidal [o-$Me_2NCH_2C_6H_4$]$_2$Cr(pyridine) (**2**) and dimeric [(o-$Me_2NC_6H_4$)$_2$Cr]$_2$ (**3**) with a supershort Cr–Cr contact. Both compounds can be thermolyzed in toluene to form the corresponding monomeric Cr(III) [$Me_2NC_6H_4$]$_3$Cr (**4**) and (o-$Me_2NCH_2C_6H_4$)$_3$Cr (**5**) derivatives. The structures of **2**–**4** have been clarified by X-ray diffraction analysis. Complex **2**: triclinic, $P1$, $a = 8.766$ (2) Å, $b = 8.825$ (1) Å, $c = 23.582$ (3) Å, $\alpha = 81.41$ (1)°, $\beta = 85.33$ (1)°, $\gamma = 60.31$ (1)°, $V = 1567.0$ (5) Å^3, $Z = 3$, $R = 0.034$ ($R_w = 0.044$), $T = 130$ K for 986 parameters and 6269 significant reflections out of 8191. Complex **3**: monoclinic, $C2/c$, $a = 10.563$ (3) Å, $b = 13.563$ (2) Å, $c = 19.813$ (8) Å, $\beta = 92.92$ (1)°, $V = 2835$ (1) Å^3, $Z = 4$, $R = 0.066$ ($R_w = 0.092$), $T = 130$ K for 261 parameters and 2583 significant reflections out of 3406. Complex **4**: trigonal, $P31c$ $a = b = 12.821$ (1) Å, $c = 7.860$ (1) Å, $V = 1118.9$ (2) Å^3, $Z = 2$, $R = 0.060$ ($R_w = 0.066$), $T = 300$ K for 92 parameters and 573 significant reflections out of 928.

Introduction

The large range of Cr–Cr quadruple bond distances formed by dimeric Cr(II) complexes with three-center chelating ligands (lantern type) and their remarkable response to the coordination of ligands[1] still remains puzzling many years after their discovery.

Elegant theoretical work from Hoffmann and Alvarez[2] has recently found a linear correlation between Cr–Cr distances and the α *pyramidality* angle of the $LCrX_4$ fragments which form the dinuclear units of "lantern-type" compounds. In other words, a pyramidal crystal field is expected to expand the lobes of the d_{z^2}, d_{xz}, and d_{yz} orbitals of the chromium atom in the region above the basal plane and therefore to enhance the ability of chromium to form M–M bonds. This sort of *orbital engineering* has recently led to the successful isolation of the first unabridged Cr–Cr multiple bond.[3] What remains unclear is which factors in the "lantern compounds" *pyramidalize* the transition metal and ultimately determine the intermetallic separation by intruding or extruding the metal in the coordination polyhedron (Chart I). Although it is possible that the Cr–Cr multiple bond is responsible for determining the intermetallic distance, it is not likely the primary factor

Chart I



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in assembling the dimetallic unit, since the well-known paradoxical weakness of Cr–Cr multiple bonds[4] has been confirmed even in the nonbridged $[TAACr]_2$ (TAA = tetramethyltetraaza[14]annulene) and $Me_8Cr_2Li_4(THF)_4$ complexes.[5] Conversely, the Cr–ligand and ligand–ligand interactions, rather than the Cr–Cr interactions,[4,5] can reasonably be expected to be the nuclearity determining factor (monomeric versus dimeric). In particular, anionic three-center chelating ligands with two donor atoms and four delocalized electrons (allylic-like) seem to possess a unique ability to favor both dimeric structures and very short Cr–Cr contacts, since supershort Cr–Cr quadruple bonds are so widely represented in this class of compounds.[6]

In order to verify that the presence of three-center chelating ligands is indeed a sufficient (but not necessary) condition for the occurrence of short Cr–Cr distances, we have prepared consistent series of Cr(II) compounds, where the three-center chelating geometry is progressively altered or restored to the ligand by either inserting or removing or replacing small units (CH_2 group or additional donor atom).[7] These modifications affect mainly the "bite" and the electronic configuration of the ligand, while the overall steric bulk of the complex is expected to remain almost unchanged. Therefore, a comparison of the structural and magnetic properties of the corresponding complexes is expected to provide important information on the ability of bridging ligands to enforce dimetallic structures and hopefully shed light on the intriguing nature of the Cr–Cr multiple bond.

Among the possible donor atoms, we have selected carbon for this work due to its apparent versatility in forming dimeric species with short Cr–Cr contacts even in the absence of three-center chelating ligands.[8] This is in contrast to the oxygen of bridging alkoxides[9] and the nitrogen of bridging amides[10] which, without three-center-chelating ligands, result in a systematic failure of Cr–Cr bond formation. In particular, we have used the chelating $[C_6H_4\text{-}o\text{-}NMe_2]^-$ (with a three-center geometry) and $[C_6H_4\text{-}o\text{-}CH_2NMe_2]^-$ (with a four-atom *bite*) because of their structural similarity. Furthermore, the complex $[C_6H_4\text{-}o\text{-}CH_2NMe_2]_2Cr$, described by Manzer several years ago as a monomeric Cr(II) square-planar species,[11] might be a suitable starting complex for the preparation of pyramidal species with which to test the Hoffmann–Alvarez relation. Since more recent attempts to prepare and characterize this species actually gave a Cr(III) monomeric derivative,[12] we were also interested in clarifying the controversy.

