

# Ligand steric bulk: a neglected factor in the formation of Cr–Cr supershort contacts

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## Abstract

The ability of three center chelating ligands to form dichromium units and to enforce short and very short Cr–Cr contacts is examined in a consistent series of cyclohexyl amidinate chromium complexes, with the aim of understanding the factors intrinsic in the nature of the bridging ligands which are able to promote or disfavor dinuclear aggregation and to determine the extent of intermetallic separation. The present study describing the crystal structures of the dinuclear  $[(\text{CyNC}(\text{H})\text{NCy})_2\text{Cr}]_2 \cdot \text{C}_6\text{H}_6$  (1) and mononuclear  $(\text{CyNC}(\text{CH}_3)\text{NCy})_2\text{Cr}$  (2),  $\{\text{CyNC}[\text{Ph}(o\text{-CH}_2\text{NMe}_2)]\text{NCy}\}_2\text{Cr} \cdot 2\text{THF}$  (3) and  $[(\text{Me}_3\text{Si})\text{NC}(\text{Ph})\text{N}(\text{SiMe}_3)]_2\text{Cr}$  (4) indicates that the steric interaction between the lateral cyclohexyl and the central amidinate group is capable of determining the nuclearity (monomeric versus dimeric) and probably the extent of intermetallic separation. Crystal data are as follows: 1:  $\text{C}_{52}\text{H}_{84}\text{N}_8\text{Cr}_2 \cdot \text{toluene}$ ,  $M = 1017.41$ , monoclinic,  $P2_1/c$ ,  $a = 13.682(5)$ ,  $b = 17.446(3)$ ,  $c = 24.521(3)$  Å,  $\beta = 90.02(5)^\circ$ ,  $V = 5853(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = -30$  °C, Mo  $K\alpha$ ,  $R = 0.104$ ,  $R_w = 0.077$  for 4030 reflections out of 10319 unique; 2:  $\text{C}_{28}\text{H}_{50}\text{N}_4\text{Cr}$ ,  $M = 494.73$ , orthorhombic,  $Prma$ ,  $a = 8.104(1)$ ,  $b = 26.572(4)$ ,  $c = 12.533(2)$  Å,  $V = 2699(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = -157$  °C, Mo  $K\alpha$ ,  $R = 0.054$ ,  $R_w = 0.069$  for 1580 reflections out of 2752 unique; 3:  $\text{C}_{44}\text{H}_{68}\text{N}_6\text{Cr} \cdot 2\text{THF}$ ,  $M = 853.16$ , triclinic,  $P\bar{1}$ ,  $a = 12.293(5)$ ,  $b = 20.437(5)$ ,  $c = 11.071(4)$  Å,  $\alpha = 94.55(3)$ ,  $\beta = 111.72(3)$ ,  $\gamma = 73.86(3)^\circ$ ,  $V = 2481(1)$  Å<sup>3</sup>,  $Z = 2$ ,  $T = -157$  °C, Mo  $K\alpha$ ,  $R = 0.093$ ,  $R_w = 0.081$  for 6492 reflections out of 8710 unique.

## Introduction

Historically, the chemistry of the Cr–Cr multiple bond began with the preparation, reported in the early 1960s by Hein and Tille, of an almost diamagnetic divalent dichromium species supported by a three-center chelating ligand [1]. The correct formulation and the presence of a Cr–Cr metal bond was correctly postulated on the basis of analytical and magnetic data. Subsequent X-ray work [2] on a closely related complex demonstrated the existence of the shortest Cr–Cr contact ever found, thus giving strong credit to the initial proposal of the existence of a direct Cr–Cr bond of high multiplicity and also giving the legitimate expectation that these bonds might be strong. Since then, the discovery of Cr–Cr supershort quadruple bonds has marked a milestone in coordination chemistry and boosted interest in the preparation, characterization and chemical reactivity of this unique functionality [3]. As a result of considerable research activity in this field, M–M multiple bonds are today widely documented across the Periodic Table [4], and a rich and diversified chemical reactivity has been discovered [5].

While very short M–M quadruple bonds are commonly encountered in the chemistry of divalent Mo and W with [6] and without bridging ligands [7], the dozens of examples of quadruply bonded dichromium systems reported in the literature to date [8] are invariably stabilized by bridging ligands, as a rule with only one exception [9]. In addition, apart from a very few cases [10], the bridging ligands employed for the stabilization of quadruply-bonded dichromium units always possess the unique three-center chelating geometry characteristic of the carboxylates and of the allylic systems in general. Since it has been proved that these ligands are able to work as binucleating ligands [11] and to enforce very short metal–metal contacts even in the absence of an M–M bond [12], the possibility that short and even supershort Cr–Cr contacts might be artifacts of the unique bridging ability of three-center chelating ligands cannot be ruled out a priori [13]. This idea, which at first glance seems to contradict with the experimental evidence, is however corroborated by theoretical work [14] which has determined that Cr–Cr quadruple bonds are so extremely weak that they are likely unable to hold together a dimetallic frame in the absence of bridging interactions: a Cr–Cr quadruple bond is expected to be as weak as a Cr–Cr single bond

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[15]. Although theoretical work on this topic [16] has been rather controversial the striking weakness of Cr–Cr quadruple bonds has been further confirmed by experimental studies on the reversible cleavage of the Cr(II) carboxylates in solution [17]. Such a chemical paradox has been interpreted in terms of a small singlet/triplet gap, where low-lying antibonding orbitals are thermally populated by electrons from high-energy metal–metal bond orbitals [18]. Unfortunately, this elegant theoretical argument clashes with the idea of a chemical bond commonly regarded as an electronic mechanism able to generate both stabilization energy and a significant attraction force between two atoms. A tantalizing question thus arises about how a paradoxically weak bond could yet be so extremely short. In other words, if a Cr–Cr quadruple bond is so extremely weak, how can the intermetallic distance possibly be so extremely short?

