A bimetallic N-heterocyclic carbene complex featuring a short Cr–Cr distance†

Kevin A. Kreisel, Glenn P. A. Yap and Klaus H. Theopold*

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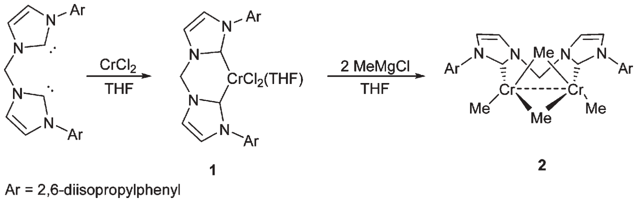
The alkylation of a chelating bis(carbene) complex of $CrCl_2$ yields an unusual bimetallic complex featuring a short Cr–Cr distance, novel ligand coordination, and CH_3 ligand exchange.

The rich chemistry of N-heterocyclic carbene (NHC) complexes has flourished in recent years due to their ability to stabilize a variety of transition metal complexes,[1] some of which are very active in catalytic reactions.[2] However, the early first row metals have been somewhat neglected in this endeavour and their NHC chemistry is fairly underdeveloped.[3] In our continuing quest to study organochromium complexes and their ability to catalytically polymerize ethylene,[4] we have decided to investigate a chelating bis(carbene) ligand to stabilize organometallic complexes of chromium.

Many examples of complexes with close Cr–Cr contacts are available in the literature, the shortest being 1.828(2) Å.[5] The strength of the M–M bonding that may coincide with such short Cr–Cr distances is controversial and is often complicated by bridging ligands that may facilitate antiferromagnetic coupling.[6] Our work with the bis(NHC) ligand 1,1′-methylene-3,3′-di-2,6-diisopropylphenylimidazole-2,2′-diylidene (L) and Cr(II) has yielded another example of such a complex.

Adding the free bis(NHC) ligand to a slurry of $CrCl_2$ in THF resulted in a color change to blue over the course of 1 h. The blue precipitate that formed was identified as $LCrCl_2(THF)$ (**1**).[7] Further treatment of **1** with MeMgCl, in an effort to make the corresponding alkyl complex ($LCrMe_2(THF)$), gave a red solution; standard work-up of the product yielded $LCr_2Me_2(\mu\text{-}Me)_2$ (**2**)‡ (Scheme 1) instead. The structure of **2** was determined by X-ray crystallography, the result of which is shown in Fig. 1.[8]

2 is a bimetallic complex consisting of one bis(carbene) ligand coordinated to two unique Cr(II) ions. Each Cr lies in a square plane formed by one arm of the bis(NHC) ligand, one terminal methyl ligand and two bridging methyl ligands. The hydrogen atoms of the bridging methyl groups were located and their positions refined in order to rule out the possibility of bridging alkylidenes. The two coordination planes about the chromium atoms intersect with an angle of 72.7°. The short Cr–Cr distance (2.0100(5) Å) and the diamagnetic nature of the ^1H NMR spectra (*vide infra*) of **2** are consistent with M–M bonding. However, the possibility of strong antiferromagnetic coupling mediated by the bridging methyl groups cannot be ruled out.



Scheme 1 Synthesis of $LCr_2Me_2(\mu\text{-}Me)_2$ (**2**).

The binucleating coordination mode of the bis(NHC) ligand and the net loss of one full bis(NHC) ligand suggest that Cr(II) is too electron rich to support the ligation of two methyl ligands and both arms of the strongly donating bis(NHC) ligand. The ejected bis(NHC) ligand apparently coordinates to the *in situ* formed $MgCl_2$ as the THF insoluble $LMgCl_2$. The IR spectrum of this precipitate contained bands consistent with the IR bands of the free bis(NHC) ligand. Comparison of the IR spectrum of $LMgCl_2$ from the reaction mixture and the IR spectrum of an independently synthesized sample of $LMgCl_2$ revealed similar stretching frequencies as well.

