The Unusual Stability of Homoleptic Di- and Tetravalent Chromium Alkyls

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Reaction of $CrCl_3(THF)_3$ with 3 equiv of R−M [R = Me_3CCH_2 (**a**), Me_3SiCH_2 (**b**)] afforded either the previously reported tetravalent homoleptic R_4Cr (**1a**, **b**) [M = MgCl] or the unprecedented divalent and tetranuclear homoleptic $[R_2Cr]_4$ (**2b**) [M = Li]. Both types of compounds display a remarkable chemical inertness toward proton transfer agents but readily react with ethylene.

Introduction

The +4 oxidation state of chromium is not easily accessible[1] despite the great potential that may be envisioned for tetravalent chromium complexes as polymerization catalysts. Homoleptic, tetravalent chromium alkyls, first isolated and characterized by Wilkinson in the 1970s, can be prepared by reaction of $CrCl_3(THF)_3$ with an equivalent amount of the Grignard reagents.[1,2] These rare species seem to possess surprising chemical inertness including resistance to the attack of acidic aqueous solutions,[3] and thus some limitations may be anticipated in using them as starting materials. Besides the tetravalent derivatives, a few air-sensitive divalent chromium alkyls, both monomeric and dimeric, are known.[3,4] A unique case of tetranuclear divalent chromium cluster was reported by Smith.[4h,i] In the case of the dinuclear complexes, the diamagnetism or residual paramagnetism was taken as an indication for the existence of a debated Cr−Cr multiple bonding interaction.[5] Trivalent chromium tris-alkyl compounds remain almost unknown[6] apart from the cyclopentadienyl derivatives.[7]

What renders chromium organometallic complexes particularly appealing is the established ability of the Cr−C bond to perform ethylene polymerization[8] or selective trimerization,[9] which is being exploited for the

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commercial production of polymers or oligomers important to a wide range of industrial applications. Thus, it is at least strange that all the chromium organometallic complexes reported to date, including species grafted on solid state supports,[10] display only moderate catalytic activity. While information about catalytic activity of tetravalent chromium species is nonexistent, theoretical calculations have predicted that the d^2 electronic configuration may be particularly promising for a performing catalyst.[11]

Following our interest in homoleptic Cr alkyls,[3m,o,p] we have now revisited the preparation of two previously reported tetravalent d^2 chromium alkyls.[1,2] In particular, we were interested in probing their ability to work both as starting materials for further functionalization and as Ziegler–Natta catalysts. We were also interested in clarifying the reaction pathway through which a trivalent chromium salt may form a homoleptic tetravalent derivative.[1,2] Finally, we were interested in elucidating the nature of the Cr–Cr interaction in the unique $[R_2Cr]_4$ tetranuclear cluster[4h,i] and evaluating its stability.

For this work we have selected the Me_3SiCH_2 and neopentyl ligands because of their well-known ability to stabilize the M–C functionality for a variety of metals. These ligands are also known to be involved in the formation of carbenes and stabilized olefin polymerization catalyst precursors.[7g,8] Herein we describe our findings.

Experimental Section

General Procedures. All operations were performed under inert atmosphere by using standard Schlenk type techniques. $CrCl_3(THF)_3$,[12] $CrCl_2(THF)_2$,[13] $(CH_3)_3SiCH_2Li$,[1414] $(CH_3)_3CCH_2MgCl$,[15] and $(CH_3)_3SiCH_2MgCl$[16] were prepared according to published procedures. Infrared spectra were recorded on Mattson 9000 and Nicolet 750-Magna FTIR instruments from Nujol mulls prepared in a drybox. Samples for magnetic susceptibility measurements were weighed inside a drybox equipped with an analytical balance and sealed into calibrated tubes. Magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room temperature for **1a** and **1b** and at variable temperature for **2b** using a Quantum Design MPMS5S SQUID magnetometer at 1.0 T, in the temperature range 2–300 K. The sample was sealed in a 5 mm quartz tube in a drybox prior to transfer to the SQUID. Sample mass was determined by difference by breaking the tube after data collection. Background data on the cleaned, empty tube were obtained under identical experimental conditions. Corrections for the quartz tube and for underlying diamagnetism were applied to the data. Elemental analyses were carried out with a Perkin-Elmer 2400 CHN analyzer for **1**. Data for the X-ray crystal structure determinations were collected on a Bruker AX SMART 1k CCD diffractometer equipped with a Smart CCD area detector.

