*Organometallics* **1994**, *13*, 4105–4108

# *Notes*

## Synthesis and Molecular Structure of the Trinuclear Mixed-Metal Complex $[\{(Me_2NCH_2CH_2CH_2)_2Cr(\mu\text{-}Cl)_2\}_2Mg]$ and of the Tetranuclear Grignard Reagent $[(Me_2NCH_2CH_2CH_2)Mg_2Cl_3(THF)_2]_2$

Umberto Casellato and Franco Ossola*

*Istituto di Chimica e Tecnologie Inorganiche e dei Materiali Avanzati, Area della Ricerca del CNR, Corso Stati Uniti 4, I-35127 Padova, Italy*

*Received April 11, 1994*[®]

*Summary: $CrCl_3{\cdot}3THF$ reacts with $[(Me_2NCH_2CH_2CH_2)Mg_2Cl_3(THF)_2]_2$ (**1**) in THF at room temperature to form the complex $[\{(Me_2NCH_2CH_2CH_2)_2Cr(\mu\text{-}Cl)_2\}_2Mg]$ (**2**). The solid-state structures of **1** and **2** have been determined by X-ray crystal analysis. **1** is triclinic, space group $P\bar{1}$ (No. 2), with a = 10.035(8) Å, b = 10.393(8) Å, c = 10.707(8) Å, α = 75.59(6)°, β = 68.61(6)°, γ = 75.28(7)°, and Z = 1 (the asymmetric unit is half of the molecule); the structure was refined to a conventional R factor of 0.079. In this tetranuclear Grignard reagent **1** Mg and Cl atoms form a system of five four-membered bridging units, where the Mg atoms exhibit five and six coordination and are connected by doubly (μ) or triply ($\mu_3$) bridging chloro ligands. **2** is triclinic, space group $P\bar{1}$ (No. 2), with a = 8.514(8) Å, b = 12.471(9) Å, c = 14.976(9) Å, α = 81.54(5)°, β = 92.52(6)°, γ = 95.32(6)°, and Z = 2; the structure was refined to R = 0.064. **2** is a trinuclear complex with two $(Me_2NCH_2CH_2CH_2)_2Cr(\mu\text{-}Cl)_2$ fragments attached either side of a central Mg atom through four Cr—Cl—Mg bridges.*

### Introduction

We are currently interested in the utilization of organometallic chromium complexes in the preparation of chromium-based materials through thermal decomposition processes.[1] Our attention is now focused on the synthesis of (σ-alkyl)chromium complexes with hydrogen atoms on the β-C atom of the ligands, stable at room temperature but susceptible to the β-elimination process at higher temperatures.

Even though the β-elimination decomposition pathway, in transition-metal derivatives, has been for years a synonym of instability and impossibility of isolation,[2] such complexes have been isolated when large, bulky ligands have been used[2,3] and, in general, when availability of the coordination site necessary for the elimination reaction has been hindered.[2]

In order to reach coordinative saturation for the metal and room-temperature stability for the compound, we are planning the synthesis of a series of chromium derivatives with alkyl ligands having a terminal Lewis basic group, e.g. 3-(dimethylamino)propyl, which could behave as a bidentate ligand and allow intramolecular coordinative saturation with nitrogen as electron donor via a five-membered ring formation.

Here we report the synthesis and molecular structure of the unusual trinuclear complex $[\{L_2Cr(\mu\text{-}Cl)_2\}_2Mg]$ (**2**) ($L = CH_2CH_2CH_2N(CH_3)_2$) and the tetranuclear Grignard reagent $[LMg_2Cl_3(THF)_2]_2$ (**1**) used in the synthesis of **2**.

### Results and Discussion

The 3-(dimethylamino)propyl ligand has been recently used in the intramolecularly base-stabilized triorgano derivatives of group III, utilized as precursors in OMVPE production of III-V semiconductor layers.[4,5] Such complexes have been obtained by the reaction of dialkylmetal chlorides with ((dimethylamino)propyl)lithium salt[4] or with the corresponding Grignard reagent,[5] but no X-ray crystal structures of the (dimethylamino)propyl reagents have been reported.