The solid state structure shown in Fig. 1 appears to persist in solution, as is evident from the ^1H NMR spectra of **2**. The spectrum in THF-d_8 appears to be that of a diamagnet (with the exception of very broad resonances for the Cr–CH_3 groups at 0.14 and −0.14 ppm) featuring fairly sharp resonances between 9.0 and

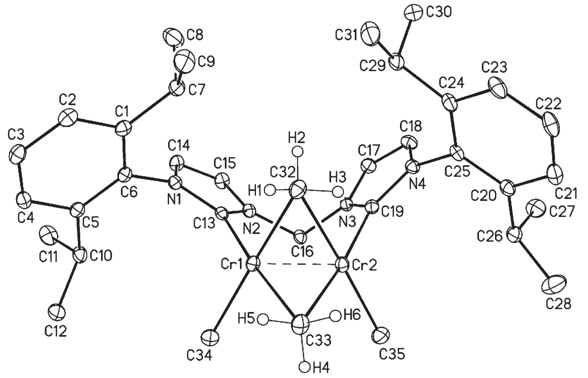
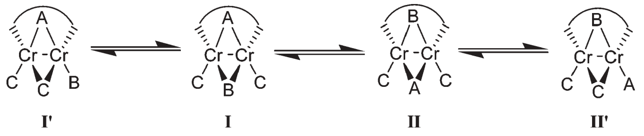


Fig. 1 The molecular structure of **2** with thermal ellipsoids at the 30% probability level. Selected distances [Å] and angles [°]: Cr1–Cr2 2.0100(5), Cr1–C13 2.127(2), Cr2–C19 2.123(2), Cr1–C32 2.225(2), Cr1–C33 2.243(2), Cr1–C34 2.115(2), Cr2–C32 2.254(2), Cr2–C33 2.202(2), Cr2–C35 2.106(2); C13–Cr1–Cr2 111.57(5), C19–Cr2–Cr1 111.17(5), C13–Cr1–C32 98.57(8), C13–Cr1–C33 172.83(8), C13–Cr1–C34 90.75(8), C19–Cr2–C32 92.86(8), C19–Cr2–C33 174.28(8), C19–Cr2–C35 92.51(9), Cr1–C32–Cr2 53.32(5), Cr1–C33–Cr2 53.76(5).

Department of Chemistry and Biochemistry, Center for Catalytic Science and Technology, University of Delaware, Newark, DE 19716, USA. E-mail: theopold@udel.edu; Fax: +1 (302)831-4269; Tel: +1 (302)831-1546

† Electronic supplementary information (ESI) available: Details of the X-ray crystal structure analysis and full structural information for **2**. See DOI: 10.1039/b616685g



Scheme 2 Methyl exchange processes in **2**.

0.5 ppm. The observation of two unique multiplets for the tertiary CH of the isopropyl groups suggests that there is no movement of the bis(NHC) ligand on the NMR time scale that would cause the bridging CH_2 group of the bis(NHC) ligand to invert. Furthermore, both of the protons of the CH_2 group are themselves unique. The three unique CH_3 resonances for the isopropyl groups in the ratio of 6 : 6 : 12 also suggest that the ligand is rigid in solution. Additionally, variable temperature ^1H NMR spectroscopy (*vide infra*) reveals no signs of a fluxional bis(NHC) ligand in solution.

At −30 °C, however, the broad Cr–CH_3 resonances are slightly shifted from their room temperature positions, as expected of a paramagnetic complex. In addition, the methyl resonances sharpened considerably, and split into three singlets in the ratio of 3 : 3 : 6. Thus, the broad nature of the Cr–CH_3 resonances must arise primarily from an exchange of the methyl ligands that is slow on the NMR time scale at low temperatures as well as from some remaining paramagnetism in the complex. Furthermore, warming **2** to 50 °C resulted in a coalescence of all of the Cr–CH_3 resonances. Thus, the variable temperature ^1H NMR data suggest that the bridging methyls and the terminal methyls are in exchange among themselves (**I** and **II**) and with each other (**I** and **I′**; **II** and **II′**) (Scheme 2). We believe this process may go by a lengthening of the Cr–Cr distance, rearrangement of the methyl ligands, followed by contraction of the Cr–Cr distance.[9]

Since each Cr atom in **2** is in the Cr(II) (d^4) oxidation state, a formal Cr–Cr quadruple bond is possible.[10] However, the square planes of each Cr ion in **2** are not parallel, as is the case for complexes like $Cr_2(2\text{-MeO-5-MeC}_6H_3)_4$.[6] The less than perfect d-orbital overlap in **2** should therefore lead to some remaining paramagnetism.[11] Accordingly, a room temperature magnetic moment revealed a μ_{eff} of 0.8(1) μ_B per Cr, which would account for the shifting and broadening of the Cr–CH_3 resonances in the ^1H NMR spectrum.