Preparation of $Cr(CH_2C(CH_3)_3)_4$ (1a). A filtered solution of freshly prepared $(CH_3)_3CCH_2MgCl$ (200 mL, 25.0 mmol, 0.125 M) in ether was added to a suspension of $CrCl_3(THF)_3$ (2.3 g, 6.1 mmol) in the same solvent (50 mL). The color of the solution initially changed to light orange-brown. After 30 min, a further color change to intense dark blue was observed. Upon stirring overnight at RT the color finally became maroon. The solvent was removed in vacuo, and the residue was suspended in hexane (150 mL). The mixture was stirred for 1 h at RT and filtered. The residue was washed with three portions of hexane (10 mL each). The combined hexane extracts were dried in vacuo, and the residue was sublimed in vacuo at 60 °C. X-ray-quality dark brown pyrophoric (**WARNING**) crystals of **1a** were thus obtained (yield 1.26 g, 3.7 mmol, 61%). Anal. Calcd (found) for $C_{20}H_{44}Cr$ (fw 336.57 g/mol): C 71.37 (72.04), H 13.18 (13.85). IR (Nujol mull, cm^{-1}): ν 1245 (vs), 1015 (w), 898 (vs), 730 (m), 693 (s), 681 (s), 612 (w), 536 (w), 515 (w). $\mu_{eff} = 2.91\ \mu_B$.

Preparation of $Cr(CH_2Si(CH_3)_3)_4$ (1b). The addition of a solution of freshly prepared $(CH_3)_3SiCH_2MgCl$ (200 mL, 30.0 mmol) in ether to a suspension of $CrCl_3(THF)_3$ (3.2 g, 8.5 mmol) in the same solvent turned the color dark purple. The mixture was stirred at RT for 1 h, then concentrated to dryness. The residue was suspended in hexane (150 mL), and the mixture was further stirred for 1 h at RT and filtered. The residue was washed with three portions of hexane (10 mL each). The combined hexane extracts were dried in vacuo, and the residue was sublimed in vacuo at 60 °C. X-ray-quality dark violet pyrophoric (**WARNING**) crystals of **1b** were obtained (yield 1.0 g, 2.5 mmol, 29%). Anal. Calcd (found) for $C_{16}H_{44}Si_4Cr$ (fw 400.87 g/mol): C 47.94 (47.88) H 11.06 (10.91). IR (Nujol mull, cm^{-1}): ν 1259 (vs), 1079 (vs), 1021 (s), 884 (s), 808 (vs), 744 (w), 694 (s), 612 (w), 536 (w), 516 (w). $\mu_{eff} = 2.89\ \mu_B$.

Preparation of $Cr_4(CH_2Si(CH_3)_3)_8$ (2b). Method A. A solution of $(CH_3)_3SiCH_2Li$ (1.7 g, 18.1 mmol) in hexane (100 mL) was added to a stirred suspension of $CrCl_3(THF)_3$ (1.8 g, 4.8 mmol) also in hexane (50 mL). The color of the slurry immediately changed to dark purple. The mixture was stirred at RT for 3 h, then filtered, and the residue was washed with three portions of hexane (10 mL each). The solution was concentrated to 50 mL and allowed to stand at −34 °C for 12 h. The color of the solution slowly turned dark brown upon standing at that temperature. X-ray-quality dark brown crystals of **2b** were formed, which were isolated by cold filtration, washed twice with precooled hexane (5 mL), and dried in vacuo (yield 0.9 g, 0.99 mmol, 83%).

Method B. A solution of $(CH_3)_3SiCH_2Li$ (1.0 g, 10.3 mmol) in hexane (100 mL) was added to a stirred suspension of $CrCl_2(THF)_2$ (1.4 g, 5.2 mmol) in the same solvent (50 mL) cooled to −50 °C. The color of the slurry immediately changed to dark brown. The mixture was allowed to warm to room temperature over a period of 2.5 h, then filtered, and the residue was extracted three times with hexane (10 mL each). The combined

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extracts were concentrated to 30 mL and allowed to stand at −34 °C. The resulting crystals were filtered while cold, washed twice with cold hexane (5 mL), and dried in vacuo (yield 0.7 g, 0.77 mmol, 60%). Anal. Calcd (found) for $C_{32}H_{88}Si_8Cr_4$ (fw 905.73 g/mol): C 42.44 (42.38) H 9.79 (9.69). IR (Nujol mull [cm^{-1}]): ν 1461 (vs), 1378 (s), 1325 (w), 1256 (m), 1244 (s), 971 (m), 945 (s), 842 (vs), 739 (s), 716 (vs), 677 (m), 570 (w), 449 (w). ^{1}H NMR (500 MHz, 25 °C, benzene-d_6): δ 0.53 (s, CH_3, 72 H), 1.40 (m, CH_2, 16 H).

Reaction of 1b with Tetraphenyldisiloxane-1,3-diol. A solution of **1b** (0.35 g; 1.0 mmol) in toluene (20 mL) was added to a solution of tetraphenyldisiloxane-1,3-diol (0.4 g, 1.0 mmol) in the same solvent (80 mL). The mixture was stirred at room temperature for 62 h, upon which the color of the solution changed from maroon to brown. The solution was concentrated in vacuo to 30 mL. Standing at −34 °C for 2 days yielded colorless crystals of $Ph_6Si_3O_3$ of apparent X-ray quality (yield 0.26 mg, 65%). Anal. Calcd (found) for $C_{36}H_{30}O_3Si_3$ (fw 594,90 g/mol): C 72.68 (72.04), H 5.08 (4.97). IR (Nujol mull, cm^{-1}): ν 1591 m, 1568 w, 1428 s, 1366 w, 1189 w, 1158 w, 1128 s, 1118 s, 1037 vs, 1016 vs, 995vs, 766 w, 744 m, 737 m, 726 s, 698 s, 678 m, 620 w, 528 vs, 487 m, 481 m.

