C–H Bond Formation

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A Tale of Two Isomers: A Stable Phenyl Hydride and a High-Spin ($S = 3$) Benzene Complex of Chromium[**]

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Stable alkyl (or aryl) hydrides of first-row transition metals are rare, presumably because the reductive elimination of alkane (or arene) is both thermodynamically favorable and kinetically facile.[1] Exceptions to this empirical rule are of considerable interest,[2] especially when both sides of the C–H activation equilibrium are directly observable. Herein, we describe a pair of such molecules and the unusual magnetic behavior of one of them.

Reaction of $[\{(\{i\mathrm{Pr}_2(\mathrm{C}_6\mathrm{H}_3)\}_2\mathrm{nacnac})\mathrm{Cr}\}_2(\mu\text{-Cl})_2]$[3] with PhMgCl in THF produced the mononuclear phenyl complex $[(\{i\mathrm{Pr}_2(\mathrm{C}_6\mathrm{H}_3)\}_2\mathrm{nacnac})\mathrm{CrPh(thf)}]$ (**1**; $\{i\mathrm{Pr}_2(\mathrm{C}_6\mathrm{H}_3)\}_2$nacnac = 2,4-pentane-*N*,*N'*-bis(2,6-diisopropylphenyl)ketiminate). Complex **1** adopts a slightly distorted square-planar coordination about the $\mathrm{Cr}^{\mathrm{II}}$ center (see the Supporting Information), and its effective magnetic moment ($\mu_{\mathrm{eff}} = 4.8(1)\,\mu_{\mathrm{B}}$ at 295 K) is consistent with the four unpaired electrons of a high-spin d^4 configuration. Exposure of **1** to H_2 gas (1 atm) yielded two metal complexes. The major product was identified spectroscopically as the previously described hydride $[\{(\{i\mathrm{Pr}_2(\mathrm{C}_6\mathrm{H}_3)\}_2\mathrm{nacnac})\mathrm{Cr}\}_2(\mu\text{-H})_2]$ (**2**), which is the product of a straightforward hydrogenolysis of **1** with subsequent dimerization. The minor product (17%) was a new compound, and it was revealed by X-ray structure determination (Figure 1 a) to be $[\{(\{i\mathrm{Pr}_2(\mathrm{C}_6\mathrm{H}_3)\}_2\mathrm{nacnac})\mathrm{Cr}\}_2(\mu\text{-Ph})(\mu\text{-H})]$ (**3**).[4] The binuclear chromium complex is held together by a bridging hydride (which was clearly located in the difference map) and a bridging phenyl ligand. The presence of the hydride ligand was confirmed by spectroscopic methods. Most importantly, the LIFDI mass spectrum of **3** (LIFDI = liquid injection field desorption ionization) showed the molecular ion (*m*/*z* 1016) as the base peak, with excellent agreement between the experimental and calculated isotope patterns.[5] Compound [D]-**3**, prepared by reaction of **1** with D_2, exhibits a similar pattern centered about *m*/*z* 1017 (M^+). The deuteride ([D]-**3**) also exhibited a band at 966 cm^{-1} in the IR spectrum (KBr), which was greatly diminished in intensity in the hydride. However, the corresponding band in the hydride is apparently obscured by strong ligand bands. The Cr–Cr separation of 2.6277(10) Å is consistent with some degree of metal–metal bonding; however, the potential-energy surface of $\mathrm{Cr}^{\mathrm{II}}$–$\mathrm{Cr}^{\mathrm{II}}$ interactions is notoriously flat, and any Cr–Cr bond in **3** would probably not be strong.[6] At $\mu_{\mathrm{eff}} = 2.4(1)\,\mu_{\mathrm{B}}$ (293 K), the magnetic moment of **3** at the very least indicates relatively strong antiferromagnetic coupling between the $\mathrm{Cr}^{\mathrm{II}}$ ions, which was confirmed by variable-temperature magnetic susceptibility measurements (see the Supporting Information). Thus, the spin ground state of **3** is $S = 0$. The formation of **3** most likely involves trapping of a mononuclear hydride formed in situ by remaining **1**. We note that **2**, once formed, does not react with **1** to produce **3**.