We found that chloro((dimethylamino)propyl)magnesium crystallizes from THF as the complex **1** having the unusual tetranuclear molecular structure shown in Figure 1. The Cl and Mg atoms form a system of five four-membered bridging units. The molecule, in fact, lies on a crystallographic inversion center with the [Mg(2)—Cl(2)]$_2$ perfectly square planar unit around it; the mean planes of the other two square units (Mg(1), Cl(1), Mg(2), Cl(2) and Mg(1), Cl(2), Mg(2′), Cl(3)) are nearly perpendicular to each other and also to the above square planar unit. This system is similar to that found in the tetranuclear Grignard reagent $[(C_2H_5)Mg_2Cl_3(C_4H_8O)_3]_2$,[6] showing comparable bonds and angles.

---

[®] Abstract published in *Advance ACS Abstracts*, August 1, 1994.

[1] (a) Maury, F.; Ossola, F. *Thin Solid Films* **1992**, *207*, 82. (b) Maury, F.; Ossola, F. *Thin Solid Films* **1992**, *219*, 24. (c) Maury, F.; Ossola, F.; Schuster, F. *Surf. Coat. Technol.* **1992**, *54/55*, 204.

[2] Davidson, P. J.; Lappert, M. F.; Pearce, R. *Chem. Rev.* **1976**, *76*, 220.

[3] (a) Kruse, W. *J. Organomet. Chem.* **1972**, *42*, C39. (b) Muller, J.; Holzinger, W. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 760.

[4] (a) Schumann, H.; Hartmann, U.; Wassermann, W. *Polyhedron* **1990**, *9*, 353. (b) Schumann, H.; Hartmann, U.; Dietrich, A.; Pickardt, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1077. (c) Schumann, H.; Just, O.; Seuss, T. D.; Görlitz, F. H.; Weimann, R. *J. Organomet. Chem.* **1994**, *466*, 5.

[5] Hostalek, M.; Pohl, L.; Brauers A.; Balk, P.; Frese, V.; Hardtdegen, H.; Hovel, R.; Regel, G. K.; Molassiotti, A.; Moser, M.; Scholz, F. *Thin Solid Films* **1989**, *174*, 1.

[6] Toney, J.; Stucky, G. D. *J. Organomet. Chem.* **1971**, *28*, 5.

0276-7333/94/2313-4105$04.50/0

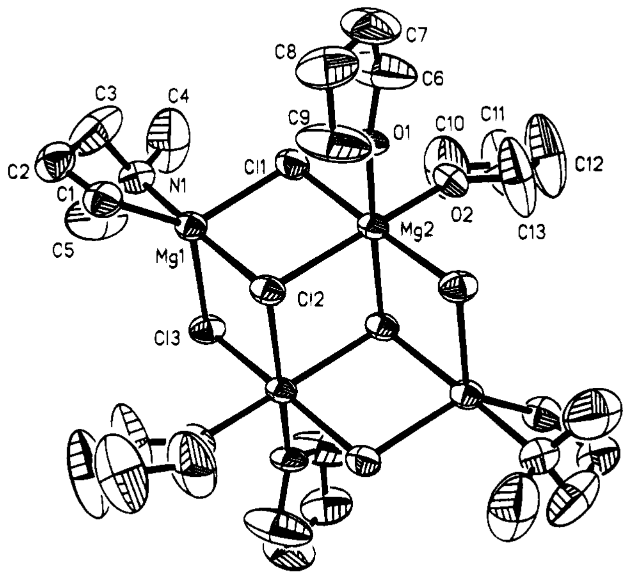

**Figure 1.** ORTEP view of the molecular structure of **1**. Thermal ellipsoids are at the 50% probability level.

The Cl(2) atom, bonded to Mg(2) and Mg(2′) (bond lengths are 2.524(4) and 2.523(4) Å, respectively) is three-coordinated, being also bonded to a third magnesium atom, Mg(1), with a bond distance of 2.779(5) Å. The Cl(1) and Cl(3) atoms are two-coordinated; the Cl(1)—Mg(1) and Cl(3)—Mg(1) bond lengths are similar, 2.397(5) and 2.401(5) Å, respectively. The five coordination around the Mg(1) atom is completed by bonding to the N(1) and C(1) atoms of the ligand L and can be described as a distorted trigonal bipyramid with Cl(2) and N(1) at the apices and C(1), Cl(1), and Cl(3) in the equatorial positions.