Experimental Section

All operations were performed under an inert atmosphere using standard Schlenk technique or in a nitrogen-filled drybox (Vacuum-Atmosphere). $CrCl_2(THF)_2$,[13] $[C_6H_4\text{-}o\text{-}NMe_2]Li$,[14] and $[C_6H_4\text{-}o\text{-}CH_2NMe_2]Li$[15] were prepared according to published procedures. Infrared spectra were recorded on a Perkin-Elmer spectrophotometer. Nujol mulls were prepared in a drybox. Elemental analyses were carried out at the Microanalytical Department of the Rijksuniversiteit of Groningen. Samples for magnetic susceptibility measurements were weighed inside a drybox equipped with a microanalytical balance and sealed into specially designed Teflon capsules. Data were recorded at variable temperatures in the range 100–298 K by using a Faraday balance (Oxford Instruments) interfaced with an Apple II computer. Plots of $1/\chi_g$ against T (K) were in satisfactory agreement with the Curie–Weiss law in all cases. Magnetic moments were calculated following standard methods,[16] and corrections for underlying diamagnetism were applied to data.[17]

$[C_6H_4\text{-}o\text{-}CH_2NMe_2]_2Cr$ (1). Solid $CrCl_2(THF)_2$ (2.1 g, 8.0 mmol) was added to a cooled solution (−30 °C) of freshly sublimed $[C_6H_4\text{-}o\text{-}CH_2NMe_2]Li$ (2.3 g, 16.3 mmol) in THF (35 mL) containing 10 mL of ether. The color of the mixture immediately turned orange-red. After the mixture was stirred for 3 h at −30 °C and for an additional 8 h at room temperature, the solvent was removed in vacuo. Bright-yellow needles of 1 (1.7 g, 5.4 mmol, 67%) were obtained upon recrystallization of the solid residue from a toluene/heptane mixture (1:3.5). Anal. Calcd (Found) for $C_{18}H_{24}N_2Cr$: C, 67.48 (67.44); H, 7.55 (7.46); N, 8.74 (8.52); Cr, 16.23 (16.19). IR (Nujol mull, cm^{-1}, KBr): 1570 (w), 1430 (m), 1395 (w), 1285 (m), 1250 (m), 1235 (s), 1190 (w), 1170 (w), 1160 (m), 1145 (w), 1140 (w), 1095 (s), 1040 (w), 1030 (m), 1020 (s), 985 (s), 970 (s), 940 (w), 860 (w), 840 (s), 820 (m), 750 (s), 735 (s), 710 (w), 645 (m), 615 (w), 500 (w), 460 (m), 410 (m). $\mu_{eff} = 4.69\mu_B$.

$[C_6H_4\text{-}o\text{-}CH_2NMe_2]_2Cr(py)$ (2). Solid $CrCl_2(THF)_2$ (1.7 g, 6.3 mmol) was added to a cooled solution (−30 °C) of freshly sublimed $[C_6H_4\text{-}o\text{-}CH_2NMe_2]Li$ (1.8 g, 13.0 mmol) in THF (30 mL) containing 15 mL of ether. The color of the mixture immediately turned orange-red. After the mixture was stirred for 3 h at −30 °C and for an additional 8 h at room temperature, the solvent was removed in vacuo. The solid residue was redissolved in ether (20 mL) containing 5 mL of THF. After filtration and addition of pyridine (5 mL), the resulting deep-red solution yielded deep-red crystals of 2 (1.6 g, 4.0 mmol, 63%) upon cooling at −80 °C. Anal. Calcd (Found) for $C_{23}H_{29}N_3Cr$: C, 69.15 (68.92); H, 7.32 (7.30); N, 10.52 (10.45); Cr, 13.02 (12.90). IR (Nujol mull, cm^{-1}, KBr): 1585 (s), 1450 (m), 1395 (w), 1350 (m), 1285 (m), 1250 (w), 1230 (m), 1210 (s), 1170 (m), 1150 (w), 1090 (m), 1060 (m), 1020 (m), 995 (s), 990 (s), 970 (m), 865 (m), 845 (s), 765 (m), 745 (s), 740 (s), 715 (s), 700 (m), 660 (w), 615 (w), 430 (w). $\mu_{eff} = 2.56\mu_B$.

Thermolysis of 2. A solution of 2 (1.83 g, 0.57 mmol) in heptane/toluene mixture (1:1) was boiled for 30 min. The color changed slowly from yellow to orange, and the boiling was continued for 18 h. A grey solid was filtered out and and the resulting orange-red solution cooled to −80 °C, yielding orange crystals of 5 (0.88 g, 1.9 mmol, 34%). Anal. Calcd (Found) for $C_{27}H_{36}N_3Cr$:

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Table I. Crystal Data and Structural Analysis Results

	complex		
	2	3	4
formula	$C_{23}H_{29}N_3Cr$	$C_{32}N_{40}N_4Cr_2$	$C_{24}H_{30}CrN_3$
fw	399.50	584.69	412.52
crystal syst	triclinic	monoclinic	trigonal
space group	*P*1	*C*2/*c*	*P*31c
a (Å)	8.766 (2)	10.563 (3)	12.821 (1)
b (Å)	8.825 (1)	13.563 (2)	12.821 (1)
c (Å)	23.582 (3)	19.813 (8)	7.860 (1)
α (deg)	81.41 (1)		
β (deg)	85.33 (1)	92.92 (3)	
γ (deg)	60.31 (1)		
V (Å^3)	1567.0 (5)	2835 (1)	1118.9 (2)
Z	3	4	2
radiatn (Mo Kα, Å)	0.71073	0.71073	0.71073
T (K)	130	130	300
d_{calcd} (g cm^{-3})	1.270	1.370	1.224
μ_{calcd} (cm^{-1})	5.4	7.7	5.1
R_F, R_w	0.034, 0.044	0.066, 0.092	0.060, 0.066

C, 71.34 (71.58); H, 7.98 (8.03); N, 9.24 (9.18); Cr, 11.42 (11.44). $\mu_{eff} = 3.67\mu_B$.