We believe that the definition of a chemical bond is not appropriate for very short Cr–Cr contacts, an efficient magnetic coupling, either through space (antiferromagnetic) or ligand (superexchange) or a combination of both, is likely a more adequate description of the intermetallic interaction. This proposal is supported by the recently described reversible cleavage of  $\text{Me}_8\text{Cr}_2\text{Li}_4$  [19] long regarded as a rare example of a supershort Cr–Cr quadruple bond without bridging ligands. Since the cleavage proceeds without modification of the coordination sphere of the chromium atom, this result has demonstrated that no significant Cr–Cr bond exists in  $\text{Me}_8\text{Cr}_2\text{Li}_4$  despite the exceedingly short Cr–Cr distance. By way of contrast, successful characterization of the first dichromium unit supported by a macrocyclic ligand  $[(\text{TAA})\text{Cr}]_2$  (TAA = tetraazaannulene) [9] and without bridging ligands, has shown that formation of a significant Cr–Cr multiple bond is indeed possible, provided that transition metal can be ‘pyramidalized’ with a ligand of suitable geometry [20]. Although these two results appear to contradict each other, the reversible cleavage of  $[(\text{TAA})\text{Cr}]_2$  obtained via coordination of pyridine [21] has confirmed that the very short Cr–Cr quadruple bond is a weak interaction even in this unbridged dimer.

While the intriguing weakness of Cr–Cr multiple bonds has so far been clearly demonstrated only in the two above-mentioned systems and carboxylates [17], it remains more difficult to verify if the large family of lantern-type systems with supershort Cr–Cr contacts is also subject to the same type of behavior. Although the idea that no Cr–Cr bonds exist in the lantern-type systems has been recently dismissed as ‘obviously inadmissible’ [18], yet three-center chelating ligands undoubtedly possess a unique ability to assemble dimetallic units with and without M–M bonds all across the Periodic Table [11, 12]. Moreover, these ligands are capable of

performing efficient magnetic couplings even when the Cr–Cr distances are elongated up to 2.6 Å [22]. Therefore, with the aim of understanding the nature of the Cr–Cr interaction in lantern-type compounds, we have undertaken a study of selected lantern-type systems where the bite of the three-center chelating ligand [23], its electronic configuration [24], the nature of the donor atom, its steric hindrance, and the magnetic properties of the final complex are evaluated in a consistent series of compounds and correlated to the nuclearity (monomeric versus dimeric).

The purpose of the present study is to verify the possibility that the ability of three-center chelating ligands both to assemble dinuclear structures and to promote formation of short M–M contacts, resides in a very favorable ‘bite’, regarded not as the distance between the two donor atoms, but instead as the normal orientation of the ligand orbitals used for ligating the two transition metals. Since the ligand steric hindrance is the factor which more effectively may affect the ‘bite’, we have examined how the steric hindrance of three-center chelating ligands determines the nuclearity of chromium complexes. For this purpose, we have prepared and characterized a novel series of monomeric and dimeric cyclohexylamidinate derivatives  $\text{CyN}=\text{C}(\text{R})-\text{NCy}$  (R = H, Me, Ph,  $\text{CH}_2\text{Ph}$ ). The choice of this particular ligand was suggested by: (i) the well established ability of the aromatic congeners to favor the formation of very short M–M contacts with many different metals [25] and (ii) the possibility of making available an ample series of ligands, where the large steric hindrance introduced by the two cyclohexyl groups may be increased or released via replacement of the R group located on the amidinate carbon atom.

## Experimental

All operations were performed under an inert atmosphere in a nitrogen-filled dry-box (Vacuum Atmosphere) or by using standard Schlenk techniques.  $\text{CrCl}_2(\text{THF})_2$  [26],  $\{[\text{Me}_3\text{Si}]\text{N}\}_2\text{C}(\text{Ph})\}\text{Li}$  [27],  $(o\text{-Me}_2\text{NCH}_2)\text{PhLi}$  [28] and  $\text{CyN}(\text{H})-\text{C}=\text{NCy}$  [29] were prepared according to published procedures.  $\text{MeLi}$ ,  $\text{PhLi}$  and  $(\text{Me}_3\text{Si})_2\text{NLi}$  were prepared following standard procedures.  $\text{CyNCNCy}$  (*i*-Pr) $\text{NCN}(\text{i-Pr})$  and  $(\text{Me}_3\text{Si})_2\text{NH}$  (Aldrich) were used as received. NMR spectra were recorded on a Varian Gemini 200 at room temperature and on a 400 Varian spectrometer at variable temperatures, by using samples sealed in vacuum in NMR tubes prepared in a dry-box. Solvents for NMR spectroscopy were dried over the appropriate drying agent, vacuum transferred into appropriate ampoules and stored inside a dry-box. IR spectra were recorded on a Perkin-Elmer 283 instrument from Nujol

mulls prepared in a dry-box. Samples for magnetic susceptibility measurements were weighed inside a dry-box equipped with an analytical balance, and sealed into calibrated tubes. Magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room temperature. The magnetic moment was calculated following standard methods [30], and corrections for underlying diamagnetism were applied to data [31].

$[CyN=C(H)-NCy]Li \cdot C_6H_{14}$

A solution of  $CyN=C(H)-N(H)Cy$  (13.3 g, 64 mmol) in hexane (160 ml) was treated with a solution of *n*-BuLi in hexane (26 ml, 2.5 M, 64 mmol) at room temperature. The resulting light yellow solution was allowed to stand at room temperature overnight upon which colorless crystals of  $[CyN-C(H)-NCy]Li$  precipitated (11.0 g, 51 mmol, 80%). IR (nujol mull, KBr,  $cm^{-1}$ ): 1565(s), 1330(s), 1295(s), 1260(m), 1230(m), 1150(w), 1100(m), 1060(m), 1030(w), 990(w), 890(m), 840(m), 805(m), 785(w), 720(m), 600(w), 580(m).  $^1H$  NMR ( $C_6D_6$ , 200 MHz, 25 °C)  $\delta$ : 8.38 (s, 1H, C-H formamidinic), 2.81 (pseudoquintet, 2H, cyclohexyl), 1.89 (m, 4H, cyclohexyl), 1.71–1.24 (series of lines, 16H, cyclohexyl).