The Mg(2) atom is six-coordinated, bonding four chlorine atoms, Cl(1), Cl(2), Cl(2′), and Cl(3′), and the oxygen atoms of the two THF molecules. The Mg(2)—Cl bond lengths vary between 2.47 and 2.52 Å, with little difference between the distances to the two- or three-coordinated chlorine atoms; the Mg(2)—O(1) and Mg(2)—O(2) bond lengths are 2.085(8) and 2.093(6) Å, respectively. The angles, around Mg(2), vary between 84 and 97° and the configuration is a distorted octahedron.

The chelating ligand L forms, with the Mg(1) atom, a five-membered ring in a puckered configuration; the torsion angle C(1)—C(2)—C(3)—N(1) is 56°. The Mg··Mg contacts are in the range 3.738(5)–3.747(5) Å, and there are no other significant contacts.

Reaction between $CrCl_3$·3THF and **1** at room-temperature gave the reddish complex **2**. **2** was found to be air sensitive but indefinitely stable at room temperature.

Its molecular structure, depicted in Figure 2, shows a very uncommon Cr—Mg—Cr trinuclear core where the central Mg atom is chloride-bridged to two $L_2Cr(\mu\text{-}Cl)_2$ fragments in opposite positions.[7] The coordination geometry of the two external chromium atoms is octahedral with the two nitrogen atoms of the ligands in "trans" positions, while the coordination geometry of the central Mg atom is tetrahedral, imposing a rotation of 90° (approximately) on the external octahedrons. The N(1)—Cr(1)—N(2) line, in fact, forms an angle of 92° to the N(3)—Cr(2)—N(4) line. The four Mg—Cl bonds are very similar, being of length between 2.31 and 2.32 Å, and are comparable to the Mg—Cl(two coordinated) bonds found for **1**, while the angles are noticeably different, varying from 96 to 117° with the lower values for angles involving Cl atoms bonded to the same Cr atom. The resulting coordination polyhedron around Mg atom is an irregular tetrahedron.

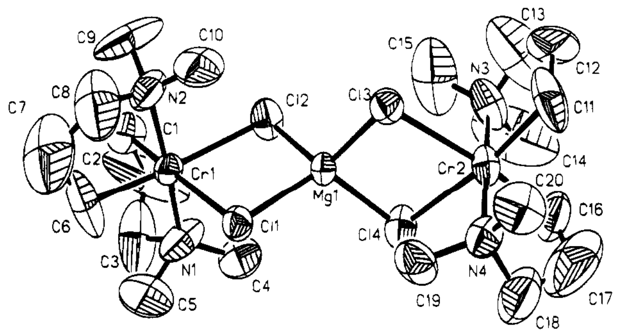

**Figure 2.** ORTEP view of the molecular structure of **2**. Thermal ellipsoids are at the 40% probability level.

Because of the diverse nature of the coordinating atoms, and the tensions which are created by the five-membered ring involving the organic part of the system, the octahedrons surrounding the two external chromium atoms are irregular. The four N—Cr—C angles are between 82 and 87° (average 84°), while the Cl(2)—Cr(1)—Cl(1) and Cl(3)—Cr(2)—Cl(4) angles are both 83°. The Cr—C bonds vary between 2.025(9) and 2.09(1) Å, and the Cr—N bonds are between 2.161(9) and 2.218(8) Å.

The five-membered rings, which the ligand forms with Cr atoms, present a different degree of puckering; the C—C—C—N torsion angles are −70° for the ring containing the N(1) atom, 34° for the N(2) ring, 2° for the N(3) ring, and −54° for the N(4) ring.

The Mg··Cr(1) and Mg··Cr(2) contacts are 3.500(3) and 3.474(3) Å, respectively.

## Experimental Section

**General Considerations.** All the operations were carried out in nitrogen-filled gloveboxes with the rigorous exclusion of oxygen and moisture. Solvents were purified by standard methods[8] and used immediately after distillation. 3-(Dimethylamino)propyl chloride was obtained from the commercially available HCl salt by treatment with sodium hydroxide solution and extraction and dried over anhydrous potassium carbonate. Other reagents were commercial products used as supplied.