X-ray Crystallography. Suitable crystals were selected, mounted on thin, glass fibers using paraffin oil, and cooled to the data collection temperature. Data were collected using 0.3° ω-scans at 0°, 90°, and 180° in ϕ. Unit cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.[17] Systematic absences in the diffraction data and unit-cell parameters were consistent with *C*2/*c* and *Cc* for **1b** and, uniquely, $P2_1/n$ for **2b**, and *Pbca* for **1a**. Refinement in the centrosymmetric space group option for **1b** yielded computationally stable and chemically reasonable results of refinement. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2. The compound molecule of **1b** is located at a 2-fold rotation axis. All carbon and hydrogen atoms for **1b** and **1a**, except the tertiary carbon atoms, were located disordered in two positions with a 50/50 site occupancy distribution. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 5.10 program library.[18] Crystal data and relevant bond distances and angles are given in Tables 1 and 2.

Density Functional Theory Calculations. All theoretical results were obtained using the Becke−Perdew exchange−correlation functional, within the Amsterdam density functional (ADF) program. The standard double-ζ basis sets were used for H, C, and Si atoms, while the standard triple-ζ basis sets were employed for the Cr atoms. The 1s electrons of C as well as the 1s−2p electrons of Si and Cr were treated as a frozen core. Graphical representations of orbitals and other functions computed by ADF have been prepared using the MOLEKEL program.

Table 1. Crystal Data and Structure Analysis Results

	1a	1b	2b
formula	$C_{20}H_{44}Cr$	$C_{16}H_{44}Si_4Cr$	$C_{32}H_{88}Si_8Cr_4$
MW	336.55	400.87	905.73
syst, space group	orthorhombic, *Pbca*	monoclinic, *C*2/*c*	monoclinic, *P*2(1)/*n*
a (Å)	15.762(2)	18.713(2)	17.081(2)
b (Å)	15.807(2)	8.358(1)	13.484(1)
c (Å)	17.837(2)	18.760(2)	22.873(2)
β (deg)	90	116.289(1)	99.603(2)
V (Å^3)	4443.8(9)	2630.5(4)	5194.3(8)
Z	8	4	4
radiation (Kα, Å)	0.71073	0.71073	0.71073
T (K)	203(2)	203(2)	203(2)
D_{calcd} (g cm^{-3})	1.006	1.012	1.148
μ_{calcd} (cm^{-1})	5.11	6.13	10.18
F_{000}	1504	880	1920
R, $R_w{}^{2\ a}$	0.0873, 0.1461	0.0904, 0.0972	0.0569, 0.1322
GoF	1.085	1.053	1.029

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = [(\sum(|F_o| - |F_c|)^2/\sum wF_o{}^2)]^{1/2}$.

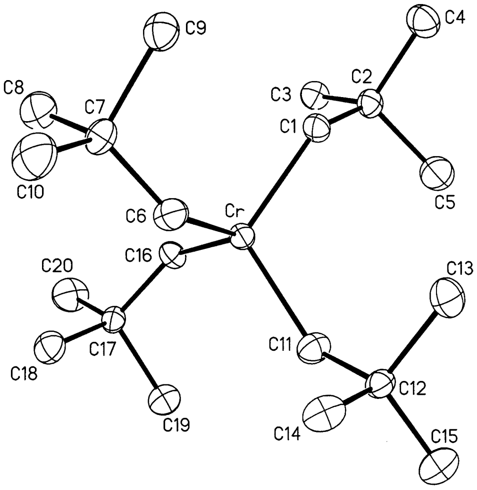

Figure 1. ORTEP drawing of **1a**. Thermal ellipsoids are drawn at the 30% probability level.

Results and Discussion

The preparation of the two homoleptic derivatives R_4Cr [R = Me_3CCH_2 (**1a**), Me_3SiCH_2 (**1b**)] was carried out according to the original preparation described by Wilkinson.[1] Reaction in ether of freshly prepared solutions of RMgCl with a suspension of $CrCl_3(THF)_3$ afforded dark brown and dark violet crystals, respectively, of the corresponding complexes which were isolated in moderate yield upon crystallization from hexane followed by sublimation. Correct combustion analysis results were obtained for the expected formulation. In good agreement with the values reported by Wilkinson for these two compounds the room-temperature magnetic moments were as expected for the high-spin d^2 electronic configuration of tetravalent chromium centers. The two complexes are thermally robust and did not show signs of decomposition upon refluxing in toluene for 24 h.