$[CyN=C(CH_3)-NCy]Li(THF)$

A solution of  $CyNCNCy$  (2.1 g, 10.2 mmol) in THF (30 ml) was cooled to  $-30$  °C and then treated with a solution of MeLi in ether (7.3 ml, 1.4 M, 10.2 mmol). After standing at room temperature overnight, the resulting yellowish solution was concentrated to a small volume (20 ml) by evaporation of the solvent *in vacuo*, filtered and allowed to stand at  $-30$  °C overnight, upon which colorless crystals of  $[CyN=C(CH_3)-NCy]Li(THF)$  precipitated (2.4 g, 8.0 mmol, 78%). IR (nujol mull, KBr,  $cm^{-1}$ ): 1510(vs), 1410(s), 1350(s), 1305(w), 1250(m), 1160(m), 1130(w), 1070(sh), 1050(s), 1020(w), 990(m), 1030(w), 990(w), 950(w), 920(m), 890(m), 840(w), 820(w), 795(m), 720(w), 650(m), 600(m), 570(m), 495(br), 460(w), 410(m).  $^1H$  NMR ( $C_6D_6$ , 200 MHz, 25 °C)  $\delta$ : 3.57 (m, 4H, THF), 3.20 (broad s, 2H, cyclohexyl), 1.99 (m, 4H, cyclohexyl), 1.88 (m, 3H,  $CH_3$ ), 1.80–1.45 (series of multiplets, cyclohexyl), 1.38 (m, 4H, THF).

$\{CyN-C[Ph(o-CH_2NMe_2)-NCy]Li(Et_2O)$

A solution of  $CyNCNCy$  (9.2 g, 44.7 mmol) in ether (200 ml) was treated at room temperature with freshly prepared (*o*- $Me_2NCH_2$ )PhLi (6.3 g, 44.7 mmol). The resulting yellowish solution was allowed to stand at room temperature overnight. The solution was concentrated to a small volume by evaporation of the solvent *in vacuo* at room temperature. The resulting solution was filtered and cooled to  $-30$  °C, upon which colorless crystals of  $\{CyN-C[Ph(o-CH_2NMe_2)-NCy]-$

$Li(Et_2O)$  precipitated (17 g, 40.4 mmol, 90%). IR (nujol mull, KBr,  $cm^{-1}$ ): 1470(s), 1410(sh), 1380(w), 1355(m), 1310(m), 1235(s), 1170(s), 1150(m), 1110(s), 1060(s), 1030(s), 980(s), 945(w), 920(w), 885(m), 860(m), 840(m), 820(w), 800(m), 770(s), 750(m), 730(s), 660(m), 560(br), 500(m), 380(br).  $^1H$  NMR ( $C_6D_6$ , 200 MHz, 25 °C)  $\delta$ : 7.81, 7.55, 7.41, 7.23 (m, 4H, phenyl), 3.63 (s, 2H, benzyl), 3.29 (q, 4H,  $Et_2O$ ), 2.80 (m, 2H, cyclohexyl), 2.30 (s, 6H, Me), 2.10, 1.80, 1.55, 1.20 (m, cyclohexyl), 1.18 (t, 6H,  $Et_2O$ ).

$\{[CyN-C(H)-NCy]_2Cr\}_2 \cdot toluene$  (1)

A suspension of  $CrCl_2(THF)_2$  (1.96 g, 7.3 mmol) in toluene (50 ml) was stirred for 2 h at room temperature in the presence of  $[CyN-C(H)-NCy]Li$  (3.24 g, 15.1 mmol). The resulting deep yellow suspension was filtered at 80 °C to eliminate a gray solid and then allowed to cool slowly to room temperature. Orange air-sensitive crystals of **1** were obtained upon standing two days at room temperature (2.5 g, 2.7 mmol, 74%). IR (nujol mull, KBr,  $cm^{-1}$ ): 1590(vs), 1360(s), 1340(s), 1320(s), 1290(vs), 1250(s), 1230(sh), 1185(m), 1150(s), 1100(s), 1080(s), 1070(s), 1020(w), 990(w), 950(m), 880(s), 840(m), 780(w), 725(vs), 690(s), 510(s), 460(m), 425(s).  $^1H$  NMR ( $C_6D_6$ , 200 MHz, 25 °C)  $\delta$ : 8.43 (s, 4H, formamidine), 7.08 (pseudo quartet, 4H, toluene), 3.11 (pseudo quintet, 8H, cyclohexyl), 2.10 (s, 3H, toluene), 2.07 (pseudo d, 16H, cyclohexyl), 1.81 (pseudo d, 16H, cyclohexyl), 1.63 (pseudo d, 8H, cyclohexyl), 1.30 (m, 40H, cyclohexyl).

$[CyN-C(CH_3)-NCy]_2Cr$  (2)

A suspension of  $CrCl_2(THF)_2$  (1.82 g, 6.8 mmol) in THF (50 ml) was stirred for 2 h at room temperature in the presence of  $[CyN-C(CH_3)-NCy]Li(Et_2O)$  (3.22 g, 14.1 mmol). The resulting purple-red solution was filtered and concentrated to a small volume. Deep red air-sensitive crystals of **2** were obtained standing two days at room temperature (0.9 g, 1.8 mmol, 26%). IR (nujol mull, KBr,  $cm^{-1}$ ): 1510(s), 1370(sh), 1360(sh), 1345(sh), 1270(w), 1255(w), 1245(w), 1200(s), 1190(s), 1140(w), 1100(sh), 1090(s), 1075(sh), 1000(s), 960(w), 920(w), 900(m), 890(s), 870(w), 850(w), 830(m), 805(m), 785(w), 725(w), 660(s), 610(m), 575(m), 505(w), 480(w), 450(w), 410(s), 370(sh).  $\mu_{eff} = 4.75 \mu_B$ .

