A stable alkyl hydride of a first row transition metal

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Hydrogenolysis of a Cr(III) dialkyl precursor produced a binuclear chromium complex with a bridging hydride and a bridging alkyl; this structurally characterized organometallic compound is thermally very stable and does not undergo the expected reductive elimination of alkane.

Organometallic compounds containing both an alkyl group (R) and a hydride ligand (H) in adjacent positions are generally unstable, decomposing by facile reductive elimination of alkane (R–H).[1] Exceptions to this rule are certain compounds containing transition metals of the second and third row, which allow the direct observation of C–H oxidative addition.[2] In contrast, the M–C and M–H bonds of first row transition metals are thought to be too weak to compensate for the loss of the C–H bond, and since the intrinsic activation barriers to C–H oxidative addition/reductive elimination are apparently small, the thermodynamically favored alkane elimination proceeds rapidly. Stable alkyl hydrides of first row transition metals are thus exceedingly rare.[3] Herein we report the synthesis and structural characterization of a dinuclear chromium alkyl hydride that is surprisingly stable.

In the context of our investigation of paramagnetic chromium alkyls as models for heterogeneous ethylene polymerization catalysts,[4] we have prepared [(2,6-Me$_2$Ph)$_2$nacnacCr(CH$_2$SiMe$_3$)$_2$] (**1**, (2,6-Me$_2$Ph)$_2$nacnac = *N,N'*-bis(2,6-dimethylphenyl)-2,4-pentanediiminato). **1** is a pseudotetrahedral Cr^{III} alkyl; despite its coordinative unsaturation (11-electron configuration) it does not catalyze the polymerization of ethylene in the absence of a co-catalyst. Reaction of **1** in pentane with excess hydrogen (1 atm, RT) yielded a red solution; standard work-up of the product gave [(2,6-Me$_2$Ph)$_2$nacnacCr)$_2$(μ-CH$_2$SiMe$_3$)(μ-H)] (**2**)† in high yield (see Scheme 1). The ^{1}H NMR spectrum of **2** exhibited several isotropically shifted and broadened resonances, as expected of a paramagnetic compound. The surprising nature of **2** was revealed by a crystal structure determination, the result of which is shown in Fig. 1.[5]‡

2 is a dinuclear chromium complex in which each chromium is coordinated by one nacnac ligand. The two chromium atoms are joined by a bridging hydride and a bridging trimethylsilylmethyl group. The hydride (H(1)) and the hydrogen atoms of the methylene group (H(2), H(3)) were located and their positions refined. The coordination geometry about each chromium is best described as distorted square planar and the dihedral angle between the two nacnac planes is 43.9°, presumably due to steric interactions between the aryl substituents and the μ-alkyl. The Cr–Cr distance of 2.6026(9) Å is
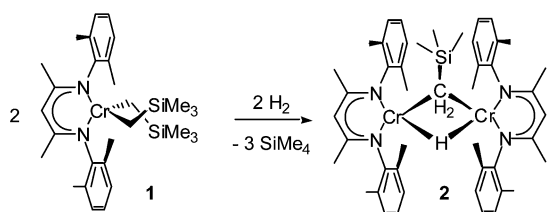
relatively long for a dinuclear Cr^{II} complex,[6] but the possibility of significant metal–metal bonding cannot be dismissed. It is supported by the low magnetic moment of **2** (μ_{eff} = 2.5(1) μ_B at 294 K, *i.e.* 1.8(1) μ_B per Cr), possibly augmented by antiferromagnetic coupling mediated by the bridging ligands.