Since crystallographic data are not available for these two complexes, an X-ray diffraction study was undertaken. Crystals of both **1a** and **1b** diffracted rather poorly. Nevertheless, it was possible after several attempts to obtain data files of sufficient quality to solve the structure of each compound and to confirm the connectivity. The two complexes possess the expected tetrahedral structure (Figures 1 and 2) with C−Cr−C angles varying in the range 106.1−115.5° for **1a** and 107.3−108.9° for **1b**. The Cr−C distances also compare rather well, ranging from 1.961 to 2.031 Å for **1a** and from 1.954 to 1.983 Å for **1b**. The geometrical parameters compare well with those of the neophyl derivative of very similar structure.[2d] Both structures displayed conformational disorder arising from the flipping over two positions of the CH_2 groups directly attached to

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Table 2. Selected Bond Distances (Å) and Angles (deg)[a]

1a	1b	2b
Cr−C(16) 1.986(12)	Cr−C(1) 1.954(14)	Cr(1)−C(5) 2.184(4)
Cr−C(6) 1.996(13)	Cr−C(5) 1.972(14)	Cr(1)−C(13) 2.188(4)
Cr−C(11) 2.002(13)		Cr(1)−Cr(2) 2.3310(10)
Cr−C(1) 2.016(12)	C(1)−Cr−C(1)#1 72.7(8)	Cr(1)−Cr(4) 2.4026(10)
	C(1)−Cr−C(5)#1 90.8(6)	Cr(2)−C(9) 2.183(4)
C(16)−Cr−C(6) 115.5(5)	C(1)#1−Cr−C(5)#1 108.9(6)	Cr(2)−C(17) 2.205(4)
C(16)−Cr−C(11) 107.0(5)	C(1)−Cr−C(5) 108.9(6)	Cr(2)−Cr(3) 2.4004(10)
C(6)−Cr−C(11) 106.1(5)	C(1)#1−Cr−C(5) 90.8(6)	Cr(3)−C(29) 2.192(5)
C(16)−Cr−C(1) 108.1(5)	C(5)#1−Cr−C(5) 155.9(9)	Cr(3)−C(21) 2.191(4)
C(6)−Cr−C(1) 106.6(5)		Cr(3)−Cr(4) 2.3396(10)
C(11)−Cr−C(1) 113.6(5)		Cr(4)−C(25) 2.200(5)
		Cr(4)−C(1) 2.207(5)
		C(5)−Cr(1)−C(13) 177.91(17)
		C(5)−Cr(1)−Cr(2) 121.74(13)
		C(13)−Cr(1)−Cr(2) 60.09(12)
		C(5)−Cr(1)−Cr(4) 59.51(13)
		C(13)−Cr(1)−Cr(4) 122.08(13)
		Cr(2)−Cr(1)−Cr(4) 90.30(3)
		C(9)−Cr(2)−C(17) 179.08(18)
		C(9)−Cr(2)−Cr(1) 60.59(12)
		C(17)−Cr(2)−Cr(1) 119.19(13)
		C(9)−Cr(2)−Cr(3) 120.26(12)
		C(17)−Cr(2)−Cr(3) 58.82(12)
		Cr(1)−Cr(2)−Cr(3) 89.90(3)
		C(29)−Cr(3)−C(21) 179.34(18)
		C(29)−Cr(3)−Cr(4) 59.87(12)
		C(21)−Cr(3)−Cr(4) 120.41(13)
		C(29)−Cr(3)−Cr(2) 121.78(13)
		C(21)−Cr(3)−Cr(2) 58.88(11)
		Cr(4)−Cr(3)−Cr(2) 90.15(3)
		C(25)−Cr(4)−C(1) 178.40(17)
		C(25)−Cr(4)−Cr(3) 59.99(12)
		C(1)−Cr(4)−Cr(3) 118.86(12)
		C(25)−Cr(4)−Cr(1) 119.70(12)
		C(1)−Cr(4)−Cr(1) 58.86(12)
		Cr(3)−Cr(4)−Cr(1) 89.65(3)
		C(29)−Cr(3)−Cr(4) 59.87(12)
		C(21)−Cr(3)−Cr(4) 120.41(13)
		C(29)−Cr(3)−Cr(2) 121.78(13)
		C(21)−Cr(3)−Cr(2) 58.88(11)
		Cr(4)−Cr(3)−Cr(2) 90.15(3)
		C(25)−Cr(4)−C(1) 178.40(17)
		C(25)−Cr(4)−Cr(3) 59.99(12)
		C(1)−Cr(4)−Cr(3) 118.86(12)
		C(25)−Cr(4)−Cr(1) 119.70(12)
		C(1)−Cr(4)−Cr(1) 58.86(12)
		Cr(3)−Cr(4)−Cr(1) 89.65(3)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x, y, -z + 1/2$.

chromium and some rotational disorder of the t-Bu and Me_3Si groups along the CH_2−C and CH_2−Si bonds. This behavior was reflected in the convergence factors, which remain unpleasantly high.