$\{CyN-C[Ph(o-CH_2NMe_2)]-NCy\}Cr \cdot 2THF$  (3)

A suspension of  $CrCl_2(THF)_2$  (0.97 g, 3.6 mmol) in THF (60 ml) was boiled for 2 min and stirred for 2 h at room temperature in the presence of  $\{CyN-C[Ph(o-CH_2NMe_2)]-NCy\}Li(THF)$  (3.53 g, 8.4 mmol). The resulting deep blue solution was filtered and concentrated to a small volume (20 ml). The mixture was boiled, filtered while hot, and allowed to cool slowly to room temperature. Deep blue air-sensitive crystals of **3** were

obtained upon standing two days at room temperature (1.2 g, 1.6 mmol, 45%). IR (nujol mull, KBr,  $\text{cm}^{-1}$ )  $\nu$ : 2770(w), 1360(s), 1345(m), 1260(s), 1215(m), 1175(w), 1150(w), 1115(w), 1080(s), 1030(s), 990(m), 940(w), 900(w), 890(w), 870(w), 850(w), 800(w), 775(s), 735(m), 720(w), 660(w), 550(w), 490(w).  $\mu_{\text{eff}} = 4.83 \mu_{\text{B}}$ .

#### $\{[Me_3Si]N\}_2C(Ph)\}_2Cr$ (**4**)

A solution of  $(Me_3Si)_2NLi$  (2.01 g, 12.0 mmol) in toluene (100 ml) was treated with PhCN (1.25 g, 12.0 mmol) at room temperature. After standing overnight at room temperature, the addition of  $CrCl_2(THF)_2$  (1.6 g, 6.0 mmol) to the mixture changed the color to purple-red. The mixture was boiled for a few minutes, stirred for 2 h at room temperature then subsequently filtered and concentrated to a small volume until crystalline material started to separate. The mixture was heated until the crystalline material redissolved, then filtered hot and allowed to cool slowly to room temperature. Subsequent standing at  $-30^\circ\text{C}$  for two days yielded dark pinkish-purple crystals of **4** (1.5 g, 2.7 mmol, 45%). IR (nujol mull, KBr,  $\text{cm}^{-1}$ )  $\nu$ : 1435(s), 1265(sh), 1245(s), 1175(w), 1080(w), 1005(m), 990(s), 925(w), 850(vs), 790(w), 765(s), 705(s), 605(w), 530(s), 450(w).  $\mu_{\text{eff}} = 4.66 \mu_{\text{B}}$ .

#### X-ray crystallography

Data were collected at a temperature of  $-160^\circ\text{C}$  using the  $\omega$ - $2\theta$  scan technique to a maximum  $2\theta$  value of  $50.0^\circ$  for a suitable air-sensitive crystal mounted on a glass fiber. Cell constants and orientation matrix were obtained from the least-squares refinement of 25 carefully centered high angle reflections. In the case of complex **1**, a monoclinic cell was obtained with twin peak deconvolution indexing routine carried out on a twin crystal measured at  $-160^\circ\text{C}$ . The structure was successfully solved in the space group  $P2_1/c$  although with high residues. Several other crystals measured at temperature above the transition phase ( $-30^\circ\text{C}$ ) invariably gave orthorhombic cells although the systematic absences clearly indicated a monoclinic system. The  $\beta$  angle of  $90^\circ$  is probably caused by a fracture in the crystal. A suitable single crystal was thus measured as monoclinic and the structure successfully solved and refined in the space group  $P2_1/c$ . The rather high values of the residuals are not surprising in the view of the poor observation/parameter ratio. Hydrogen atom positions were located but not refined. The intensities of three representative reflections were measured after every 150 reflections to monitor crystal and electronic stability. Data were corrected for Lorentz and polarization effects but not for absorption. The structures were solved by direct methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were located in the difference Fourier maps and refined

isotropically in the case of favorable observation/parameter ratio. The final cycle of full-matrix least-squares refinement was based on the number of observed reflections with ( $I > 2.5\sigma(I)$ ). Neutral atomic scattering factors were taken from Cromer and Waber [32]. Anomalous dispersion effects were included in  $F_{\text{calc}}$ . All calculations were performed using the TEXSAN package [33] on a Digital VAX station. Details on data collection and structure refinement are reported in Table 1. Selected bond distances and angles are given in Table 2. See also 'Supplementary material'.

#### Description of the crystal structures

##### Complex 1

The structure of the complex shows the typical dimeric arrangement (lantern-type) of the well-known quadruply-bonded complexes of dichromium (Fig. 1). The molecule is formed by a  $Cr_2$  unit bridged by four formamidinate groups. Each formamidinate ligand adopts the classical three-center chelating geometry where each of the two donor atoms of one ligand molecule binds one of the two metal centers, forming a five-membered ring with the  $Cr_2$  unit. In common with the other complexes reported in this work, the coordination geometry of the chromium atom is square planar ( $N1-Cr1-N3 = 173.8(5)$ ,  $N3-Cr1-N7 = 90.3(6)$ ,  $N1-Cr1-N7 = 89.4(6)^\circ$ ) with the chromium atom slightly elevated above the plane defined by the four nitrogen atoms ( $Cr2-Cr1-N$  angles ranging from  $93.1(3)$  to  $97.6(4)^\circ$ ). The  $Cr-Cr$  distance ( $Cr1-Cr2 = 1.913(3) \text{ \AA}$ ) places complex **1** in the family of the quadruply-bonded dichromium complexes with a supershort intermetallic contact. The  $Cr-N$  bonding distances are normal ( $Cr1-N1 = 2.06(1)$ ,  $Cr1-N3 = 2.06(1)$ ,  $Cr1-N5 = 2.06(1)$ ,  $Cr1-N7 = 2.03(1) \text{ \AA}$ ) and compare well with those of other monomeric and dimeric  $Cr(II)$  complexes. The five-membered metallacycles formed by the four ligands with the two chromium atoms are planar. The angles formed by the formamidinic carbon with the nitrogen donor atoms ( $N7-C46-N8 = 118(1)$ ,  $N3-C20-N4 = 119(1)$ ,  $N5-C33-N6 = 124(1)$ ,  $N1-C7-N2 = 122(2)^\circ$ ) are on average (av. angle =  $121^\circ$ ) larger than those of the monomeric species. The angles formed by the nitrogen donor atoms with the cyclohexyl rings and formamidinic carbon atoms (ranging from  $115(1)$  to  $120(1)^\circ$ ) are on average (av. angle =  $117^\circ$ ) smaller than in the case of the monomeric species as a result of a smaller steric hindrance. Short H...H contacts are observed between the formamidinic hydrogen atoms and some of the hydrogens of the cyclohexyl rings ( $H33...H28a = 1.89$ ,  $H46...H48b = 1.93$ ,  $H46...H41b = 2.01 \text{ \AA}$ ).