[(C$_6$H$_4$-*o*-NMe$_2$)$_2$Cr]$_2$ (3). A freshly prepared solution of [C$_6$H$_4$-*o*-NMe$_2$]Li (26.3 mL, 1.0 M) in THF (30 mL) was added dropwise to a cooled suspension (−10 °C) of CrCl$_2$(THF)$_2$ (3.5 g, 13.0 mmol) in THF (40 mL). The resulting deep-red mixture was warmed to room temperature and stirred for 10 h. After solvent evaporation in vacuo, the solid residue was recrystallized from ether (40 mL) containing 10 mL of THF. Brick-red crystals of **3** were obtained upon cooling at −30 °C (3.15 g, 5.4 mmol, 83%). Anal. Calcd (Found) for $C_{32}H_{40}N_4Cr_2$: C, 65.74 (65.47); H, 6.90 (6.87); N, 9.58 (9.51); Cr, 17.79 (17.57). IR (Nujol mull, cm^{-1}, KBr): 1586 (m), 1430 (s), 1395 (m), 1180 (s), 1290 (w), 1250 (s), 1180 (w), 1170 (w), 1160 (s), 1150 (s), 1105 (m), 1100 (s), 1050 (w), 1020 (s), 1010 (s), 920 (s), 910 (w), 850 (m), 845 (w), 770 (s), 750 (s), 710 (s), 650 (m), 610 (w), 590 (m), 570 (s), 460 (m), 430 (m). $\mu_{eff} = 0.43\mu_B$.

[C$_6$H$_4$-*o*-NMe$_2$]$_3$Cr (4). A red solution of [C$_6$H$_4$-*o*-NMe$_2$]$_4$Cr$_2$ (2.7 g, 4.7 mmol) in toluene (1300 mL) containing 10 mL of THF was refluxed for 21 h. The color turned orange, and a black amorphous solid precipitated. The orange solution was filtered and cooled to −80 °C, upon which large light-orange crystals of **4** separated (0.6 g, 1.5mol, 32%). Anal. Calcd (Found) for $C_{24}H_{30}N_3Cr$: C, 69.88 (69.78); H, 7.33 (7.23); N, 10.19 (10.09); Cr, 12.60 (12.74). IR (Nujol mull, cm^{-1}, KBr): 1590 (m), 1550 (w), 1370 (s), 1300 (m), 1255 (s), 1245 (m), 1155 (m), 1145 (m), 1135 (w), 1120 (w), 1090 (m), 1010 (s), 975 (w), 925 (s), 770 (s), 740 (m), 725 (s), 690 (w), 630 (w), 520 (w). $\mu_{eff} = 3.73\mu_B$.

X-ray Crystallography. Complex 2. A suitable single crystal was selected in a drybox, glued on the top of a glass fiber, and mounted under nitrogen into the cold nitrogen stream of a locally modified low-temperature unit of a CAD-4F Enraf-Nonius diffractometer. Unit cell dimensions and their standard deviations were determined from the setting angles of 22 reflections in the range 14.94° < θ < 20.48°. Crystal and/or instrumental instability was monitored by measuring the intensities of three reference reflections every 3 h of X-ray exposure time; there was no indication of crystal decomposition. A 360° ψ-scan for the reflection close to axial (320) showed an intensity variation up to 4% about the mean value. The net intensities of the data were corrected for the scale variation, Lorentz, and polarization effects, but not for absorption. Standard deviations $\sigma(I)$ in the intensities were increased according to an analysis of the excess variance of the reference reflections. Variance was calculated on the basis of counting statistics, and the term (P^2P^2) ($P_{\text{(instability const)}} = 0.038$) was derived from the excess variance in the reference reflections. Equivalent reflections were averaged, resulting in 6269 reflections satisfying the $I \geq 2.5\sigma(I)$ criterion of observability. The structure was solveed by Patterson methods and subsequent partial structure expansion (SHELXS86).[18] The positions and anisotropic thermal parameters for the non-hydrogen atoms were refined with block-diagonal least-squares procedures (XTAL)[19] minimizing the function $Q = \sum_h[w(|F_o| - |F_c|^2]$. A subsequent difference Fourier synthesis gave all the hydrogen atoms. All the hydrogen atom coordinates and thermal parameters were refined isotropically. A final difference Fourier map did not show residual features. Crystal data and experimental details on data collection and refinement are given in Table I. The final atomic coordinates and isotropic thermal parameters are given in Table II. Molecular geometry data are given in Table V. All calculations were carried out on the CDC-Cyber 962-31 computer at the University of Groningen with the program packages XTAL[19] and EUCLID[20] (calculation of geometric data) and an extended version of the program PLUTO[21] (preparation of the illustrations).