Both **1a** and **1b** are pyrophoric and immediately ignite upon exposure to air (**Warning!**). Nevertheless, these species display, in agreement with Wilkinson's observation, a remarkable inertness toward protic reagents. No reaction was observed upon refluxing in toluene, while reaction with either phenols or carboxylic acid took place *only after refluxing in toluene for 15 h*, affording decomposition. In sharp contrast to this surprising inertness toward protic agents, a smooth reaction took place at room temperature with tetraphenyldisiloxane-1,3-diol, producing the trimeric $[Ph_2SiO]_3$ in good yield. Regrettably, the fate of the chromium moiety remained unclear despite repeated attempts to isolate a tractable product. The formation of $[Ph_2SiO]_3$ implies a formal abstraction of one molecule of water from the disilanolate. Thus, different perspectives might be envisioned about the grafting of CrR_4 on

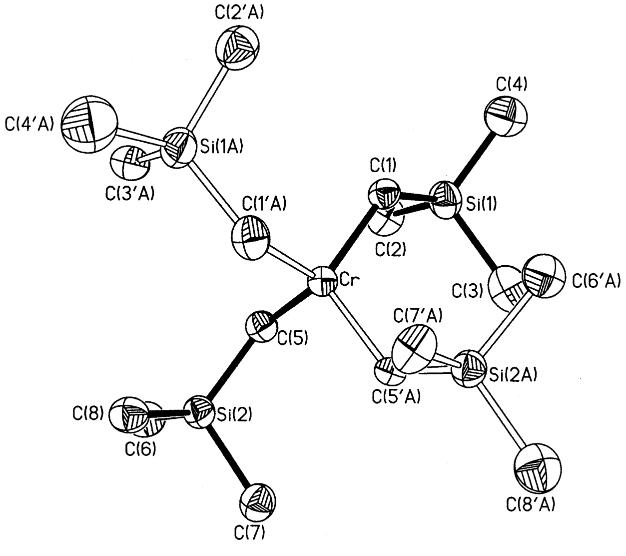

Figure 2. ORTEP drawing of **1b**. Thermal ellipsoids are drawn at the 30% probability level.

silica surfaces,[10] where a similar dehydration might actually occur as an alternative to the grafting process.

Solutions of **1** do not react appreciably with ethylene or other α-olefins at room temperature and atmospheric pressure. However, in the presence of 2 equiv of $AlCl_3$ a vigorous reaction forming polyethylene took place. The catalytic activity of **1b** of 1.1 kg of PE/mol/h/atm is moderate and in the range of the other homogeneous chromium catalysts reported so far in the literature.[19,20] The polyethylene displayed a fairly high MW of 699 500 and rather broad polydispersity (5.0).

The formation of tetravalent **1** starting from a trivalent salt and by using reducing Grignard reagents can in principle be ascribed to a disproportionation reaction of an unstable and in situ generated R_3Cr intermediate. However, the fact that the yields are above 50% in the case of **1a** might dismiss this possibility. Attempts to identify divalent chromium species as possible byproducts of the reaction were inconclusive possibly due to the presence of magnesium salts as byproducts which would be likely to be engaged with chromium in the formation of polymeric structures. However, when the reaction of $CrCl_3(THF)_3$ was carried out with the corresponding lithium reagent Me_3SiCH_2Li, the *divalent* and tetrameric species $[(Me_3SiCH_2)_2Cr]_4$ (**2b**) previously reported by Smith[4h,i] was isolated in 83% yield. Compound **2b** was conveniently prepared by reacting $CrCl_2(THF)_2$ with 2 equiv of the lithium reagent. Attempts to prepare a neopentyl derivative, which we presumed would proceed in a similar manner, afforded only intractable materials. The formation of **2b** in high yield via reduction of a trivalent species is not particularly surprising given the well-known ability of organolithium reagents to act as reductants. We have analyzed the mother liquor solutions for the possible presence of **1b** as a partner product of a disproportionation process. However, not even traces of **1b** could be detected upon sublimation of the dried residues, thus ruling out that its formation might be due to a disproportionative pathway.

Since the atomic coordinates and the geometrical parameters of **2b** were not available from the patent literature, we have undertaken another crystal structure determination, thus confirming the tetrameric structure of **2b** as composed of four square-planar divalent chromium centers bridged by the eight methylene groups of the trimethylsilyl groups (Figure 3). Each chromium is connected to two neighbor chromium centers by two bridging trimethylsilylmethyl groups, while the four chromium atoms define a nearly regular square plane [deviation from the plane 0.0173 Å, Cr−Cr−Cr angles ranging between 89.65° and 90.30°]. The overall structure can be described in terms of a nearly regular cube, with the eight methylene groups of the CH_2SiMe_3 groups occupying each corner and the chromium atoms located in the center of the four side faces while the top and bottom faces remain unoccupied. The coordination geometry around each of the chromium centers is regular square-planar and rather similar to that of $Cr_2(CH_2SiMe_3)_4(PMe_3)_2$ and $[Cr_2(CH_2SiMe_3)_6]^{2-}$.[3d,q] The Cr−C−Cr angles range between 62.98° and 65.22° and are as expected for CH_2-trimethylsilyl bridging groups.