We have prepared a bimetallic complex of chromium that exhibits a short Cr–Cr distance and an unusual binding motif of a bis(NHC) ligand. The short Cr–Cr distance is consistent with considerable d-orbital overlap, which is also insinuated by the near diamagnetism of the complex. The solution dynamics of the methyl ligands include an exchange of the bridging methyl and the terminal methyl ligands that occurs rapidly on the NMR time scale at room temperature.

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Notes and references

‡ **2**: [$LCrCl_2$(THF)] (**1**, 0.195 g, 0.295 mmol) was suspended in 15 mL of THF and the solution cooled to −30 °C. MeMgCl (0.20 mL, 3.0 M, 0.590 mmol) was slowly added and the reaction mixture allowed to reach room temperature. After stirring for 1 h, the solvent was removed and the residue extracted with Et_2O and filtered. The resulting red solution was concentrated, layered with toluene, and cooled to −30 °C overnight to yield red crystals (0.059 g, 57% yield) of **2**. ^1H NMR (250 MHz, THF-d_8): δ = 8.28 (1 H, d, CH_2, J_{HH} = 4 Hz), 7.83 (2 H, s, CH(imid)), 7.19 (4 H, s, CH(aromatic)), 7.16 (2 H, s, CH(imid)), 6.92 (2 H, s, CH(aromatic)), 6.45 (1 H, d, CH_2, J_{HH} = 4 Hz), 2.88 (2 H, m, CH(i-Pr), J_{HH} = 6 Hz), 1.89 (2 H, m, CH(i-Pr), J_{HH} = 6 Hz), 1.44 (6 H, d, CH_3(i-Pr), J_{HH} = 6 Hz), 1.09 (6 H, d, CH_3(i-Pr), J_{HH} = 6 Hz), 0.72 (12 H, d, CH_3(i-Pr), J_{HH} = 6 Hz), 0.14 (6 H, br, Cr–CH_3), −0.14 (6 H, br, Cr–CH_3) ppm; IR (KBr): ν = 3124 (w), 3072 (w), 2963 (s), 2931 (s), 2869 (s), 1464 (s), 1383 (m), 1364 (m), 1247 (w), 1214 (w), 1180 (w), 1060 (w), 1031 (w), 804 (m), 761 (m), 471 (w) cm^{-1}; UV/Vis (THF): λ_{max} (ε) = 633 (88 M^{-1} cm^{-1}) nm; mp = 131 °C (dec.); MS (15 eV): *m*/*z* 524 (M^+ − Cr, − 4Me); elemental analysis calcd (%) for $C_{35}H_{52}N_4Cr_2$: C 66.44, H 8.28, N 8.85; found: C 66.09, H 8.52, N 8.61.

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8 **2**: $C_{39}H_{62}Cr_2N_4O$, M = 706.93, monoclinic, $P2_1/n$, a = 12.375(2) Å, b = 17.081(2) Å, c = 18.753(3) Å, β = 96.698(2)°, V = 3937.0(9) Å^3, Z = 4, D_{calc} = 1.193 g cm^{-1}, θ = 1.62–25.00°, Mo Kα λ = 0.71073 Å, T = 120 K, 33 353 reflections, R_{int} = 0.0247, μ = 0.585 mm^{-1}, max and min transmission: 0.9713 and 0.8821, solved by direct methods and refined by full-matrix least-squares procedures using SHELXTL (6.01),[12] 6929 unique reflections, 445 parameters, $R1$ = 0.0392, w$R2$ = 0.1020 ($I > 2\sigma(I)$). CCDC 618496. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b616685g.

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