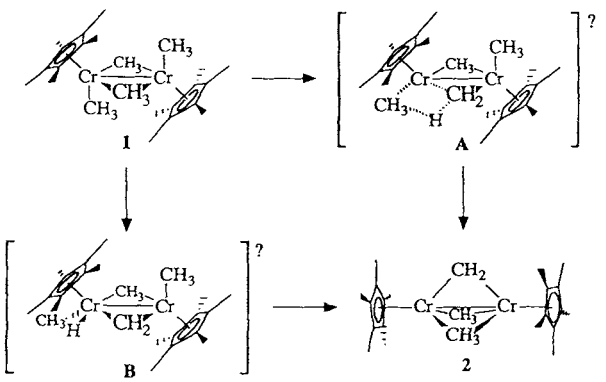
A Paramagnetic μ-Methylene Complex with a Short Cr^{III}–Cr^{III} Bond**

By *Seok Kyun Noh, Robert A. Heintz, Christoph Janiak, Shawn C. Sendlinger*, and *Klaus H. Theopold**

Despite the intensive study of μ-methylene complexes,[1] representatives of this class of organometallic compounds with unpaired electrons are rare,[2] and μ-CH_2 complexes of chromium are unknown. Our ongoing study of the reactivity of paramagnetic chromium(III) alkyls[3] has now produced an unusual molecule with one bridging methylene group and two bridging methyl ligands spanning a Cr–Cr bond. From an inorganic viewpoint this complex represents an unprecedented example of metal–metal bonding between two Cr^{III} ions of a face-sharing bioctahedron.[4]

We have recently reported the synthesis of the methyl-bridged dimer $[Cp^*(CH_3)Cr(\mu\text{-}CH_3)]_2$ (**1**) (Cp^* = pentamethylcyclopentadienyl).[3g] In solution this electron-deficient compound decomposed with a half-life of ca. 4.5 hours at room temperature. Toepler pump experiments and gas-chromatographic analysis showed that 0.92 equivalents of methane were produced in this reaction. In the ^1H NMR spectrum the Cp^* resonance of **1** ($\delta = 0.56$ in C_6D_6) was cleanly replaced with a new signal at $\delta = 3.0$. Recrystallization of the organometallic product from hexanes at $-30\,^\circ C$ yielded analytically pure $[\{Cp^*Cr(\mu\text{-}CH_3)\}_2(\mu\text{-}CH_2)]$ (**2**) in 45% yield (Scheme 1).[5] The mechanism of this intramolecular C–H activation may involve either a concerted "σ-bond metathesis" (transition structure **A**) or an oxidative addition yielding the *cis*-(alkyl)hydride **B** as an intermediate. While the former reaction pathway is well precedented only for d^0 alkyls,[6] the intermediacy of **B** is made plausible by the existence of alkyls and hydrides of Cr^{IV}.[7]



Scheme 1.

The crystal structure of **2** was determined by X-ray diffraction at $-65\,^\circ C$ (Fig. 1).[8] Complex **2** is a binuclear chromium complex and possesses no crystallographic symmetry.