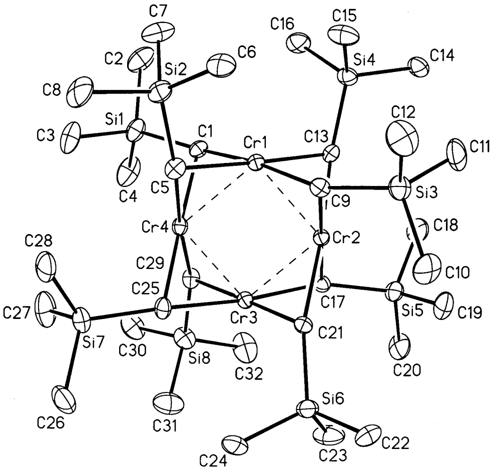

Figure 3. ORTEP drawing of **2b**. Thermal ellipsoids are drawn at the 30% probability level.

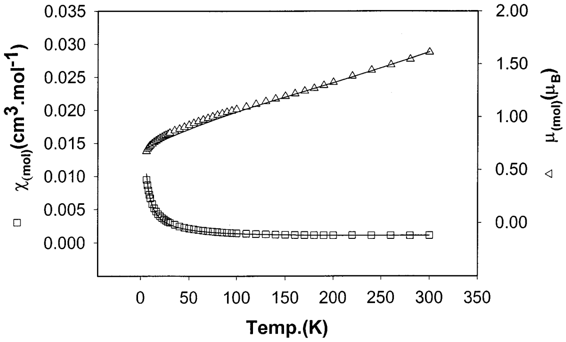

Figure 4. Plot of the $1/\chi$ and of the μ_{eff} against T for **2b**. Best fitting was obtained with $g = 2.188$, $J = -510$, TIP = 0.00079, $\rho = 0.004$, $\theta = -0.05$.

The Cr···Cr distances in **2b** (ranging from 2.331 to 2.402 Å) fall in a range consistent with metal−metal multiple bonding,[5] yet the complex is paramagnetic at room temperature with a low magnetic moment of about 1.61 μ_B (mol) at 300 K, dropping to 0.3 μ_B at 2 K (Figure 4). High-spin mononuclear Cr(II) systems in a weak square-planar field are expected to show much higher moments at room temperature (4.7−4.9 μ_B), with minor depression of the moment as temperature is lowered. For a low-spin system, significant spin−orbit coupling effects can lead to significant depression of the moment from room-temperature values around 3−3.3 μ_B to 0 μ_B, but only at temperatures approaching 0 K. The mononuclear Cr(IV) complexes **1a** and **1b** have moments at room temperature consistent with the presence of two unpaired electrons, as would be expected. The Cr centers in **2b** are nominally square-planar and so might be expected to exist in a high-spin configuration (d^4). However the very low overall moments exhibited by **2b** and the significant drop on lowering temperature are more reasonably associated with intramolecular spin coupling, through a superexchange mechanism, which would be antiferromagnetic in nature. The data for **2b** were fitted to an isotropic exchange model for four Cr(II) centers arranged in a square with a single exchange integral, according to the appropriate Hamil-