##### Complex 2

The molecule is monomeric with the chromium atom in the center of the rectangular plane

TABLE 1. Crystal data and structural analysis results for complexes 1–3

	1	2	3
Formula	C <sub>59</sub> H <sub>92</sub> N <sub>8</sub> Cr <sub>2</sub>	C <sub>28</sub> H <sub>50</sub> N <sub>4</sub> Cr	C <sub>52</sub> H <sub>84</sub> N <sub>6</sub> O <sub>2</sub> Cr
Formula weight	1017.41	494.73	853.16
Crystal system	monoclinic	orthorhombic	triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>Pnma</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	13.682(5)	8.104(1)	12.293(5)
<i>b</i> (Å)	17.446(3)	26.572(4)	20.437(5)
<i>c</i> (Å)	24.521(3)	12.533(2)	11.071(4)
$\alpha$ (°)			94.55(3)
$\beta$ (°)	90.02(5)		111.72(3)
$\gamma$ (°)			73.86(3)
<i>V</i> (Å <sup>3</sup> )	5853(3)	2699(1)	2481(1)
<i>Z</i>	4	4	2
Radiation (Mo K $\alpha$ ) (Å)	0.71069	0.71069	0.71069
<i>T</i> (°C)	–30	–157	–157
<i>D</i> <sub>calc</sub> (g cm <sup>–3</sup> )	1.155	1.217	1.142
$\mu$ <sub>calc</sub> (cm <sup>–1</sup> )	4.0	4.34	2.3
<i>R</i> <sub>F</sub> , <i>R</i> <sub>w</sub>	0.104, 0.077	0.054, 0.069	0.093, 0.081
<i>GOF</i>	5.72	3.34	5.08
Parameters	588	158	572
Observations	4030	1580	6492

TABLE 2. Selected bond distances (Å) and angles (°)

1	2	3			
Cr1–Cr2	1.913(3)	Cr1–N1	2.088(4)	Cr1–N1	2.122(4)
Cr1–N1	2.06(1)	Cr1–N2	2.078(4)	Cr1–N2	2.091(4)
Cr1–N3	2.06(1)	C1–N2	1.326(5)	N1–C1	1.325(6)
Cr1–N5	2.06(1)	N1–C15	1.331(5)	N2–C1	1.336(6)
Cr1–N7	2.03(1)	N1–C8	1.462(6)	N1–C11	1.451(6)
N1–C7	1.32(2)	N2–C2	1.475(6)	N2–C17	1.468(6)
N2–C7	1.33(2)	C1–C14	1.51(1)	N1–Cr1–N1a	179.9
N7–C46	1.31(2)	C15–C16	1.52(1)	N2–Cr1–N1	116.4(2)
N8–C46	1.31(2)	C8–N1–C15	122.1(4)	N1–C1–N2	113.0(4)
N1–C7–N2	122(2)	N1–C15–N1a	112.8(6)	C1–N1–C11	120.4(4)
N3–C20–N4	119(1)	C2–N2–C1	121.0(4)	C1–N2–C17	122.6(4)
N5–C33–N6	124(2)	N2–C1–N2a	112.2(6)	N2–Cr1–N1–C1	177.9(4)
N7–C46–N8	118(1)	N1–Cr1–N2	179.9(2)	N2–C1–N1–C11	0.5(3)
C7–N2–C8	117(1)	N1–Cr1–N1a	64.2(2)	H17...C2	2.48
C14–N3–C20	118(1)	N1–Cr1–N2a	115.9(1)	H11...C2	2.44
C20–N4–C21	115(1)	Cr1–N2–C1–N2a	6.4(6)		
H33...H28a	1.89	Cr1–N1–C15–N1a	7.2(6)		
H46–H48b	1.93	H3...H25	1.99		
H41b–H46	2.01	H1...H14	2.14		

(N1–Cr1–N2 = 179.9(2), N1–Cr1–N1a = 64.2(2), N1–Cr1–N2a = 115.9(1)°) defined by the four nitrogen donor atoms of the two acetamidinate ligands (Fig. 2). The Cr–N distances (Cr1–N1 = 2.088(4), Cr1–N2 = 2.078(4) Å) are very comparable with those of the other two monomeric complexes reported in this work. The two metallacycles formed by the two chelating ligands slightly deviate from planarity (Cr1–N1–C15–N1a = –7.2(6), Cr1–N2–C1–N2a = –6.4(6)°). The angles formed by the amidinic carbon atom (N1–C15–N1a = 112.8(6), N2–C1–N2a = 112.2(6)) with the two nitrogens and by the nitrogen atoms with the

rings and the amidinic carbon (C8–N1–C15 = 122.1(4), C1–N2–C2 = 121.0(4) Å) compare very well with those of the other monomeric complexes. The four cyclohexyl rings are perpendicular with respect to the plane of the metallacycle and parallel to each other. The distorted trigonal planar geometry of the nitrogen atoms (Cr1–N1–C8 = 145.3(3), Cr1–N2–C2 = 145.0(3)°) is also very similar to those of the other monomeric complexes, thus indicating that the steric interaction between the bulky cyclohexyl groups is comparable. As in the previous case, short non-bonding contacts are present between the hydrogen atoms of the methyl groups with the

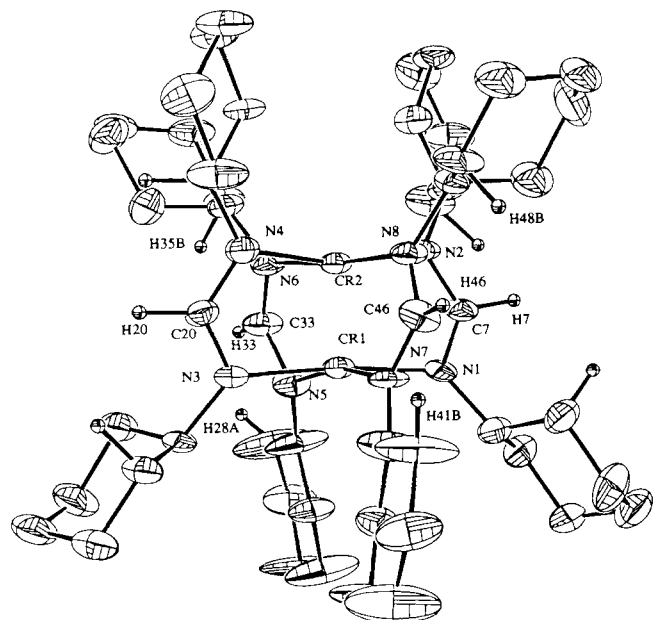


Fig. 1. ORTEP plot of 1. Thermal ellipsoids are drawn at the 50% probability level.