Table II. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for 2

atom	*x*	*y*	*z*	U_{eq}[a] (Å^2)
Cr(1)	0.00000 (0)	0.00000 (0)	0.00000 (0)	0.0145 (2)
N(1)	0.1102 (5)	0.1445 (5)	0.9446 (2)	0.019 (1)
N(2)	−0.1198 (5)	−0.1358 (5)	1.0555 (2)	0.019 (1)
N(3)	0.2669 (5)	−0.2668 (5)	0.9962 (2)	0.021 (1)
C(1)	0.0597 (6)	0.1170 (6)	1.0626 (2)	0.018 (1)
C(2)	−0.0037 (6)	0.1600 (6)	1.1185 (2)	0.020 (1)
C(3)	0.0515 (6)	0.2472 (6)	1.1493 (2)	0.023 (1)
C(4)	0.1743 (6)	0.2962 (6)	1.1256 (2)	0.024 (1)
C(5)	0.2374 (6)	0.2620 (6)	1.0706 (2)	0.022 (1)
C(6)	0.1816 (6)	0.1734 (6)	1.0401 (2)	0.020 (1)
C(7)	0.2499 (6)	0.1347 (6)	0.9804 (2)	0.021 (1)
C(8)	−0.0246 (6)	0.3315 (6)	0.9311 (2)	0.025 (1)
C(9)	0.1887 (6)	0.0732 (7)	0.8902 (2)	0.025 (1)
C(10)	−0.1451 (6)	−0.0327 (5)	0.9380 (2)	0.016 (1)
C(11)	−0.2133 (6)	0.0533 (6)	0.8835 (2)	0.019 (1)
C(12)	−0.3117 (6)	0.0069 (6)	0.8519 (2)	0.023 (1)
C(13)	−0.3488 (6)	−0.1241 (6)	0.8752 (2)	0.023 (1)
C(14)	−0.2910 (6)	−0.2082 (6)	0.9301 (2)	0.022 (1)
C(15)	−0.1914 (6)	−0.1641 (6)	0.9605 (2)	0.019 (1)
C(16)	−0.1257 (6)	−0.2580 (6)	1.0197 (2)	0.022 (1)
C(17)	−0.3009 (6)	−0.0069 (6)	1.0710 (2)	0.025 (1)
C(18)	−0.0212 (7)	−0.2381 (6)	1.1090 (2)	0.027 (1)
C(19)	0.3026 (6)	−0.3638 (6)	0.9530 (2)	0.021 (1)
C(20)	0.4547 (6)	−0.5214 (6)	0.9499 (2)	0.026 (1)
C(21)	0.5747 (6)	−0.5868 (6)	0.9943 (2)	0.023 (1)
C(22)	0.5388 (6)	−0.4903 (6)	1.0394 (2)	0.024 (1)
C(23)	0.3858 (6)	−0.3317 (6)	1.0385 (2)	0.023 (1)

[a] $U_{eq} = {}^1/_3\sum_i\sum_jU_{ij}a^*_ia^*_ja_i{\cdot}a_j$.

Complex 3. The cell parameters and orientation matrix were obtained from the least-squares refinement of 22 reflections in the range 10.32° < θ < 17.34°. The space group was obtained from the systematic absence and was checked for higher symmetry. The Patterson map showed three highest peaks of the same weight with distance vectors of 1.0, 1.6, and 1.9 Å, respectively, which were interpreted as disordered Cr atom positions. The disorder was modeled by assuming the Cr(1) and Cr(2) atoms were disordered over the positions defined by the 2-fold axis (0, *y*, $^1/_4$) with a 50% occupancy. Crystal and instrumental stabilities were monitored by measuring the intensities of three reference reflections measured every 3 h of X-ray exposure time. Data were corrected for scale variation, Lorentz, and polarization effects. No absorption corrections were applied. Standard deviations in the intensities based on counting statistics were increased according to an analysis of the excess variance of the three reference reflections. The average of the equivalent reflections resulted in 2588 reflections satisfying the $I \geq 2.5\sigma(I)$ observability criterion. The structure was solved by Patterson methods and subsequent partial structure expansion (SHELXS86).[18] The position coordinates and thermal parameters for non-hydrogen atoms were anisotropically refined with block diagonal least-squares procedures. Hydrogen atoms were located in difference Fourier maps and isotropically refined. Weights were introduced in the final cycle,

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(18) Sheldrick, G. M. SHELXS86. University of Gottingen, Gottingen, FRG, 1986. (Program for crystal structure solution)

(19) Hall, S. R., Stewart, J. M., Eds. XTAL2.6 User's manual. Universities of Western Australia and Maryland.

(20) Spek, A. L. The EUCLID package in *Computational Crystallography*; Sayre, D., Ed.; Clarendon Press: Oxford, UK, 1982; p 528.

(21) Meetsma, A. Extended version of the program PLUTO. University of Groningen, Groningen, The Netherlands (unpublished).

Table III. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for 3

atom	*x*	*y*	*z*	U_{eq}[a] (Å^2)
Cr(1)	0.07371 (9)	0.18153 (7)	0.25906 (5)	0.0135 (3)
Cr(2)	−0.07460 (9)	0.10380 (7)	0.25707 (5)	0.0143 (3)
N(1)	0.2138 (3)	0.0947 (2)	0.3326 (2)	0.0265 (9)
N(2)	−0.2046 (3)	0.1908 (2)	0.3280 (1)	0.0240 (9)
C(1)	0.0138 (5)	0.115 (3)	0.3266 (3)	0.053 (1)
C(2)	−0.0664 (5)	−0.0610 (3)	0.3521 (3)	0.058 (2)
C(3)	−0.0419 (4)	−0.1078 (3)	0.4133 (3)	0.036 (1)
C(4)	0.0682 (3)	−0.0839 (3)	0.4519 (2)	0.025 (1)
C(5)	0.1527 (3)	−0.0159 (3)	0.4270 (2)	0.023 (1)
C(6)	0.1238 (3)	0.0280 (2)	0.3655 (2)	0.022 (1)
C(7)	0.2804 (4)	0.1615 (3)	0.3806 (2)	0.035 (1)
C(8)	0.3070 (9)	0.0329 (4)	0.3007 (4)	0.070 (3)
C(9)	−0.0037 (5)	0.2729 (3)	0.3275 (3)	0.047 (1)
C(10)	0.0796 (5)	0.3441 (3)	0.3553 (3)	0.058 (2)
C(11)	0.0639 (4)	0.3875 (3)	0.4181 (3)	0.037 (1)
C(12)	−0.0397 (4)	0.3628 (3)	0.4535 (2)	0.028 (1)
C(13)	−0.1288 (3)	0.2969 (3)	0.4262 (2)	0.023 (1)
C(14)	−0.1095 (3)	0.2550 (2)	0.3640 (2)	0.0203 (9)
C(15)	−0.2681 (4)	0.1231 (3)	0.3734 (2)	0.031 (1)
C(16)	−0.3004 (7)	0.2556 (4)	0.2950 (4)	0.060 (2)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a^*_ia^*_ja_i{\cdot}a_j$.