Elemental analyses were performed by Dornis U. Kolbe Mikroanalytisches Laboratorium, Mulheim/Ruhr, Germany.

Infrared spectra were recorded with a Mattson Galaxy Series FTIR 3000 apparatus; samples were prepared in the glovebox as KBr pellets and sandwiched between KBr plates in an airtight holder.

The electronic absorbtion spectra were measured with a Cary 17 D double-beam spectrophotometer; $^1H$ and $^{13}C$ NMR spectra were recorded with a Bruker 200 AC instrument and were referred to TMS = 0.00 ppm.

---

[7] A similar transition-metal/magnesium trinuclear chloride-bridged linear arrangement has been recently found for titanium, but in this molecule Ti atoms were pseudotetrahedrally coordinated, being bonded to Cp rings, and magnesium was octahedrally coordinated, being also bonded to two coordinating THF molecules; see: Stephan, W. *Organometallics* **1992**, *11*, 996.

[8] Perrin, D. D.; Armarego, W. L.; Perrin, D. R. In *Purification of Laboratory Chemicals*; 2nd ed.; Pergamon: Oxford, U.K., 1982.

**Table 1. Crystal and Intensity Data for 1 and 2**

| | complex | |
|---|---|---|
| | **1** | **2** |
| formula | $C_{26}H_{56}N_2Cl_6O_4Mg_4$ | $C_{20}H_{48}N_4Cl_4Cr_2Mg$ |
| color, habit | white, plate | reddish, prallelepiped |
| fw | 770.7 | 584.5 |
| system | triclinic; $P\bar{1}$ (No. 2) | triclinic; $P\bar{1}$ (No. 2) |
| cell | | |
| $a$ (Å) | 10.035(8) | 8.514(8) |
| $b$ (Å) | 10.393(8) | 12.471(9) |
| $c$ (Å) | 10.707(8) | 14.976(9) |
| α (deg) | 75.59(6) | 81.54(5) |
| $\beta$ (deg) | 68.61(6) | 92.52(6) |
| $\gamma$ (deg) | 75.28(7) | 95.32(6) |
| $V$ (Å$^3$) | 990(1) | 1565(1) |
| $D_c$ (g cm$^{-3}$) | 1.29 | 1.30 |
| molec/cell ($Z$) | 1[a] | 2 |
| $F$(000) | 408 | 648 |
| μ(Mo Kα) (cm$^{-1}$) | 4.7 | 10.0 |
| scan mode | $\omega-2\theta$ | |
| scan speed | 2 deg/min | |
| $2\theta$ max (deg) | 52 | |
| unique reflns | 1526 | 4164 |
| obsd reflns [$I > 3\sigma(I)$] | 1482 | 2623 |
| corrections | Lp, absorption | |
| max and min abs coeff | 1.84, 1.00 | 1.34, 1.03 |
| residual ($R$) | 0.079 | 0.064 |

[a] The asymmetric unit is half of the molecule.

**Table 2. Fractional Coordinates with Equivalent Isotropic Thermal Parameters (Å$^2$) for 1**

| atom | $x$ | $y$ | $z$ | $U_{eq}$[a] |
|---|---|---|---|---|
| Cl(1) | 0.3241(3) | 0.8622(3) | 0.3639(3) | 0.0699(8) |
| Cl(2) | −0.0227(3) | 0.8395(3) | 0.5756(3) | 0.0564(7) |
| Cl(3) | 0.1560(3) | 0.9865(3) | 0.7072(3) | 0.0641(9) |
| Mg(1) | 0.2508(4) | 0.7867(3) | 0.6055(3) | 0.0543(9) |
| Mg(2) | 0.0832(4) | 0.9456(3) | 0.3300(3) | 0.0505(9) |
| C(1) | 0.241(1) | 0.5841(9) | 0.7147(9) | 0.077(1) |
| C(2) | 0.385(1) | 0.5268(9) | 0.741(1) | 0.092(1) |
| C(3) | 0.503(1) | 0.597(1) | 0.635(1) | 0.157(1) |
| N(1) | 0.4726(8) | 0.7447(8) | 0.6245(8) | 0.069(1) |
| C(4) | 0.587(1) | 0.789(1) | 0.518(1) | 0.197(1) |
| C(5) | 0.470(1) | 0.769(1) | 0.744(1) | 0.210(1) |
| O(1) | 0.1115(7) | 0.7696(6) | 0.2561(6) | 0.066(1) |
| C(6) | 0.230(1) | 0.720(1) | 0.151(1) | 0.170(1) |
| C(7) | 0.201(1) | 0.594(1) | 0.135(1) | 0.143(1) |
| C(8) | 0.100(1) | 0.546(1) | 0.258(1) | 0.121(1) |
| C(9) | 0.037(1) | 0.663(1) | 0.325(1) | 0.149(1) |
| O(2) | 0.1838(7) | 1.0492(6) | 0.1367(6) | 0.064(1) |
| C(10) | 0.301(1) | 1.112(1) | 0.104(1) | 0.178(1) |
| C(11) | 0.312(1) | 1.213(1) | −0.008(1) | 0.180(1) |
| C(12) | 0.233(1) | 1.191(1) | −0.064(1) | 0.221(1) |
| C(13) | 0.136(1) | 1.110(1) | 0.032(1) | 0.193(1) |