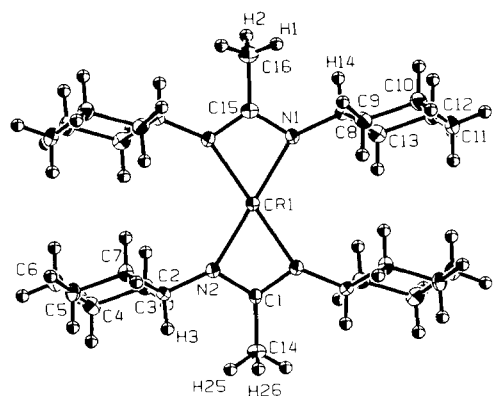


Fig. 2. ORTEP plot of 2. Thermal ellipsoids are drawn at the 50% probability level.

methyne hydrogen atoms of the cyclohexyl rings ( $H1\dots H14=2.14$ ,  $H3\dots H25=1.99$  Å).

### Complex 3

Two crystallographically independent, but chemically identical, molecules were found in the unit cell together with two disordered molecules of THF. The complex is monomeric (Fig. 3) and is formed by a square planar chromium atom placed in the center of the square plane defined by the four nitrogen atoms of the two benzamidine ligands ( $N1-Cr1-N2=116.4(1)$ ,  $N1-Cr1-N2a=63.6(2)$ ,  $N1-Cr1-N1a=179.9^\circ$ ). The Cr-N distances ( $Cr1-N1=2.122(4)$ ,  $Cr1-N2=2.091(4)$  Å) compare well with those of the above complex. The two metallacycles formed by the two chelating ligands are also planar ( $Cr1-N1-C1-N2=0.5(3)^\circ$ )

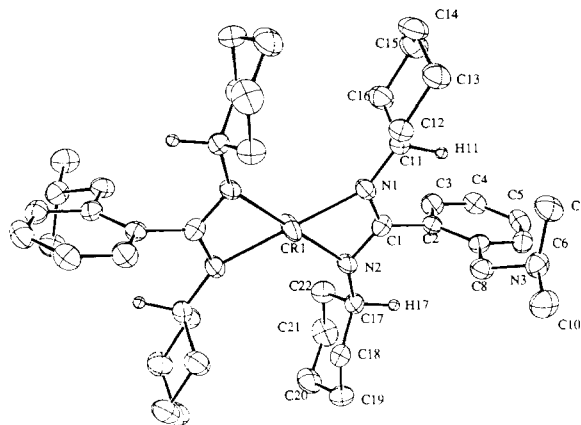
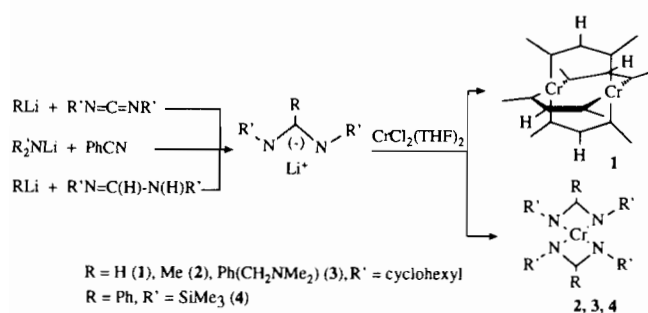


Fig. 3. ORTEP plot of 3. Thermal ellipsoids are drawn at the 50% probability level.

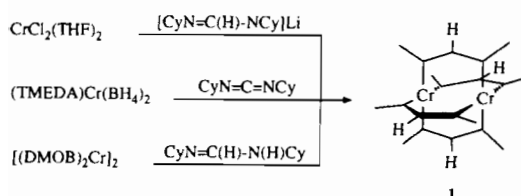
with similar C-N distances ( $C1-N1=1.325(6)$ ,  $C1-N2=1.336(6)$  Å) and angles ( $Cr1-N1-C1=91.1(3)$ ,  $N1-C1-N2=113.0(4)^\circ$ ). The planes bound by the phenyl and cyclohexyl rings are perpendicular to the metallacycle plane and to each other. The dimethylamino-methyl group placed in the *ortho* position of the two phenyl rings has the nitrogen atom pointing away from the chromium atom and does not cause any significant distortion or bending. The considerable steric interaction between the four cyclohexyl rings is shown by the wide angles formed by the distorted trigonal planar nitrogen atoms with the first carbon atom of the cyclohexyl ring and chromium ( $Cr1-N1-C11=148.3(3)$ ,  $Cr1-N2-C17=144.4(3)^\circ$ ). The angles formed by the nitrogen donor atoms with the cyclohexyl rings and the benzamidine carbon atoms ( $C1-N1-C11=120.4(4)$ ,  $C1-N2-C17=122.6(4)^\circ$ ) are very comparable to those of the other monomeric derivatives. Once again, a short intramolecular non-bonding contact can be observed between the hydrogen of the cyclohexyl rings and the carbon atoms of the phenyl ring ( $C2\dots H11=2.48$ ,  $C2\dots H17=2.44$  Å).