Table IV. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for 4

atom	*x*	*y*	*z*	U_{eq}[a] (Å^2)
Cr	$^1/_3$	$^2/_3$	0.292	0.0260 (5)
N	0.3277 (9)	0.5060 (9)	0.4270 (12)	0.049 (3)
C(1)	0.2341 (9)	0.5068 (11)	0.1689 (14)	0.040 (3)
C(2)	0.2480 (9)	0.4345 (9)	0.2884 (16)	0.045 (3)
C(3)	0.1935 (11)	0.3106 (10)	0.2736 (18)	0.063 (4)
C(4)	0.1228 (13)	0.2563 (12)	0.131 (2)	0.076 (5)
C(5)	0.1098 (11)	0.3254 (15)	0.093 (19)	0.071 (5)
C(6)	0.1637 (9)	0.4472 (11)	0.0268 (14)	0.044 (3)
C(7)	0.2678 (13)	0.4702 (12)	0.5977 (15)	0.059 (5)
C(8)	0.4366 (10)	0.4950 (12)	0.4292 (15)	0.058 (4)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a^*_ia^*_ja_i{\cdot}a_j$.

giving a satisfactory convergence. Crystal data and experimental details on structure determination and refinement are given in Table I. Atomic coordinates are given in Table III. Relevant bond distances and angles are given in Table V. Neutral atom scattering factors were used with anomalous dispersion corrections. All calculations were carried out on the CDC-Cybers 962-31 computer at the University of Groningen with the program packages XTAL,[19] EUCLID[20] (calculation of geometric data), and an extended version of PLUTO[21] (preparation of illustrations).

Complex 4. X-ray data were collected for a rod-shaped crystal sealed in a Lindemann glass capillary on an Enraf-Nonius CAD4T diffractometer equipped with a rotating anode at 10 kW (graphite-monochromated Mo Kα radiation). Cell parameters were derived from SET4 setting angles of 25 reflections in the range $17 < 2\theta < 37°$ range. Intensities were corrected for *Lp* but not for absorption. The structure was solved by direct methods (SHELXS86)[18] and refined by full-matrix least-squares techniques (SHELX76)[22] to a final $R = 0.060$ for 573 reflections. Hydrogen atoms were introduced at calculated positions and refined with two common isotropic parameters. The absolute structure was tested by refinement of the inverted model, resulting in slightly higher *R* values. Neutral scattering factors were used,[23] corrected for anomalous dispersion.[24] Pertinent results on data collection and structure refinement are reported in Table I. Atomic coordinates are given in Table IV. Relevant bond distances and angles are given in Table V. Calculations were carried out on a DEC5000/Ultrix system. The program PLATON[25] was used for geometry calculations and the preparation of the thermal ellipsoid plot.

Table V. Selected Bond Distances (Å) and Angles (deg)

2			
Cr(1)–N(1)	2.186 (4)	Cr(1)–C(1)	2.154 (5)
Cr(1)–N(2)	2.193 (4)	Cr(1)–C(10)	2.152 (5)
Cr(1)–N(3)	2.366 (4)		
N(1)–Cr(1)–N(3)	91.0 (1)	C(1)–Cr(1)–N(1)	79.5 (2)
N(2)–Cr(1)–N(3)	91.1 (1)	C(1)–Cr(1)–C(10)	159.9 (2)
N(1)–Cr(1)–N(2)	177.9 (1)	C(10)–Cr(1)–N(3)	98.7 (2)
C(1)–Cr(1)–N(3)	101.4 (2)	C(10)–Cr(1)–N(2)	79.4 (2)
C(1)–Cr(1)–N(2)	100.2 (2)	C(10)–Cr(1)–N(1)	100.2 (2)
3			
Cr(1)–Cr(2)	1.887 (1)	Cr(1)–N(2)	2.332 (3)
Cr(1)–N(1)	2.341 (3)	Cr(1)–C(9)	2.037 (5)
N(1)–Cr(1)–N(2)	96.43 (9)	N(1)–Cr(1)–Cr(2)	103.28 (9)
N(1)–Cr(1)–C(9)	160.07 (9)	N(2)–Cr(1)–Cr(2)	102.53 (9)
4			
Cr–N	2.286 (10)	Cr–C(1)	2.037 (12)
C(1)–Cr–N	85.0 (4)	N–Cr–N(a)	100.2 (4)
N–C(2)–C(1)	11.6 (9)	N–Cr–C(1a)	97.9 (5)
Cr–N–C(2)	85.2 (6)	C(1)–Cr–C(1a)	99.3 (5)