In view of the unusual chemical nature of **2** and the diminished utility of NMR spectroscopy for its characterization, it was important to rule out alternative structures, such as a mixed-valent (Cr^{II}, Cr^{III}) μ-alkylidene. While the determination of hydrogen atom positions by X-ray diffraction is always compromised by a systematic error,[7] the detection of H(1)–H(3) in a difference map leaves little doubt about their presence. Furthermore, the gross structural features, bond distances and magnetic moment of **2** are very similar to those of a class of Cr^{II} dimers including—*inter alia*—[(2,6-Me$_2$Ph)$_2$nacnacCr)$_2$(μ-H)$_2$] (**3**).[8] Dihydride **3** was the product of an attempt to synthesize [(2,6-Me$_2$Ph)$_2$nacnacCr(CH$_2$CH$_3$)$_2$]; while this dialkyl appeared to be formed as an intermediate, it apparently suffered facile β-hydrogen elimination. Both the formation of **2** and **3** presumably involve binuclear reductive eliminations (of SiMe$_4$ for **2** and C$_2$H$_6$ or H$_2$ for **3**). The molecular structure of **3** is shown in Fig. 2;[9] like **2**, it is a dinuclear Cr–Cr-bonded compound (Cr–Cr = 2.6207(7) Å, μ_{eff} = 1.2(1) μ_B/Cr). The metal–ligand distances in both compounds are essentially identical and the effective magnetic moments of **2** and **3** are similar in magnitude and consistent with significant metal–metal interactions. This correspondence in physical properties strongly suggests that **2** and **3** belong in the same class and that the organic ligand of **2** is a bridging alkyl rather than a μ-alkylidene. Additional evidence for this was provided by
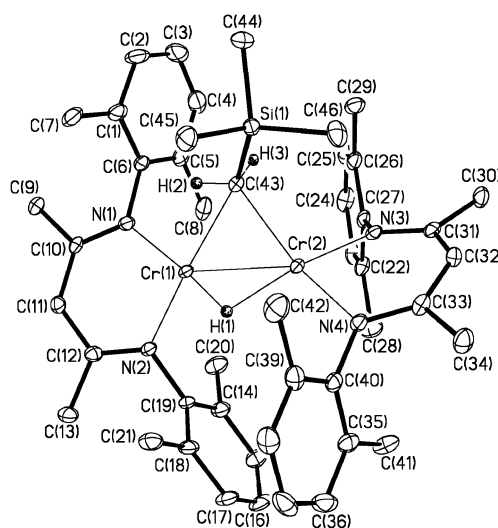

Fig. 1 The molecular structure of **2**. Selected distances [Å] and angles [°]: Cr(1)–Cr(2) 2.6026(9), Cr(1)–C(43) 2.288(4), Cr(2)–C(43) 2.190(4), Cr(1)–H(1) 1.67(7), Cr(2)–H(1) 1.78(7), Cr(1)–N(1) 2.080(4), Cr(1)–N(2) 2.026(3), Cr(2)–N(3) 2.062(4), Cr(2)–(N4) 2.061(4); Cr(1)–C(43)–Cr(2) 71.01(13), Cr(1)–H(1)–Cr(2) 97(4); Cr(1)–C(43)–Si(1) 144.4(3), Cr(2)–C(43)–Si(1) 105.1(2), N(1)–Cr(1)–N(2) 89.0(1), N(3)–Cr(2)–N(4) 88.4(1).
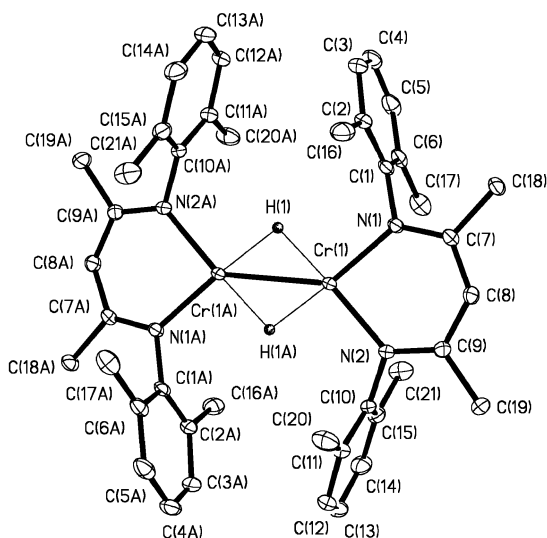

Scheme 1 Hydrogenolysis of [(2,6-Me$_2$Ph)$_2$nacnacCr(CH$_2$SiMe$_3$)$_2$] (**1**).