[a] $U_{eq}$ is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

**Table 3. Selected Bond Distances, Contacts, and Angles for 1[a]**

| | | | |
|---|---|---|---|
| | Bond Distances (Å) | | |
| Cl(1)—Mg(1) | 2.397(5) | Cl(1)—Mg(2) | 2.479(5) |
| Cl(2)—Mg(1) | 2.779(5) | Cl(2)—Mg(2) | 2.524(4) |
| Cl(3)—Mg(1) | 2.401(5) | Mg(1)—C(1) | 2.146(9) |
| Mg(2′)—Cl(3) | 2.473(5) | Mg(2′)—Cl(2) | 2.523(4) |
| Mg(1)—N(1) | 2.23(1) | Mg(2)—O(1) | 2.085(8) |
| Mg(2)—O(2) | 2.093(6) | C(1)—C(2) | 1.51(1) |
| C(2)—C(3) | 1.51(1) | C(3)—N(1) | 1.47(1) |
| N(1)—C(4) | 1.47(1) | N(1)—C(5) | 1.45(2) |
| | Contacts (Å) | | |
| Mg(1)···Mg(2) | 3.747(5) | Mg(1)···Mg(2′) | 3.739(5) |
| Mg(2)···Mg(2′) | 3.738(5) | | |
| | Bond Angles (deg) | | |
| Mg(1)—Cl(1)—Mg(2) | 100.4(2) | Mg(1)—Cl(2)—Mg(2) | 89.8(2) |
| Cl(2)—Mg(1)—Cl(3) | 82.9(2) | Cl(1)—Mg(1)—Cl(3) | 106.4(2) |
| Cl(1)—Mg(1)—Cl(2) | 82.4(2) | Cl(3)—Mg(1)—N(1) | 97.8(3) |
| Cl(3)—Mg(1)—C(1) | 125.1(3) | Cl(2)—Mg(1)—N(1) | 178.7(3) |
| Cl(2)—Mg(1)—C(1) | 96.2(3) | Cl(1)—Mg(1)—N(1) | 96.3(3) |
| Cl(1)—Mg(1)—C(1) | 128.1(3) | C(1)—Mg(1)—N(1) | 84.3(4) |
| Cl(1)—Mg(2)—Cl(2) | 86.3(2) | Cl(2)—Mg(2)—O(2) | 172.0(3) |
| Cl(2)—Mg(2)—O(1) | 93.8(2) | Cl(1)—Mg(2)—O(2) | 89.5(3) |
| Cl(1)—Mg(2)—O(1) | 88.4(3) | O(1)—Mg(2)—O(2) | 92.8(3) |
| Cl(2′)—Mg(2)—Cl(1) | 96.8(3) | Cl(2′)—Mg(2)—Cl(2) | 84.4(3) |
| Cl(2′)—Mg(2)—Cl(3′) | 87.1(3) | Cl(2′)—Mg(2)—O(2) | 89.4(3) |
| Cl(2′)—Mg(2)—O(1) | 174.4(3) | Mg(1)—N(1)—C(3) | 98.8(7) |
| Mg(1)—C(1)—C(2) | 107.5(6) | C(1)—C(2)—C(3) | 110.2(9) |
| C(2)—C(3)—N(1) | 114.4(9) | | |

[a] Symmetry code: ′ = $-x$, $2 - y$, $1 - z$.