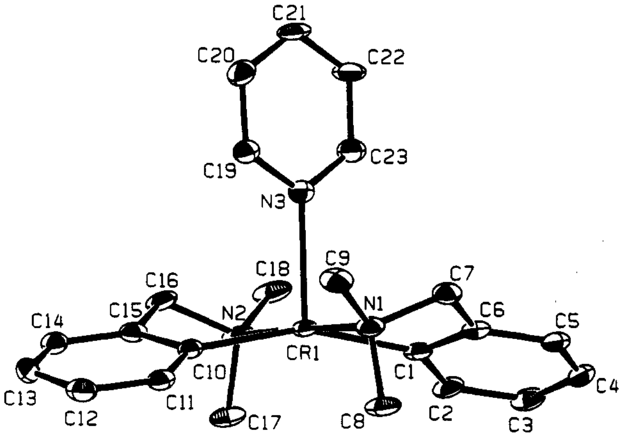
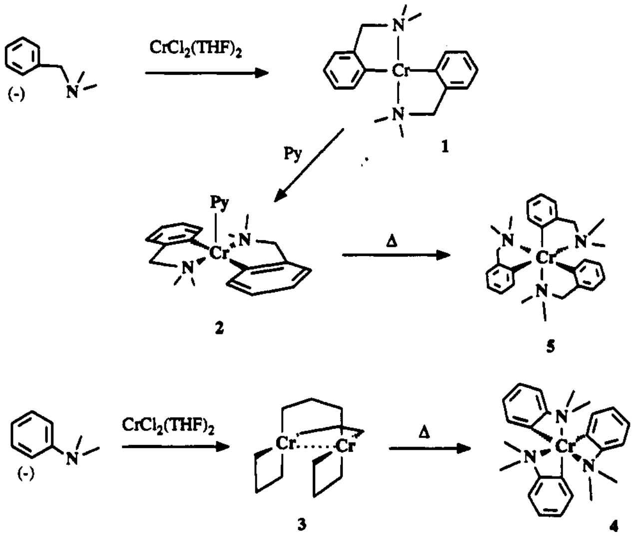


Figure 1. ORTEP plot of 2. Thermal ellipsoids are drawn at the 50% probability level.

Scheme I



Results

The reaction of $CrCl_2(THF)_2$ with 2 equiv of $[C_6H_4\text{-}o\text{-}CH_2NMe_2]Li$ led to the formation of bright-yellow needles which gave analytical results consistent with the formulation $[C_6H_4\text{-}o\text{-}CH_2NMe_2]_2Cr$ (1) (Scheme I). The magnetic moment ($\mu_{eff} = 4.69\mu_B$) suggests the square-planar geometry commonly found in monomeric d^4 Cr(II) com-

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[22] Sheldrick, G. M. SHELX76 Crystal Structure Analysis Package. University of Cambridge, Cambridge, England, 1976.

[23] Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321.

[24] Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

[25] Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

plexes. Unfortunately, attempts to grow crystals suitable for X-ray analysis have been frustrated due to the unfavorable crystal habit. Further reaction of 1 with pyridine produced a red solution, and red crystals of $[C_6H_4\text{-}o\text{-}CH_2NMe_2]_2Cr(py)$ (2) were isolated in good yield upon cooling. The crystal structure of 2 has been determined by X-ray analysis. The overall geometry may be described in terms of distorted square-based pyramid, with the two chelating aryl groups and the chromium atom defining the basal plane and one molecule of pyridine situated on the axial position. In analogy with the isostructural pyramidal $(pyrrolyl)_2Cr(py)_3$[26] the Cr–N distance formed by the axial pyridine molecule is rather elongated [Cr–N(3) = 2.366 (4) Å]. Conversely, the Cr–N distances formed by the two amino groups [Cr–N(1) = 2.186 (4) Å, Cr–N(2) = 2.193 (4) Å] and the Cr–C distances [Cr–C(1) = 2.154 (5) Å, Cr–C(10) = 2.151 Å] are normal. While the two amino groups are linearly placed trans to the chromium atom [N(1)–Cr–N(2) = 177.9 (1)°], the angle subtended at chromium by the two aryl groups is significantly bent [C(1)–Cr–C(10) = 159.9 (2)°]. Therefore, the coordination geometry of the chromium atom can also be regarded as a severely distorted trigonal bipyramid. The bending of the phenyl–Cr–phenyl axis is rather curious since the major steric interaction can be expected between the axial pyridine and the two Me_2N groups. We believe that the bending is probably caused by geometry optimization of the five-membered rings formed by the two chelating $C_6H_4\text{-}o\text{-}CH_2NMe_2$ ligands.

In analogy with the isostructural $(pyrrolyl)_2Cr(py)_3$,[26] the magnetic moment of complex 2 ($\mu_{eff} = 2.57\mu_B$) is consistent with a d^4 low-spin electronic configuration.

The reaction of $CrCl_2(THF)_2$ with 2 equiv of $[C_6H_4\text{-}o\text{-}NMe_2]Li$ proceeds in a similar manner, forming the dinuclear $[C_6H_4\text{-}o\text{-}NMe_2]_2Cr_2$ (3). Analytical results are in agreement with the proposed formulation, while the low residual paramagnetism ($\mu_{eff} = 0.43\mu_B$) typical of the lantern-type Cr(II) complexes suggests a dimeric structure with a considerable electronic coupling between the two metal centers.

The structure of 3 has been confirmed by X-ray analysis. The unit cell consists of discrete dimeric units. The coordination geometry of each chromium atom is square pyramidal with the basal plane defined by two nitrogen and two carbon atoms from four molecules of ligand, and the apical position occupied by the second chromium atom. Two of the four $C_6H_4\text{-}o\text{-}NMe_2$ ligands on the same side of the dimetallic unit adopted the typical three-center chelating bonding mode between two chromium atoms. Conversely, the other two work as normal chelating ligands with the two donor atoms coordinated to the same metal atom. In spite of the considerably different bonding modes, the Cr–N and Cr–C bond distances formed by the bridging and nonbridging ligands are comparable [Cr(1)–N(1) = 2.341 (3) Å, Cr(1)–N(2) = 2.332 (3) Å, and Cr(1)–C(1) = 2.051 (5) Å, Cr(1)–C(9) = 2.037 (5) Å]. The angles subtended at the central atom of the chelating ligand are also very similar in the two differently bonded chelating ligands [C(1)–C(6)–N(1) = 113.1 (3)°, C(9)–C(14)–N(2) = 113.2 (3)°], suggesting that the two different bonding modes (bridging–chelating and chelating) do not imply any particular distortion in the internal geometry of the ligand. The value of the Cr–Cr distance [Cr(1)–Cr(2) = 1.883 (4) Å] collocates complex 3 in the class of the quadruply bonded complexes with a supershort Cr–Cr distance.