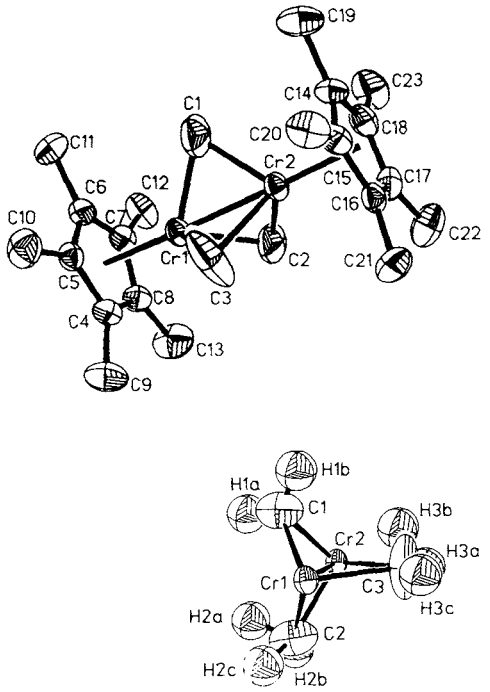


Fig. 1. The molecular structure of $[\{Cp^*Cr(\mu\text{-}CH_3)\}_2(\mu\text{-}CH_2)]$ (**2**). Selected bond distances [Å] and angles [°]: Cr1-Cr2 2.394(1), Cr1-C1 2.033(7), Cr2-C1 2.050(8), Cr1-C2 2.119(8), Cr2-C2 2.103(6), Cr1-C3 2.177(6), Cr2-C3 2.197(7), C1-H1a 0.905, C1-H1b 0.981, C2-H2a 1.064, C2-H2b 0.936, C2-H2c 1.086, C3-H3a 1.007, C3-H3b 0.868, C3-H3c 0.826; Cr1-C1-Cr2 71.8(3), Cr1-C2-Cr2 69.1(2), Cr1-C3-Cr2 66.3(2), C1-Cr1-C2 90.4(3), C1-Cr1-C3 92.0(3), C2-Cr1-C3 91.2(3), C1-Cr2-C2 90.4(3), C1-Cr2-C3 91.0(3), C2-Cr2-C3 91.1(3).

Each chromium is bonded to an η^5-Cp^* ligand, one bridging methylene group, and two bridging methyl ligands, thus placing the metal atom in the pseudooctahedral coordination environment of a three-legged piano stool. The two individual octahedra are joined via a trigonal face, resulting in a very close interaction between the two chromium atoms. Indeed, the Cr–Cr distance of 2.394(1) Å falls squarely within the range found in binuclear Cr^{II} carboxylates (2.28–2.54 Å), which are generally assigned quadruple bonds.[9] Thus **2**, which exhibits the shortest Cr^{III}–Cr^{III} distance found to date, certainly contains a metal–metal bond (see below). All hydrogen atoms of the bridging ligands were located in a difference map, and their positions were refined. Considering the limitations of an X-ray diffraction experiment, the C–H distances and H–C–H angles are reasonable, adding some credibility to the structural results overall. The Cr–C bonds to the methylene group (2.033(7) and 2.050(8) Å) are somewhat shorter than comparable σ bonds to terminal alkyl groups (ca. 2.09 Å).[3] Unexpectedly, the two methyl groups exhibit significantly different Cr–C bond lengths. While the bonds to C3 (2.177(6) and 2.197(7) Å) are similar to those found in **1** (2.170(5) and 2.206(4) Å), C2 features much shorter Cr–C distances (2.103(6) and 2.119(8) Å).

The extremely short Cr–Cr distance of **2** might be expected to lead to pairing of the d electrons in bonding molecular orbitals and thus we were surprised to find that the effective magnetic moment of **2** at room temperature substantially exceeds that of **1** (2.1 μ_B at room temperature), which exhibits a longer Cr–Cr distance (2.606(4) Å). The magnetic susceptibility of solid **2** in the temperature interval 60–280 K was measured with a Faraday balance; μ_{eff} increased with temperature and reached a value of 3.3 μ_B at room temperature. This behavior is consistent with merely antiferromagnetic coupling[10] of the two chromium centers (note that

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$[Cp^*Cr(\mu\text{-}Cl)CH_3]_2$ has no Cr–Cr bond (d_{Cr-Cr}: 3.278 Å)[11] and $\mu_{eff} = 3.5\ \mu_B$ at 280 K[3e]).

To address the extent of metal–metal bonding in **2** and to reconcile the structural data with the magnetic measurements, we have performed an EHMO calculation on the model compound $[\{\eta^5\text{-}Cp)Cr(\mu\text{-}CH_3)\}_2(\mu\text{-}CH_2)]$ (**2a**).[12] It is important to realize that one does not have to invoke metal–metal bonding to explain the short metal–metal contact found in **2**. A simple geometric calculation—assuming average $Cr\text{–}C_{bridge}$ bond distances of 2.11 Å and ideal octahedral geometry (all C–Cr–C angles 90°)—yields a Cr–Cr distance of 2.44 Å for a confacial bioctahedral structure. Thus, a strong metal–metal interaction may be a consequence rather than the cause of the observed structure. Figure 2 shows a partial interaction diagram of the fragment orbitals of two CpCr moieties and the hybrid orbitals of the bridging