**Table 4. Fractional Coordinates with Equivalent Isotropic Thermal Parameters (Å$^2$) for 2**

| atom | $x$ | $y$ | $z$ | $U_{eq}$[a] |
|---|---|---|---|---|
| Cr(1) | 0.0447(2) | 0.2502(1) | 0.8533(1) | 0.0624(4) |
| Cl(1) | 0.2684(3) | 0.3935(2) | 0.8976(2) | 0.0684(5) |
| Cl(2) | 0.0456(4) | 0.3768(2) | 0.7022(2) | 0.0917(6) |
| Mg(1) | 0.2450(4) | 0.4938(2) | 0.7548(2) | 0.0566(6) |
| Cl(3) | 0.1947(3) | 0.6750(2) | 0.7481(2) | 0.0751(6) |
| Cl(4) | 0.4731(3) | 0.5253(2) | 0.6732(2) | 0.0903(6) |
| Cr(2) | 0.4383(2) | 0.7317(1) | 0.6461(1) | 0.0713(5) |
| C(1) | −0.1161(9) | 0.1359(7) | 0.8041(7) | 0.1111(7) |
| C(2) | 0.0019(9) | 0.0761(9) | 0.7547(8) | 0.2856(7) |
| C(3) | 0.147(1) | 0.0456(9) | 0.8136(9) | 0.2243(7) |
| N(1) | 0.2178(8) | 0.1522(7) | 0.8121(7) | 0.1327(7) |
| C(4) | 0.3356(9) | 0.2071(8) | 0.7524(7) | 0.1268(7) |
| C(5) | 0.305(1) | 0.1073(8) | 0.9041(9) | 0.1807(7) |
| C(6) | 0.034(1) | 0.1739(8) | 0.9870(7) | 0.1695(7) |
| C(7) | −0.104(1) | 0.2105(8) | 1.0376(8) | 0.2519(7) |
| C(8) | −0.147(1) | 0.3173(8) | 0.9896(8) | 0.2500(7) |
| N(2) | −0.1368(8) | 0.3417(7) | 0.8971(6) | 0.1009(7) |
| C(9) | −0.2901(9) | 0.3102(9) | 0.8555(9) | 0.1973(7) |
| C(10) | −0.1105(9) | 0.4611(7) | 0.8836(8) | 0.1217(7) |
| C(11) | 0.375(1) | 0.8913(7) | 0.6215(7) | 0.1494(7) |
| C(12) | 0.257(1) | 0.896(1) | 0.5393(8) | 0.2398(8) |
| C(13) | 0.229(1) | 0.803(1) | 0.4950(9) | 0.2758(7) |
| N(3) | 0.3005(9) | 0.7119(7) | 0.5240(6) | 0.1208(7) |
| C(14) | 0.406(1) | 0.689(1) | 0.4549(8) | 0.3202(7) |
| C(15) | 0.162(1) | 0.6369(9) | 0.5316(8) | 0.2423(7) |
| C(16) | 0.6384(9) | 0.7664(9) | 0.5753(7) | 0.1282(7) |
| C(17) | 0.755(1) | 0.8074(9) | 0.6463(7) | 0.2783(7) |
| C(18) | 0.751(1) | 0.7503(9) | 0.7464(7) | 0.1588(7) |
| N(4) | 0.5866(8) | 0.7537(6) | 0.7687(5) | 0.0827(7) |
| C(19) | 0.5593(9) | 0.6683(8) | 0.8489(6) | 0.1022(7) |
| C(20) | 0.562(1) | 0.8602(7) | 0.7957(7) | 0.1176(7) |

[a] $U_{eq}$ is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

**Synthesis of 1.** **1** was synthesized by the reaction either between iodine-activated magnesium turnings and 3-(dimethylamino)propyl chloride in benzene[9,10] followed by extraction with THF (48% yield) or between finely powdered activated magnesium (prepared by the reduction of anhydrous magnesium chloride with potassium[10]) and 3-(dimethylamino)propyl chloride in THF (67% yield). **1** melts at 145 °C.