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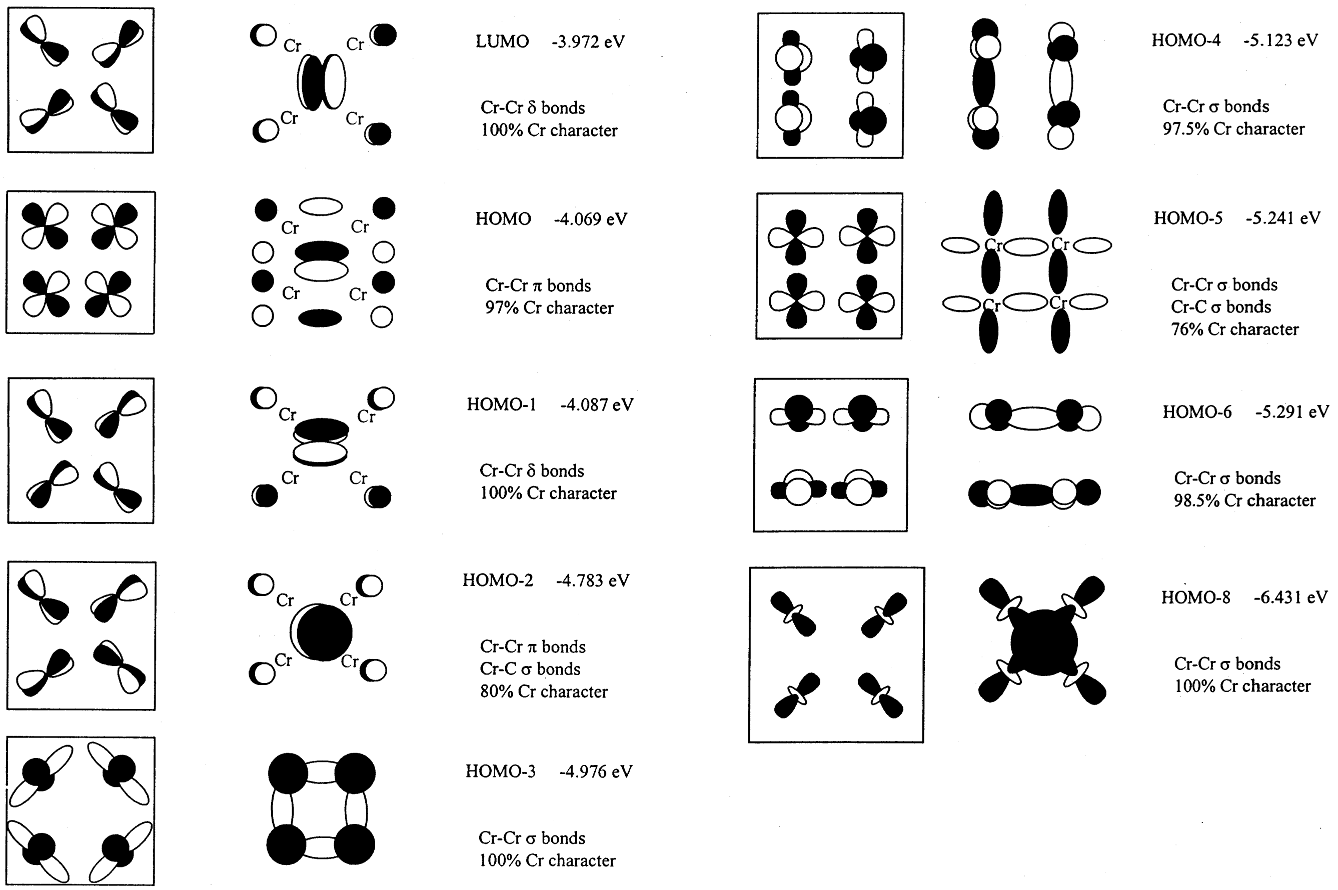
(19) (a) Liang, Y.; Yap, G. P. A.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1996**, *15*, 5284. (b) White, P. A.; Calabrese, J.; Theopold, K. H. *Organometallics* **1996**, *15*, 5473.

(20) Kim, W. K.; Fevola, M. J.; Liable-Sands, L. M.; Rheingold, A. L. Theopold, K. H. *Organometallics* **1998**, *17*, 4541.

Chart 1



tonian expression (eq 1).

$$H = -J\{S_1\cdot S_2 + S_2\cdot S_3 + S_3\cdot S_4 + S_1\cdot S_4\} \qquad (1)$$

$$\chi_{\mathrm{M}}f = \frac{N\beta^2 g^2 \rho \sum S(S'+1)(2s'+1)\exp[-E(S')/kT]}{3k(T-\theta)\sum S'(2S'+1)\exp[-E(S')/kT]} \qquad (2)$$

$$\chi_{\mathrm{M}} = \chi_{\mathrm{M}'}(1-\rho) + \frac{2N\beta^2 g^2 \rho}{3kT} + \mathrm{TIP} \qquad (3)$$

Using the vector coupling scheme, the appropriate energy levels and spin states were derived and substituted into the Van Vleck equation (eq 2), and corrections made for TIP (temperature independent paramagnetism), Weiss-like temperature effects (θ), and paramagnetic impurity fraction (ρ) (eq 3).[21] A satisfactory fitting of the magnetic data was obtained by using the integrated software package MAGMUN 4.0.[22] The data for **2b** were fitted to eq 3 for both low-spin (d^2) and high-spin (d^4) cases. Reasonable fits were obtained in both cases with $g = 2.188$, $J = -510$ cm^{-1}, TIP = 0.00079 cm^3·mol^{-1}, $\rho = 0.004$, $\theta = -0.05$, ($10^2R = 6.1$; $R = [(\chi_{\mathrm{obs}} - \chi_{\mathrm{calc}})^2/\chi_{\mathrm{obs}}{}^2]^{1/2}$) for the d^4 case and $g = 2.193$, $J = -475$ cm^{-1}, TIP = 0.000765 cm^3·mol^{-1}, $\theta = 0.012$, $\theta = 0$ ($10^2R = 6.4$) for the d^2 case. The solid line in Figure 4 is calculated with the best fit data for the high-spin case. The data below 6 K show quite a sharp drop in moment, perhaps indicative of zero-field splitting effects. These data have not been included in the data fit. However since zero-field splitting is likely to be very much smaller than $|J|$, the exchange coupling clearly dominates.

Since both models can account reasonably for the data with large $|J|$ values, it is clear that the magnetic properties of **2b** can be interpreted in terms of very strong intramolecular antiferromagnetic coupling. This could be manifested through superexchange via the bridging methylene groups, although the close proximity of the chromium(II) centers within the square and the possibility of direct metal−metal interactions might also be a significant contributing factor in the overall exchange process. On the other hand, complex **2b** displays an unusual chemical inertness (see below) that in principle could be ascribed to the existence of a robust Cr−Cr direct bonding interaction.