Both 2 and 3 have a moderate thermal stability since reflux in toluene formed the corresponding Cr(III) species $[o\text{-}Me_2NC_6H_4]_3Cr$ (4) and the previously reported $(o\text{-}Me_2NCH_2C_6H_4)_3Cr$ (5),[12] respectively, together with small amount of grey tarry solid.

The crystal structure of 4 has confirmed the expected monomeric nature.[27] The molecule consists of discrete octahedrally distorted monomers with six donor atoms from three molecules of ligand defining the coordination octahedron. The three molecules of ligand impose an overall propeller-shaped geometry on the molecule [N–Cr–C(1) = 85.0 (4)°]. The angle subtended at the central atom of the ligand [N–C(2)–C(1) = 111.6 (9)°] compares well with those of complex 3, indicating once more that the different mode of ligation does not significantly affect the normal geometry of the ligand. The Cr–N and Cr–C distances [Cr–N = 2.286 (10) Å, Cr–C(1) = 2.037 (12) Å] are normal.

The magnetic moment of 4 ($\mu_{eff} = 3.73\mu_B$) is as expected for a monomeric d^3 Cr(III) octahedral complex.

Discussion

The removal of the CH_2 group in $C_6H_4CH_2N(CH_3)_2$ to form $C_6H_4N(CH_3)_2$ introduces two major modifications. First of all, the four-atom bite is now reduced to three which, when adopting the normal chelating mode, can form only a strained four-membered ring with the transition metal. The second major modification is the introduction of electronic conjugation between the two donor atoms, which is probably important for establishing efficient magnetic exchanges between the two chromium atoms of dimeric units.

The supershort Cr–Cr distance of the corresponding dinuclear 3 [Cr–Cr = 1.88 (1) Å] is in line with the wide pyramidality angle (average $\alpha = 96.02°$) formed by the four ligand donor atoms with the intermetallic axis (calculated Cr–Cr = 1.88). Conversely, an average α angle of 84.5° can be observed in the monomeric 2, which, according to the Hoffman equation, should correspond to a Cr–Cr distance of about 2.6 Å in the hypothetical $[Mz_2CrPy]_2$ (Mz = $o\text{-}Me_2NCH_2C_6H_4$) dimer. However, complex 2 is pyramidal and monomeric, and if we assume that a significant attraction force between two pyramidal or square-planar Cr(II) atoms does really exist and is responsible for the formation of unusually short metal–metal multiple bonds capable of holding together Cr_2 units, then a legitimate question arises about which factors in complex 2 inhibited the formation of both dimeric structure and Cr–Cr bond.

The monomeric nature of 2 can only be explained by the existence of unfavorable steric repulsions between two monomeric units, able to prevent formation of Cr–Cr bonds. Conversely, the dimeric aggregation and the very short Cr–Cr distance of 3 might be ascribed to two main factors: the Cr–Cr quadruple bond and the binucleating ability of the three-center chelating ligand. Although there is a possibility that the Cr–Cr supershort distance is the result of the existence of a Cr–Cr multiple bond, it is doubtful that such a bond is the driving force for assembling dimeric units, since the energy profiles of Cr–Cr quadruple bonds are usually very shallow[28] and the bonds are paradoxically weak[4] and easily cleaved via coordination of Lewis bases.[4d,e,5] In this respect, it is worth noting that in a solution of pyridine even the nonbridged $[TAACr]_2$ is in equilibrium with the monomeric low-spin octahedral $TAACr(py)_2$,[5a] while $Me_8Cr_2Li_4$ can be cleaved simply via

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[26] Edema, J. J. H.; Gambarotta, S.; Meetsma, A.; van Bolhuis, F.; Spek, A. L.; Smeets, W. J. J. *Inorg. Chem.* **1990**, *29*, 2147.

[27] von Hein, F.; Tille, D. *Z. Allg. Anorg. Chem.* **1964**, *329*, 72.

[28] (a) Hall, M. B. *Polyhedron* **1987**, *6*, 679, and references cited therein. (b) Benard, M. *J. Am. Chem. Soc.* **1978**, *100*, 2354.

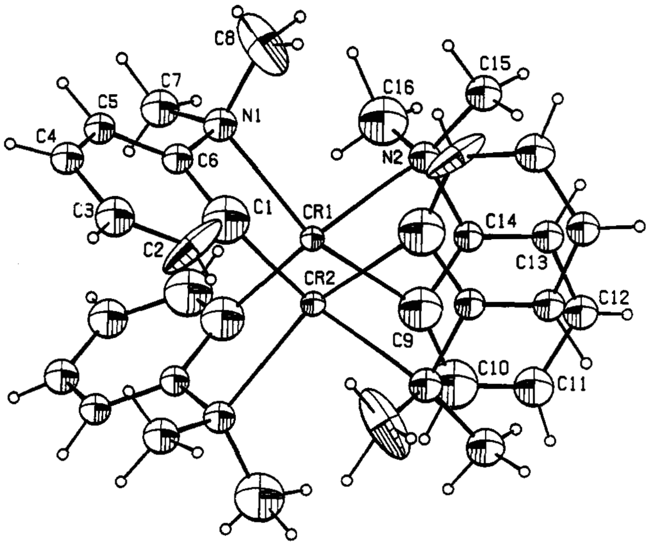

Figure 2. ORTEP plot of 3. Thermal ellipsoids are drawn at the 50% probability level.