$^1$H NMR ($C_6D_6$, $T$ = 297 K): $\delta$ 0.14 (t, 4H, α-$CH_2$), 1.39 (m, 16H, $\beta$-$CH_2$(THF)), 2.26 (s, 12H, N($CH_3$)$_2$), 2.20–2.50 (8H, $\beta$-$CH_2$ and $\gamma$-$CH_2$), 3.86 (m, 16H, α-$CH_2$(THF)).

$^{13}$C {$^1$H} NMR ($C_6D_6$, $T$ = 297 K): $\delta$ 2.80 (α-C), 25.20 ($\beta$-C(THF)), 45.53 (C(Me)), 65.42 ($\gamma$-C), 69.85 (α-C(THF)). The $\beta$-C signal is most likely buried in the $\beta$-C(THF) signal; the $^{13}$C proton undecoupled spectrum shows the appearance of a triplet for the α-C signal, a quartet for the C(Me) signal and a triplet for the $\gamma$-C signal.

Anal. Calcd for $C_{26}H_{56}N_2Cl_6O_4Mg_4$: C, 40.51; H, 7.27; N, 3.64; Cl, 27.65; Mg, 12.63. Found: C, 40.64; H, 7.25; N, 3.59; Cl 27.58; Mg, 12.56.

**Synthesis of 2.** A solution of **1** (2.035 g, 2.64 mmol) in 30 mL of THF was added dropwise over 1 h to a solution of $CrCl_3$·3THF (1.741 g, 4.65 mmol) in THF while stirring, and the resulting red-brown mixture was stirred overnight. The solvent was removed under vacuum and the residue dissolved

---

[9] Rosseels, G.; Matteazzi, J.; Wouters, G.; Bruckner, P.; Prost, M. *Synthesis* **1970**, 302.

[10] Lai, Yee-Hing *Synthesis* **1981**, 585 and references therein.

**Table 5. Selected Bond Distances and Angles for 2**

| | | | |
|---|---|---|---|
| Bond Distances (Å) | | | |
| Cr(1)—Cl(1) | 2.620(3) | Cr(1)—Cl(2) | 2.561(3) |
| Cr(1)—C(1) | 2.075(9) | Cr(1)—N(1) | 2.165(9) |
| Cr(1)—C(6) | 2.09(1) | Cr(1)—N(2) | 2.180(8) |
| Cl(1)—Mg(1) | 2.323(4) | Cl(2)—Mg(1) | 2.323(4) |
| Mg(1)—Cl(3) | 2.325(4) | Mg(1)—Cl(4) | 2.313(4) |
| Cl(3)—Cr(2) | 2.613(3) | Cl(4)—Cr(2) | 2.589(3) |
| Cr(2)—C(11) | 2.085(9) | Cr(2)—N(3) | 2.161(9) |
| Cr(2)—C(16) | 2.025(9) | Cr(2)—N(4) | 2.218(8) |
| Bond Angles (deg) | | | |
| Cl(1)—Cr(1)—Cl(2) | 83.1(1) | Cr(1)—Cl(1)—Mg(1) | 90.0(1) |
| Cr(1)—Cl(2)—Mg(1) | 91.4(1) | Cl(1)—Cr(1)—N(1) | 90.9(2) |
| Cl(2)—Cr(1)—N(1) | 93.4(3) | Cl(2)—Cr(1)—N(2) | 88.5(2) |
| Cl(1)—Cr(1)—N(2) | 91.4(3) | Cl(2)—Cr(1)—C(1) | 92.4(3) |
| Cl(1)—Cr(1)—C(6) | 91.0(3) | C(1)—Cr(1)—N(1) | 83.7(3) |
| N(1)—Cr(1)—N(2) | 177.2(3) | N(3)—Cr(2)—N(4) | 178.1(3) |
| C(6)—Cr(1)—N(2) | 82.1(3) | Cl(1)—Mg(1)—Cl(2) | 95.5(2) |
| Cl(3)—Mg(1)—Cl(4) | 96.8(2) | Cl(1)—Mg(1)—Cl(3) | 117.0(2) |
| Cl(1)—Mg(1)—Cl(4) | 115.6(2) | Cl(2)—Mg(1)—Cl(3) | 117.0(2) |
| Cl(2)—Mg(1)—Cl(4) | 116.4(2) | Mg(1)—Cl(3)—Cr(2) | 89.2(2) |
| Mg(1)—Cl(4)—Cr(2) | 90.1(2) | Cl(3)—Cr(2)—Cl(4) | 83.7(1) |
| Cl(4)—Cr(2)—N(3) | 90.0(3) | Cl(4)—Cr(2)—N(4) | 90.2(2) |
| Cl(3)—Cr(2)—N(3) | 92.7(3) | Cl(3)—Cr(2)—N(4) | 89.2(2) |
| Cl(4)—Cr(2)—C(16) | 92.6(3) | Cl(3)—Cr(2)—C(11) | 90.2(3) |
| C(11)—Cr(2)—N(3) | 84.5(4) | C(16)—Cr(2)—N(4) | 87.1(3) |
| Cr(1)—Mg(1)—Cr(2) | 176.9(1) | | |