Given the magnetic behavior, density functional theory (DFT) calculations were carried out on the singlet state. In good agreement with this working hypothesis, the LUMO (−3.972 eV), HOMO (−4.069 eV), and HOMO-1 (−4.087 eV) are nearly degenerate, with a HOMO−LUMO gap of only 0.097 eV (Chart 1), thus explaining the appearance of magnetism by incrementing the temperature. The reason for the incomplete degeneracy is likely to be ascribed to the unequal Cr−Cr bond distances, ranging from 2.34 to 2.40 Å. Among the frontier orbitals, the HOMO, HOMO-1, HOMO-3, HOMO-4, HOMO-6, and HOMO-8 all are between 97 and 100% Cr-centered (Chart 1), indicating a surprising nonparticipation of the ligand bridging carbon atoms and the presence of a substantial Cr−Cr bond interac-

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[21] Kambe, R. K. *J. Phys. Soc. Jpn.* **1950**, *5*, 38.

[22] Xu, Z.; Thompson, L. K.; He, K.; Waldmann, O. MAGMUN4.0 Available free of charge from http://www.chem.mun.ca/resinst/ (no source codes available).

tion. The LUMO and the HOMO-1 are pure Cr−Cr δ-bonds with identical shapes but different orientation in the sense that the two vertical nodal planes are perpendicular to each other, while the horizontal nodal plane coincides for both orbitals with the molecular plane. Both MOs are generated by the overlap of the d orbitals orthogonal to the molecular plane (Chart 1), forming four lobes in the center of the tetrametallic unit. The HOMO can be described as a combination of two Cr−Cr π-bonds each between one couple of chromium atoms generated by in-plane combination of d orbitals forming four out-of-phase lobes lying on the molecular plane. A second MO with a strong π-character is provided by HOMO-2 (−4.783 eV) formed by the in-phase hybrid combination of d orbitals perpendicular to the molecular plane and oriented toward the center of the molecule. The main feature consists of two large lobes located on the two sides of the molecular plane. There is, however, a small but nonnegligible participation of the bridging carbon atom's p orbitals (20%). On the same line, HOMO-7 (−6.340 eV) also is a Cr−Cr π-bond, again forming two large lobes in the center of the molecules above and below the plane defined by the tetrametallic unit. In this MO however, the participation of the bridging carbon atoms appears to be more significant, the Cr−Cr bond character being only 60%. The Cr−Cr σ-bonding interaction is realized through a series of five MOs (from HOMO-3 to HOMO-6) arising from overlap of the lobes of d orbitals located either coplanar or perpendicular to the tetrametallic unit. Particularly appealing is HOMO-8 (−6.431 eV), consisting of a large lobe located in the center of the molecule. The orbital appears to be formed by hybrid combination of d atomic orbitals strongly reminiscent in shape of the d_{z^2} lying on the molecular plane and directed toward the center of the molecule. Though not considered in great detail in this report, frontier orbitals HOMO-9 through HOMO-14 all exhibit some Cr−Cr bonding character but with a major participation of the ligand bridging carbon atoms.

Similar to the case of **1a** and **1b**, complex **2b** displays a remarkable chemical inertness toward protic agents, and to our surprise no reactivity could be observed even with carboxylic acid, phenols, pyrroles, etc. In contrast to the case of $Me_8Cr_2Li_4(THF)_4$, whose short Cr−Cr quadruple bond could be reversibly cleaved via coordination of Lewis base,[3o] the tetranuclear structure of **2b** seems to be surprisingly robust since no cleaving was observed upon treatment with TMEDA and unreacted **2b** was always recovered in good yield. Nevertheless, a smooth reaction with ethylene took place at room temperature in toluene solution, producing substantial amounts of polyethylene (MW = 510 000, PD = 2.4). Although the catalytic activity was very modest (0.5 kg of PE/mol/h/atm), as expected for a divalent chromium species, we found it remarkable that the reaction does not require the presence of a cocatalyst.

In conclusion, the ability of the Cr−C bond in these complexes to perform ethylene insertion reactions along with the surprising inertness toward H-transfer reactions might be the key to understanding the tremendous efficiency of the Cr catalyst commercially used for ethylene homopolymerization. A strong tendency to perform ethylene insertion, counterbalanced by poor, if any, tendency of the Cr−C bond to undergo hydrogen transfer, may well account for the formation of high molecular weight polymers with virtual no branching. Thus, understanding the factors determining this behavior will be critical for the design of more efficient catalysts and provides motivation for the development of new Cr-based catalysts.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Council of Canada (NSERC) and by Canada Foundation for Innovation (CFI) through an infrastructure grant.

Supporting Information Available: Listings of atomic coordinates, thermal parameters, and bond distances and angles for structures reported in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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