modification of the coordination sphere of the alkali cation.[5b] Conversely, three-center chelating ligands show, within a variety of molecular arrangements and with the majority of metals, a great ability to form dimers.[29] In some cases, very short M–M contacts have been observed with these ligands even in the absence of any direct bonding interaction.[30] However, if the structural comparison between 2 and 3 clearly indicates that the presence of a three-center chelating ligand is a driving force for dimeric aggregation, then the monomeric structure of 4 (with three three-center chelating ligands) demonstrates that, with this type of ligand, dimeric aggregation may not necessarily be expected and that other factors, in addition to ligand geometry, may determine the nuclearity.

The dimeric structure of 3 and the monomeric one of 4 can be explained exclusively with the different electronic configurations (d^4 versus d^3) of the two oxidation states +II and +III, since both the ligand and the transition metal are just the same in the two complexes. A literature survey on the chemistry of the two oxidation states has shown that, in agreement with simple ligand field considerations, the two electronic configurations are characterized respectively by square-planar (or square-pyramidal) and octahedral coordination geometry.[31] Molecular models show that the assembling of dimeric structures with two octahedral Cr(III) atoms and six three-center chelating ligands is possible only through a considerable increase in steric hindrance and by imposing unusually distorted coordination geometries on two or more bridging donor atoms. Conversely, two square-planar or square-pyramidal Cr(II) atoms can be easily coupled together by these ligands with the classical lantern-type geometry. Whether the intermetallic distance is long, short, or supershort in these complexes would not be able to significantly affect the normal geometry of the ligand and the steric interactions within the molecule.

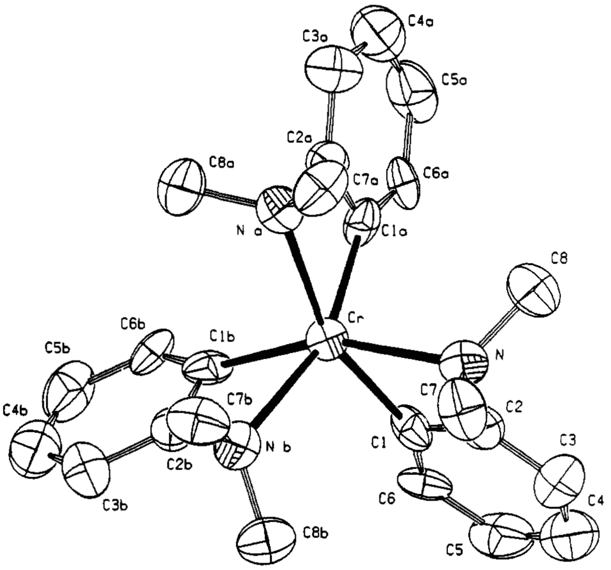

Figure 3. Thermal ellipsoid plot of 4 drawn at the 50% probability level.

In conclusion, these results have shown that the binucleating ability of three-center chelating ligands provides a unique driving force for assembling dimetallic unit, provided that the preferential coordination geometry imposed on the transition metal by the crystal field stabilization energy does not introduce unfavorable geometries in the dinuclear structure.

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Supplementary Material Available: Tables listing crystal structure data, atomic positional parameters, anisotropic thermal parameters, and complete bond distances and angles for 2–4 (29 pages). Ordering information is given on any current masthead page.

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(29) For some selected examples of other transition metals, see the following. (a) Vanadium: Edema, J. J. H.; Gambarotta, S.; Hao, S.; Bensimon, C. *Inorg. Chem.* **1991**, *30*, 2586. (b) Copper: Figgis, B. N.; Martin, R. L. *J. Chem. Soc. A* **1956**, 3837. (c) Titanium: Tarkhova, T. N.; Gladkikh, E. A.; Grishin, I. A.; Lineva, A. N.; Khalmalov, V. V. *Zh. Strukt. Khim.* **1976**, *17*, 1052. (d) Oro, L. A.; Ciriano, M. A.; Villaroya, B. E.; Tiripicchio, A.; Lahoz, F. J. *J. Chem. Soc., Dalton Trans.* **1985**, 1891. (e) Gold: Briant, C. E.; Hall, K. P.; Mingos, M. P. *J. Organomet. Chem.* **1982**, *229*, C5. (f) Platinum: Schagen, J. D.; Overbeek, A. R.; Schenk, H. *Inorg. Chem.* **1978**, *17*, 1938. (g) Tin: Bandoli, G.; Clemente, D. A.; Panattoni, C. *J. Chem. Soc., Chem. Commun.* **1971**, 311. (h) Iron: Tolman, W. B.; Bino, A.; Lippard, S. J. *J. Am. Chem. Soc.* **1989**, *111*, 8522. Turowski, P. N.; Armstrong, W. H. Roth, M. E.; Lippard, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 681. (i) Yttrium: Poncelet, O.; Hubert-Pfalzgraf, L. G.; Doran, J. C. *Polyhedron* **1990**, *9*, 1305. (j) Nickel: Corbett, M.; Hoskins, B. F.; McLeod, N. *Aust. J. Chem.* **1975**, *28*, 2377.

(30) (a) van Koten, G.; Noltes, J. G. *J. Organomet. Chem.* **1975**, *102*, 551. (b) Harder, S.; Boersma, J.; Brandsma, L.; van Henteren, A.; Kanters, J. A.; Bauer, W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 7802.

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