Fig. 2 The molecular structure of **3**. Selected distances [Å] and angles [°]: Cr(1)–Cr(1A) 2.6207(7), Cr(1)–H(1) 1.77(3), Cr(1)–H(1A) 1.76(3), Cr(1)–N(1) 2.0179(18), Cr(1)–N(2) 2.0268(19); Cr(1)–H(1)–Cr(1A) 95.9(9); N(1)–Cr(1)–N(2) 90.56(8).

labeling experiments coupled with mass spectroscopy. Thus, the mass spectrum (EI, 15 eV) of **2** exhibited a molecular ion at m/z 802 ($C_{46}H_{62}Cr_2N_4Si$) with the requisite chromium isotope pattern. The product of the reaction of **1** with D_2 showed a molecular ion at m/z 803, consistent with the formation of [(2,6-Me$_2$Ph)$_2$nacnacCr)$_2$(μ-CH$_2$SiMe$_3$)(μ-D)] (**2**-d$_1$).[10] GC-MS analysis of the volatile products of the reaction of **2** in toluene with D_2O was consistent with the formation of (CH$_3$)$_3$SiCH$_2$D as the sole organic product; in particular, there was no indication of the formation of (CH$_3$)$_3$SiCHD$_2$, the expected product of deuterolysis of an alkylidene species. Based on all these observations the assignment of **2** as an alkyl hydride complex is unambiguous.

2 is remarkably stable. For example, heating of a toluene-d$_8$ solution of **2** to 100 °C for several days did not produce any signs of decomposition. Prolonged photolysis did not induce any chemical change either. Finally, reaction of **2** with excess H_2 or D_2 had no discernible effect. To our knowledge, such resistance to alkane reductive elimination is unprecedented. We are considering two possible rationalizations of this phenomenon. First, it is conceivable that the inorganic product of the alkane elimination—presumably [((2,6-Me$_2$Ph)$_2$nacnacCr)$_2$]—is too unstable thermodynamically to allow its formation. The other possibility is that the reductive elimination faces an insurmountable kinetic barrier. Maybe electron–electron repulsion with the metal–metal bond prevents the development of overlap between the valence orbitals of the hydride and the alkyl group. However, we note that steric interactions force the core of **2** into a butterfly configuration; thus the dihedral angle between the planes defined by Cr(1)–C(43)–Cr(2) and Cr(1)–H(1)–Cr(2) is 47°. The nonbonded C(43)⋯H(1) distance of 2.74 Å and the C(43)–Cr–H(1) angles of 86° are characteristic of a *cis*-relationship of these two ligands; they provide no structural evidence for a repulsive interaction with a Cr–Cr bond. We are conducting further experiments and calculations to explore the unusual stability of **2** and to delineate the reactivity of this class of dinuclear Cr(II) organometallics.

Notes and references

† **2**: [(2,6-Me$_2$Ph)$_2$nacnacCr(CH$_2$SiMe$_3$)$_2$] (**1**, 0.700 g, 1.32 mmol) was placed in a large ampoule and dissolved in 25 mL pentane. The solution was degassed and the ampoule was filled with H$_2$ (1 atm). The reaction mixture

was stirred overnight at room temperature, whereupon its color had changed to dark red. After evaporation of the pentane the residual solid was extracted with Et$_2$O. Cooling of the concentrated Et$_2$O solution to −30 °C yielded dark red crystals (0.500 g, 95% yield) of **2**. ^{1}H NMR (C_6D_6): δ = 14.7 (br), 6.4 (br), 4.7 (br), 2.6 (br) ppm; IR (KBr): ν = 3056 (m), 3016 (m), 2954 (s), 2915 (s), 2852 (m), 1533 (s), 1435 (s), 1384 (s), 1285 (m), 1259 (m), 1241 (s), 1182 (s), 1094 (m), 1022 (m), 979 (s), 857 (s), 761 (s), 673 (m) cm^{-1}; UV/Vis (Et$_2$O): λ_{max} (ε) = 480 (663 M^{-1} cm^{-1}) nm; mp: 194–197 °C; μ_{eff} (294 K) = 2.5(1) μ_B; MS (15 eV): m/z 802 (M$^+$); elemental analysis calcd (%) for $C_{46}H_{62}Cr_2N_4Si_1$: C 68.80, H 7.78, N 7.00; found: C 68.72, H 7.66, N 6.82.