### Results and discussion

The lithium amidinate ligands used in this work were prepared by using three different synthetic procedures (Scheme 1). Addition reaction of several RLi (R = Me, Bz, Ph, Ph(*o*-CH<sub>2</sub>NMe<sub>2</sub>)) reagents to *N,N'*-dicyclohexylcarbodiimide, or of lithium amide to benzonitrile gave the corresponding series of alkyl cyclohexylamidinate lithium derivatives [ $R'N-C(R)-NR'$ ]Li (R = Me, Ph [34], Bz [34], Ph(*o*-Me<sub>2</sub>NCH<sub>2</sub>); R' = cyclohexyl, SiMe<sub>3</sub>). The cyclohexylformamidinate lithium salt was obtained from treatment of the *N,N'*-cyclohexylformamidine with *n*-BuLi in hexane. Preparation of the chromium complexes was rather straightforward and



Scheme 1.



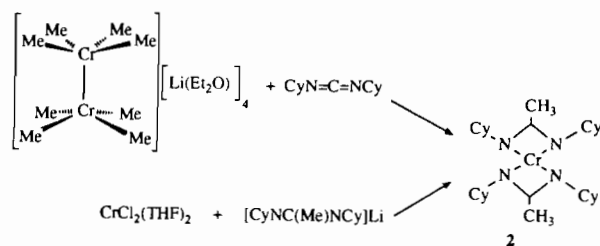
Scheme 2.

was carried out at room temperature via reaction of the appropriate lithium amidinate with CrCl<sub>2</sub>·THF<sub>2</sub> starting material in either toluene or THF.

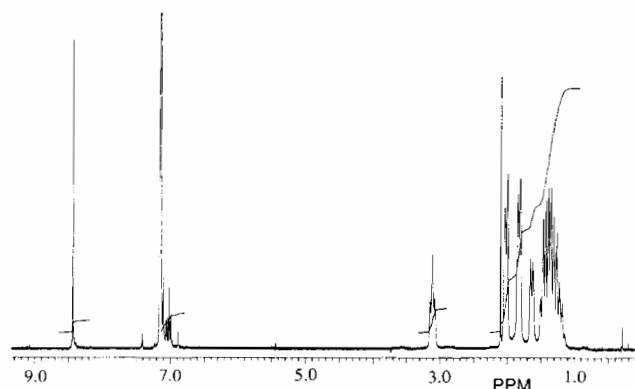
The nuclearity of **1** and **2** was not affected by that of the starting material. In fact, dimeric **1** was also obtained via an insertion reaction of the monomeric (TMEDA)Cr(BH<sub>4</sub>)<sub>2</sub> [35] with *N,N'*-cyclohexylcarbo-diimide (Scheme 2). The product was obtained in good yield although co-crystallization of the (BH<sub>3</sub>)<sub>2</sub>TMEDA\* byproduct made the purification of **1** via fractional crystallization difficult. Complex **1** was conveniently identified in this case on the basis of IR and NMR spectra. The same result was obtained using a dimeric starting material with a supershort Cr–Cr distance. By way of contrast, attempts to prepare a dimeric cyclohexyl acetamidinate complex by using a dinuclear starting material with a very short Cr–Cr contact yielded the same monomeric and paramagnetic **2** as obtained from the reaction of CrCl<sub>2</sub>(THF)<sub>2</sub> and lithium acetamidinate (Scheme 3).

As expected, the cyclohexylformamidinate complex **1** possesses the characteristic lantern-type geometry (Fig. 1) of complexes formed by three-center chelating ligands, and a very short Cr–Cr contact (Cr1–Cr1a = 1.913 Å) which assigns this species to the family of the quadruply-bonded systems. Furthermore, complex **1** is diamagnetic as indicated by both the well-resolved sharp <sup>1</sup>H NMR spectrum (Fig. 4) and the complete absence of line broadening and shifting as a

\*Crystal data: C<sub>6</sub>H<sub>22</sub>B<sub>2</sub>N<sub>2</sub>, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 5.552(1), *b* = 16.612(1), *c* = 5.915(2) Å, β = 113.30(5)°, *V* = 501.0(8) Å<sup>3</sup>, *Z* = 4, *T* = –160 °C, Mo Kα, *R* = 0.076, *R*<sub>w</sub> = 0.116 for 47 parameters and 467 reflections out of 643 unique.



Scheme 3.

Fig. 4. <sup>1</sup>H NMR spectrum of **1**.

function of the temperature in the range 5–80 °C. The perfect diamagnetism indicates that the singlet–triplet gap [36] is in this case not particularly small and that all the features which indicate the existence of a real Cr–Cr quadruple bond (short Cr–Cr contact and efficient electronic coupling) are present in complex **1**. However, we have recently observed that Me<sub>8</sub>Cr<sub>2</sub>Li<sub>4</sub>(THF)<sub>4</sub>, which has a Cr–Cr distance (Cr–Cr = 1.968(2) Å) only 0.038 Å longer than in the diamagnetic [(*p*-tolyl)-formamidinateCr]<sub>2</sub> [37] and 0.055 Å than in complex **1**, displays the characteristic small residual paramagnetism which is diagnosed by line broadening and significant chemical shift variation as a function of the temperature [36]. This indicates that the nature of the bridging ligand (and probably its electronic configuration) is the factor which, rather than the Cr–Cr distance alone, is capable of determining the extent of electronic coupling.

An interesting observation can be made by comparing the structure of **1** with that of the recently reported *p*-tolylformamidinate dichromium isostructural complex [37]. In spite of the fact that the steric hindrance introduced by the eight cyclohexyl groups of **1** is considerably larger than in the case of the aromatic homologue, the Cr–Cr distance of **1** is slightly but significantly shorter, not longer, as it would first be expected on the basis of the behavior of the multiple bonds between main group elements, where larger steric hindrance usually results in longer bonds. Furthermore, an increased steric interaction among the alkyl groups at

the periphery of the complex should pull the chromium atoms out of the coordination polyhedron in order to transform the square-pyramidal coordination geometry of the two metals into a more roomy square-planar. Therefore, should this trend be confirmed, it will imply that a larger encumbrance of the amidinic ligand, with resulting increased repulsion between the central group and the two lateral ones, will determine shorter intermetallic distances.