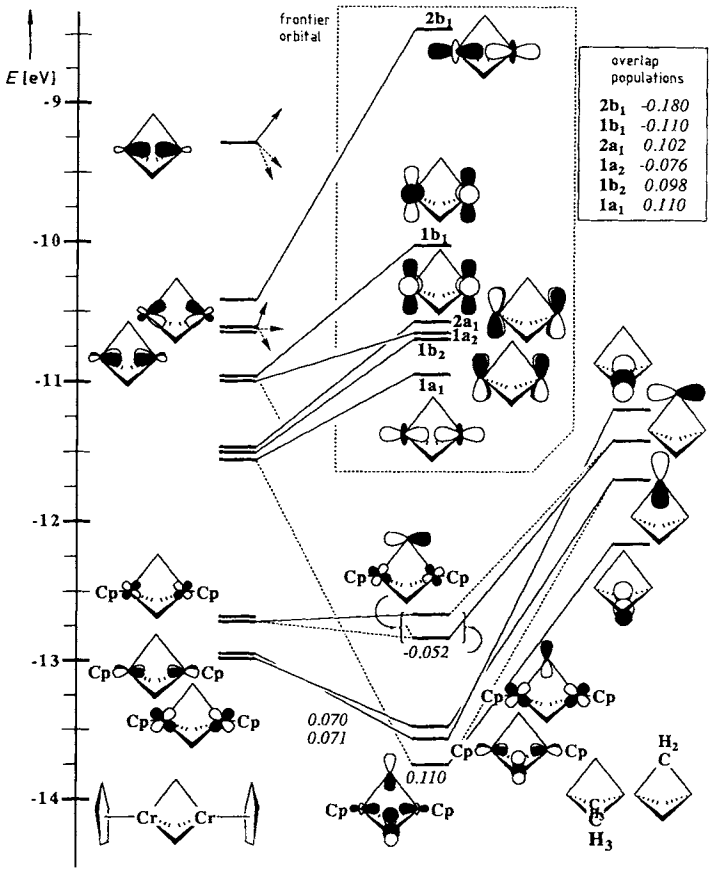

Fig. 2. Partial interaction diagram for $[\{CpCr(\mu\text{-}CH_3)\}_2(\mu\text{-}CH_2)]$ (**2a**). Numbers in italics are overlap populations; symmetry labels were assigned assuming C_{2v} symmetry. The overlap populations for the frontier d orbitals (inner box) were calculated for doubly occupied levels. Cp denotes substantial charge density on the cyclopentadienyl ligand.

ligands. As in the theoretical analysis of **1**,[3g] we find that the two three-center two-electron methyl bridges provide for substantial M–M overlap population (0.206) due to core orbitals. The three-center four-electron methylene bridge, on the other hand, makes only a minor contribution, as its filled Cr–C bonding combinations also give rise to metal–metal antibonding core levels.

Concerning the frontier d orbitals, Figure 2 shows the lower six levels (the two "t_{2g} sets" of the local octahedra) of the general 4-over-6 pattern expected for a confacial bioctahedron.[13] In idealized D_{3h} symmetry these are split into a_1' (σ), e′ (δ), e″ (δ^*), and a_2'' (σ^*) levels, the details of the pattern and energy gaps depending strongly on the metal and the M–X–M bridge angles. In the present case the σ^* level ($2b_1$ in C_{2v} symmetry) is too high in energy (1.5 eV above $1b_1$) to be populated in the electronic ground state. The remaining five levels lie within 1.0 eV and are available for filling with a total of six electrons. The extended Hückel method[14] does not take into account electron–electron interactions and thus cannot reliably predict the ground state of **2a**. However, the calculations are entirely consistent with a spin equilibrium between singlet, triplet, and pentet configurations. Herein lies the explanation for the higher magnetic moment of **2** when compared with **1**. Complex **1** features both σ and π bonding between the metals; both σ^* and π^* levels are thus destabilized beyond possible occupation, leaving only four MOs for six electrons (possible spin multiplicities $S = 0,1$). However, **2** exhibits σ and δ overlap and only the σ^* orbital is destabilized sufficiently to prevent occupation by electrons, thus leaving five MOs to be filled with six electrons (possible spin multiplicities $S = 0, 1, 2$).

We believe **2** is best described as having a chromium–chromium single bond. One aim of further experiments in our laboratory is the preparation of molecules with even shorter Cr^{III}–Cr^{III} distances. The "supershort" Cr^{II}–Cr^{II} quadrupole bonds (down to 1.828(2) Å)[9] provide a challenge, and the discovery of further examples of metal–metal bonding involving trivalent chromium is anticipated.

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1, 124242-59-7; **2**, 127446-27-9; **2a**, 127446-28-0.

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[4] a) F. A. Cotton, D. A. Ucko, *Inorg. Chim. Acta 6* (1972) 161; b) D. B. Morse, T. B. Rauchfuss, S. R. Wilson, *J. Am. Chem. Soc. 112* (1990) 1860; in contrast to these authors we do not believe that the Cr–Cr distance of 3.00(1) Å in $[Cp_2^*Cr_2(\mu\text{-}I)_3]^{\oplus}$ indicates significant metal–metal bonding between two Cr^{III} ions.