3: [(2,6-Me$_2$Ph)$_2$nacnacCrCl$_2$(THF)$_2$] (0.440 g, 0.768 mmol) was dissolved in 10 mL Et$_2$O and the solution cooled to −30 °C. A 3.0 M Et$_2$O solution of EtMgBr (0.533 mL, 1.6 mmol) was added *via* syringe, resulting in a rapid color change from red to green. The solution was warmed to room temperature and stirred overnight, whereupon the color had changed to a dark orange. Filtering, concentrating, and cooling to −30 °C yielded orange crystals of **3**. ^{1}H NMR (C_6D_6): δ = 19.3 (br), 13.7 (br), 7.0 (br), 6.8 (br), 2.0 (br) ppm; IR (KBr): ν = 3055 (m), 3014 (m), 2958 (s), 2917 (s), 2856 (m), 1522 (s), 1454 (s), 1378 (s), 1260 (m), 1240 (s), 1180 (s), 1096 (m), 1022 (m), 851 (s), 762 (s) cm^{-1}; μ_{eff} (294 K) = 1.7(1) μ_B; MS (15 eV): m/z 716 (M$^+$); elemental analysis calcd (%) for $C_{42}H_{52}Cr_2N_4$: C 70.36, H 7.31, N 7.81; found: C 68.88, H 7.63, N 6.25.

‡ CCDC 196911 and 205747. See http://www.rsc.org/suppdata/cc/b3/b301943h/ for crystallographic data in .cif or other electronic format.

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5 **2**: $C_{46}H_{62}Cr_2N_4Si$, M = 803.09, monoclinic, $P2_1/n$, a = 12.33630(10) Å, b = 20.9724(3) Å, c = 17.6709(3) Å, β = 106.0100(10)°, V = 4394.52(10) Å^3, Z = 4, D_{calc} = 1.214 g cm^{-1}, θ = 1.54–25.00°, MoK$_\alpha$ λ = 0.71073 Å, T = 173 K, 16789 reflections, μ = 0.557 mm^{-1}, max and min transmission: 0.9211 and 0.8734, solved by direct methods and refined by full-matrix least-squares procedures using SHELXTL (5.1), 490 parameters, R = 0.0687, wR = 0.1912. CDCC reference number 196911.
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8 Similar compounds featuring a related nacnac ligand are [(2,6-^{i}Pr$_2$Ph)$_2$nacnacCr)$_2$(μ-CH$_3$)$_2$] (Cr–Cr 2.597(10) Å, Cr–N$_{avg}$ 2.09 Å, Cr–C$_{avg}$ 2.21 Å, μ_{eff} = 2.5(1) μ_B) and [(2,6-^{i}Pr$_2$Ph)$_2$nacnacCr)$_2$(μ-H)$_2$] (Cr–Cr 2.676(13) Å, Cr–N$_{avg}$ 2.05 Å, Cr–H$_{avg}$ 1.71 Å, μ_{eff} = 3.5(1) μ_B); these will be included in a forthcoming full paper; L. A. MacAdams, PhD thesis, University of Delaware, 2002.
9 **3**: $C_{42}H_{52}Cr_2N_4$, M = 716.88, monoclinic, $C2/c$, a = 23.4971(13) Å, b = 10.7216(6) Å, c = 15.0645(9) Å, β = 92.4850(10)°, V = 3791.6(4) Å^3, Z = 4, D_{calc} = 1.256 g cm^{-1}, θ = 2.09–28.28°, MoK$_\alpha$ λ = 0.71073 Å, T = 150 K, 11853 reflections, μ = 0.607 mm^{-1}, max and min transmission: 0.9145 and 0.8882, solved by direct methods and refined by full-matrix least-squares procedures using SHELXTL (5.1), 221 parameters, R = 0.0471, wR = 0.1375. CDCC reference number 205747.
10 A comparison of the IR spectra of **2** and **2**-d$_1$ did not reveal any significant differences; presumably the hydride (deuteride) stretches are obscured by ligand bands.