in benzene. The resulting solution was filtered, the solvent removed under vacuum, and the reddish residue recrystallized from a hexane-cooled solution and identified as **2** (343 mg, 42.3% yield). **2** decomposes at 195–200 °C.

IR (KBr pellets): 1470 (s), 1225 (w), 1170 (w), 1045 (w), 1010 (m), 975 (m), 955 (m), 885 (m), 770 (m), 590 (w), 505 (w), and 470 (w) cm$^{-1}$.

Near-IR–vis $\lambda_{max}$ (benzene): 515 nm.

$^1$H NMR ($C_6D_6$, $T$ = 297 K): very broad overlapped signals centered at −3.85 and −25.26.

Anal. Calcd for $C_{20}H_{48}N_4Cl_4Cr_2Mg$: C, 39.07; H, 7.81; N, 9.12; Cl, 23.12; Cr 16.93; Mg 3.96. Found: C, 38.68; H, 7.62; N, 8.60; Cl, 23.36; Cr, 17.13; Mg, 3.94.

**Crystal Structure Determination.** Crystals, of maximum dimension 0.2 mm, were selected and used for X-ray analysis. Data was collected using a Philips PW 1100 (FEBO System) diffractometer with Mo Kα radiation ($\lambda$ = 0.7107 Å), monochromatized by a highly oriented graphite crystal. Each crystal was mounted under nitrogen inside a Lindman glass capillary which was hermetically sealed. The intensities of three standard reflections periodically measured showed slow decomposition during data collection for each of the crystal structures.

Cell dimensions were determined by least-square refinement of 25 medium-angle settings. The structures were solved by Patterson and Fourier methods, alternated by cycles of least-square refinement of the atomic parameters. Hydrogen atoms were located on the Fourier-difference maps but were generally introduced in calculated positions with fixed C—H distances and isotropic temperature factors (C—H = 1.08 Å, $U_{iso}$ = 0.08 Å$^2$). Anisotropy was introduced for all non-hydrogen atoms. Refinement of scale factor and positional and thermal parameters was performed minimizing the function $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1$. The ligand atoms in **2** show large vibrational motion and disordered atomic positions, and the disorder and the thermal motion are closely linked. Many attempts were made to find models which could be refined taking into account the statistical disorder of the ring atoms, but all were unsuccessful because the parameters tended to oscillate rather than converge. The reported positional parameters are those corresponding to the model which we have found to be the most successful. Form factors for the atoms were supplied internally by the SHELX[11] program system. Crystal and intensity data for the compounds are reported in Table 1; final atomic parameters and bond distances and angles are listed in Tables 2–5. The programs for the ORTEP drawings were from ref 12. The absorption correction applied was from ref 13.

**Supplementary Material Available:** Tables of thermal parameters of non-hydrogen atoms, fractional coordinates of the hydrogen atoms, and complete bond distances and bond angles (3 pages). Ordering information is given on any current masthead page. Structure factor amplitudes are available from the authors.

OM940268X

---

[11] Sheldrick, G. M. *SHELX 76*: *Program for Crystal Structure Determination*; Univ. of Cambridge: Cambridge, U.K., 1976.

[12] Johnson, C. K. *ORTEP-II*. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

[13] North, A.C.T.; Phillips D.C.; Matteus, F. S. *Acta Crystallogr., Sect. A.* **1968**, *24*, 351.