Closer analysis of the structural features of **1** has revealed that one hydrogen of each of the two cyclohexyl rings forms a short contact with the formamidinic hydrogen ( $H...H = 1.8\text{--}2.0 \text{ \AA}$ ). Comparable  $H...H$  non-bonding distances ( $H...H = 2.1 \text{ \AA}$ ) between the cyclopentadienyl rings of the two  $Cp_2Zr$  moieties of the  $[Cp_2ZrX]_2$  ( $X = I, PR_2$ ) dimers are responsible for introducing a destabilization energy estimated in the range of  $6 \text{ kcal mol}^{-1}$  but which rapidly increases up to  $38 \text{ kcal mol}^{-1}$  when the  $H...H$  distances become slightly shorter. These  $H...H$  repulsions are thought to be responsible for the considerable stretching of the  $Zr\text{--}Zr$  bonds (up to  $3.67 \text{ \AA}$  from a distance otherwise expected to be in the range of  $3.05 \text{ \AA}$ ) [38]. The crystal structure of the monomeric **2** has shown that short  $H...H$  non-bonding contacts ( $H...H = 1.99\text{--}2.14 \text{ \AA}$ ) are also formed by the methine H atoms of the two cyclohexyl rings with the methyl hydrogen atoms of the acetamidinate group. Replacement of the methyl group by a phenyl ring did not significantly modify the steric hindrance with respect to complex **2**. The complex is still monomeric and the shorter contact between the phenyl and cyclohexyl groups is realized between the hydrogen atoms of the cyclohexyl ring and three carbon atoms of the central phenyl ring ( $C...H = 2.44\text{--}2.48 \text{ \AA}$ ). Finally, the large increase in steric bulk introduced by the trimethylsilyl groups of complex **4** not only determines the monomeric structure (see ref. 39 and 'Supplementary material') but also results in a significant deviation of the core from the planarity, now forced to adopt a rather unusual flattened tetrahedral coordination geometry (Fig. 5).

The monomeric structures of **2**, **3** and **4** indicate that replacement of the formamidine hydrogen atom with

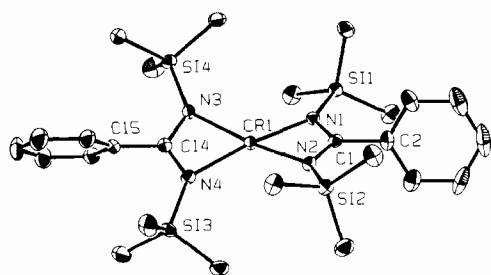
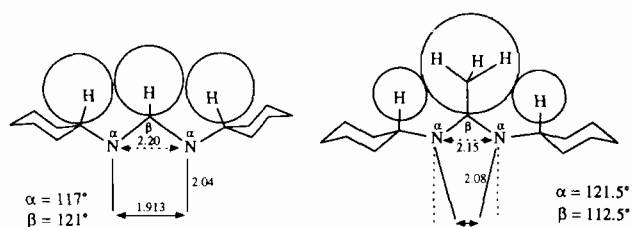


Fig. 5. ORTEP plot of **4**. Thermal ellipsoids are drawn at the 50% probability level.

alkyl groups (methyl, phenyl), and consequent increase of steric repulsion between the central amidinate group and the peripheral cyclohexyls, suppresses the ligand's ability to accommodate a dimetallic unit (Scheme 4). In the case of **2**, **3** and **4**, the ligands are obviously unable to overlap with the orbitals of the dimetallic unit and thus behave as normal mononucleating chelating ligands.

While the differences in bond distances in **1**, **2** and **3** are rather small (including the  $Cr\text{--}N$  and  $N...N$  distances) considering the completely different structures (monomeric versus dimeric), small but probably significant variations can be observed in the angles formed by the N atom with the ring and the amidinic group ( $\alpha$ ), and by the central amidinic carbon atom with the two donor atoms ( $\beta$ ) (Scheme 4). Unfortunately, only a few structures of amidinate complexes are available to enable a significant comparative structural analysis. However, the data reported in Table 3 indicate that the intermetallic separation and the nuclearity are related to the variation of steric interaction within the ligand as probed by the two  $\alpha$  and  $\beta$  angles. In particular, the  $\alpha$  angle, which in the series of complexes reported in Scheme 4 is directly determined by the intramolecular contacts between the ligand 'wings' and the central amidinic group, displays a trend which is rather consistent with the increase of steric crowding and the shortening of  $Cr\text{--}Cr$  distance. Conversely, the  $\beta$  angle shows a significant variation only in the monomeric complexes and it is therefore difficult to evaluate whether the narrowing of  $\beta$  is the cause or rather an effect of the monomeric structure.

It is obviously impossible to draw from these empirical observations a definitive conclusion on how the steric



Scheme 4.

TABLE 3. Comparative structural data

	a	<b>1</b>	b	c	<b>2</b>	<b>3</b>
$N...N$ ( $\text{\AA}$ )	2.29	2.19	2.27	2.27	2.15	2.25
$Cr\text{--}Cr$ ( $\text{\AA}$ )	1.93	1.91	1.84	1.84	monomer	monomer
$\alpha$ ( $^\circ$ )	116	117	118	118	121.5	121.5
$\beta$ ( $^\circ$ )	119	121	121	121	112.5	113

a = (*p*-tolyl)formamidinate [37]; b = (*i*-Pr)formamidinate [35]; c = (methyl)benzamidinate [40].



hindrance of the ligand does determine so spectacularly the existence of Cr–Cr supershort contacts. However, what has been demonstrated is that the steric interactions within the ligand, which have never before been regarded as a factor capable of determining the nuclearity and of promoting the formation of very short Cr–Cr contacts, does indeed determine the existence of the dichromium unit, since simple replacement of the hydrogen by a methyl group formed only monomeric species.

Although these argumentations are only qualitative, we believe that they deserve some attention. Should theoretical calculations confirm that the steric repulsions within the ligand are capable of determining not only the existence of the dimetallic unit but also the extent of the intermetallic separation (as these results seem to suggest), a significant progress will be achieved towards the understanding of the nature of the intermetallic interaction of Cr–Cr supershort contacts.

### Supplementary material

Tables listing atomic positional parameters, temperature factors, torsion angles, bond angles and distances, and hydrogen atom positional parameters associated with complexes **1**, **2**, **3** and **4** (93 pages) are available from the authors on request.

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