[5] **2**: ^1H NMR (C_6D_6): $\delta = 3.0$ (br, Cp*), 85.7 (v br, CH_3 and CH_2?). IR (KBr): $\tilde{\nu} = 2908$(s), 2852(m), 1437(m), 1375(s), 1161(w), 1109(w), 1024(m), 912(w), 565(w), 498(w) cm^{-1}. Correct elemental analysis.

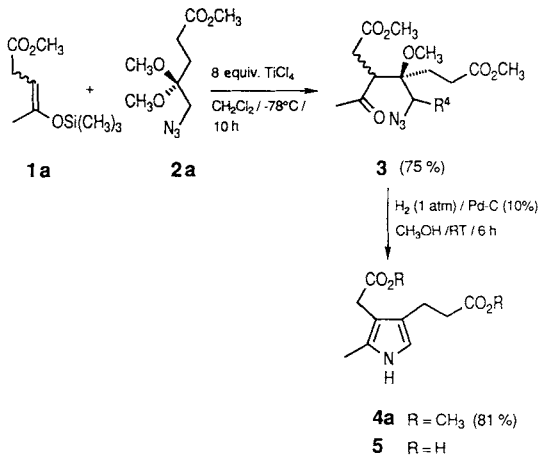
[6] M. E. Thompson, S. E. Baxter, A. R. Bulls, B. J. Burger, M. C. Nolan, B. D. Santarsiero, W. P. Schaefer, J. E. Bercaw, *J. Am. Chem. Soc. 109* (1987) 203.

[7] F. A. Cotton, G. Wilkinson: *Advanced Inorganic Chemistry*, 5th ed, New York 1988, p. 691.

[8] Purple crystals from hexanes; monoclinic $P2_1/c$; $a = 10.166(2)$, $b = 14.260(4)$, $c = 16.328(3)$ Å, $\beta = 106.26(2)°$; $Z = 4$; $R = 0.060$. Further details of the crystal structure determination are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD-54477, the names of the authors, and the journal citation.

[9] a) F. A. Cotton, R. A. Walton, *Multiple Bonds Between Metal Atoms*, Wiley, New York 1982, p. 150, b) *Struct. Bonding (Berlin) 62* (1985) 1.

[10] a) R. L. Martin in E. A. V. Ebsworth, A. G. Maddock, A. G. Sharp (Eds.): *New Pathways in Inorganic Chemistry*, Cambridge University Press, Cambridge 1968, Chapter 9; b) R. L. Carlin: *Magnetochemistry*, Springer Verlag, Berlin, 1986, Chapter 5; c) C. J. Cairns, D. H. Busch, *Coord. Chem. Rev. 69* (1986) 1.
[11] W. A. Herrmann, W. R. Thiel, E. Herdtweck, *J. Organomet. Chem. 353* (1988) 323.
[12] The computations were performed within the extended Hückel formalism with weighted H_{ij}'s [14]. The atomic and geometric parameters were (H_{ii}, ζ): Cr4s, − 8.66 eV, 1.70; 4p, − 5.24 eV, 1.70; 3d, − 11.22 eV, 4.95, 1.60 (coefficients for double ζ expansion: 0.4876, 0.7205) [15]; C 2s, − 21.4 eV, 1.625; 2p, − 11.4 eV, 1.625; H 1s, − 13.6 eV, 1.3 [14]. Cr-Cr 2.40 Å, Cr-CH_2 2.04 Å, Cr-CH_3 2.15 Å, C-H 0.96 Å, Cr-Cp(center) 1.906 Å, C-C (Cp) 1.41 Å; idealized C_{2v} symmetry.
[13] R. H. Summerville, R. Hoffmann, *J. Am. Chem. Soc. 101* (1979) 3821.
[14] a) R. Hoffmann, *J. Chem. Phys. 39* (1963) 1397; b) R. Hoffmann, W. N. Lipscomb, *ibid. 36* (1962) 2179, *37* (1962) 2872; c) J. H. Ammeter, H. B. Bürgi, J. C. Thibeault, R. Hoffmann, *J. Am. Chem. Soc. 100* (1978) 3686.
[15] T. A. Albright, P. Hofmann, R. Hoffmann, C. P. Lillya, P. A. Dobosk, *J. Am. Chem. Soc. 105* (1983) 3396.



Scheme 1. Synthesis of the pyrrole **4a** via crossed aldol reaction (RT = room temperature).

A Novel Pyrrole Synthesis**

By *Hugo Bertschy, Anne Meunier*, and *Reinhard Neier**

The importance of pyrroles as natural products can be traced to the many functions which are fulfilled by tetrapyrrolic ligands.[1] The most important example of a natural alkyl-substituted pyrrole is porphobilinogen, the precursor for all tetrapyrrolic ligands. Biosynthetically, porphobilinogen is formed with the help of δ-aminolevulinic acid dehydratase (EC 4.2.1.24) in a condensation reaction starting from two molecules of δ-aminolevulinic acid.[2] Formally, this transformation corresponds to a Knorr pyrrole synthesis. Up to now, however, this synthetic path could not be imitated in vitro.

Two mechanisms have been postulated for the enzyme-catalyzed synthesis of porphobilinogen, but no unequivocal proof for either of them has been put forward.[3] The mechanism proposed by *Shemin* is especially attractive for chemists, because the reaction sequence starts with the key step, the formation of the C–C bond. The problem of regioselectivity is solved right at the beginning and all the successive steps follow from the natural reactivity of the intermediates. This is in contrast to the proposed mechanism for the Knorr pyrrole synthesis,[4] where the C–N bond is formed first. In the Knorr synthesis the C–C bond formation occurs regioselectively only if the intermediate enamine is stabilized by conjugation. It is therefore difficult to synthesize alkyl-substituted pyrroles using a Knorr reaction.

We report here the regioselective synthesis of alkyl-substituted pyrroles, which follows *Shemin*'s proposal for the biosynthesis of porphobilinogen. Regioselectively formed silyl enol ethers are used in a crossed aldol reaction[5] (Scheme 1). The aldol products are transformed into mono-, di-, tri-, and tetraalkyl-substituted pyrroles (Table 1). Annelated and aryl-substituted pyrroles can also be synthesized via this sequence. The substitution pattern is determined by the aldol reaction. This sequence allows the synthesis of pyrroles starting with aldol products under very mild conditions.

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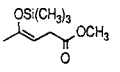
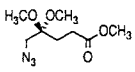
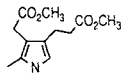
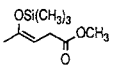
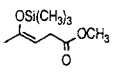
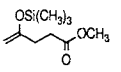
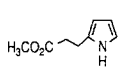
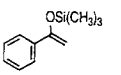
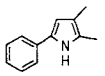
In order to use *Mukaiyama*'s crossed aldol reaction for the synthesis of pyrroles, adequate derivatives of α-amino ketones had to used. The azido group has been used successfully as a synthetic equivalent for amino groups. The acetal of α-azido ketones can be easily synthesized in two steps starting from α-halo ketones.[6] The synthesis of the second component, the silyl enol ethers, has been described already.[7]

Table 1. Synthesis of alkylpyrroles using the regioselective aldol reaction followed by cyclization.

No.	Silyl enol ether [a]	Acetal [b]	Reaction conditions [c]	Product (yield [%]) [d]
1	 **1a**	 **2a**	1. A, 75 % 2. B, 81 %	 **4a** (61 %)
2	 **1a**	 **2b**	1. A, 84 % 2. B, 52 %	 **4b** (44 %)
3	 **1a**	 **2c**	1. A, 80 % 2. B, 63 %	 **4c** (50 %)
4	 **1b**	 **2c**	1. A, 98 % 2. B, 26 %	 **4d** (25%)
5	 **6**	 **2b**	1. A, 85 % 2. C, 89 %	 **4e** (76%)

[a] Acetal:silyl enol ether = 1:1.1. [b] Acetals **2a** and **2b** were synthesized starting from the azido ketones [6]. Compound **2c** was synthesized starting from commercially available 2-bromo-1,1-dimethoxyethane (1.5 equiv. NaN_3/DMSO/KI (cat.)/90 °C/5 d). [c] A: 6 equiv. $TiCl_4/CH_2Cl_2/-78$ °C/6–8 h (trial 1:8 equiv. $TiCl_4$), yield calculated starting from the acetal; B: H_2/Pd-C 10%/CH_3OH/room temperature 6 h–2 d; C: PBu_3/C_6H_6/room temperature/5 d. yield relative to the unpurified aldol product; after crystallization (trial 1), after flash chromatography (hexane/EtOAc) (trials 4, 5), after kugelrohr distillation (80–120 °C/10^{-3} Torr) (trials 2, 3). [d] Total yield.