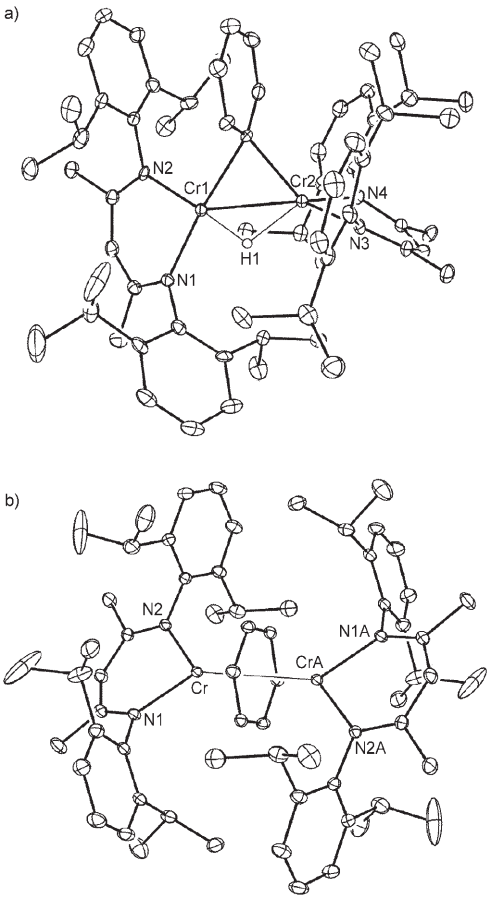

Figure 1. The molecular structures of isomers **3** (a) and **5** (b); thermal ellipsoid are set at 30% probability, and hydrogen atoms other than the hydride ligand in **3** are omitted for clarity. Selected interatomic separations [Å] and angles [°] for **3**: Cr1–Cr2 2.6277(10), Cr1–C64 2.265(2), Cr2–C64 2.158(2), Cr1–H1 1.70(3), Cr2–H1 1.69(3); Cr1-C64-Cr2 72.86(8) and for **5**: Cr–C_{av} 2.271 (range: 2.252(3)–2.289(3)), C–C(av) 1.437 (range: 1.433(4)–1.443(4)), Cr–CrA 3.515(2).

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As a consequence of the distorted square-planar coordination geometry about both chromium atoms of **3** and the *cis*-chelating nature of the nacnac ligands, the phenyl group and the hydride are necessarily in a *cis* arrangement. Thus, the C_{ipso}-Cr-H angles are 79.5° and 83.0°, respectively, and the nonbonded C_{ipso}–H separation is a modest 2.57 Å. In view of this close proximity and the potential formation of a rather strong ($D_{\text{C-H}} = 113\ \text{kcal mol}^{-1}$) aromatic C–H bond,[7] reductive elimination of a molecule of benzene from **3** might be expected to be facile. However, **3** is indefinitely stable at room temperature, and its thermolysis proceeded very slowly even at 80 °C (approximate half life greater than one month). Among the multiple products of its decomposition were benzene (identified by ^{1}H NMR spectroscopy) and $[\{(\{i\text{Pr}_2(\text{C}_6\text{H}_3)\}_2\text{nacnac})\text{Cr}\}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-CH}_2(\text{CH}_2)_3\text{O})]$ (**4**; identified by X-ray diffraction, see the Supporting Information); the latter is the result of a C–O bond activation of the THF solvent. Repetition of the thermolysis in $[\text{D}_{18}]$octane revealed very little decomposition of **3** up to 120 °C.

Hypothetical C–H bond formation in **3** without loss of benzene might form a benzene complex. Chromium has a pronounced tendency for the formation of η^6-arene complexes,[8] and the stability of this structural motif ($D_{\text{Cr-Ar}} = 39\ \text{kcal mol}^{-1}$)[9] should be another contribution to the thermodynamic driving force for the reductive elimination. The envisioned compound can indeed be prepared, albeit not by the path suggested. Instead, magnesium reduction of $[\{(\{i\text{Pr}_2(\text{C}_6\text{H}_3)\}_2\text{nacnac})\text{Cr}\}_2(\mu\text{-Cl})_2]$ in THF in the presence of a small amount of benzene yielded a black solution, from which crystals of $[\{(\{i\text{Pr}_2(\text{C}_6\text{H}_3)\}_2\text{nacnac})\text{Cr}\}_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_6\text{H}_6)]$ (**5**) could be isolated in 58 % yield. The molecular structure of **5** is shown in Figure 1 b.[4] Two $\{(\text{nacnac})\text{Cr}^\text{I}\}$ fragments are joined by a bridging benzene ligand, which keeps the two Cr atoms at a distance of 3.515(2) Å.[10] Thermolysis of **5** also required high temperatures (over 80 °C), eventually yielding benzene and **4** without any evidence of **3** being formed. Complex **5** is a paramagnet with an unusually large room-temperature magnetic moment ($\mu_{\text{eff}} = 7.4(1)\mu_\text{B}$ per dimer at 293 K). This value is close to the spin-only moment for a strongly coupled system with six unpaired electrons ($S = 3$, $\mu_{\text{eff}} = 6.93\mu_\text{B}$). Two magnetically independent chromium ions would result in moments of either $8.4\mu_\text{B}$ (two $S = 5/2$ ions) or $5.5\mu_\text{B}$ (two $S = 3/2$ ions), both of which are inconsistent with the measured moment. The results of variable-temperature magnetic measurements on **5** are shown in Figure 2.

Its molar magnetic susceptibility followed the Curie–Weiss law, with a temperature-independent moment of $7.4\mu_\text{B}$. Saturation magnetization measurements at 5 K (see the Supporting Information) were consistent with a spin ground state of $S = 3$. The only reasonable interpretation of these results posits extremely strong ($|J| > 500\ \text{cm}^{-1}$) ferromagnetic coupling between the two metal centers (Cr^I, d^5, $S = 3/2$), mediated by the bridging benzene ligand.[11]

Complexes **3** and **5** are isomers related by a simple C–H bond formation/cleavage. However, we have not observed any interconversion between them; thus our belief—based on bond-strength considerations[12]—that **5** is the thermodynamically more stable isomer remains tentative. The kinetic barrier separating **3** and **5** is surprisingly high, and its origin is not at all clear. Possible reasons include the presence of a direct metal–metal bond in **3**, which prevents the development of overlap between the valence orbitals of the phenyl *ipso* carbon atom and the hydride ligand by coulombic repulsion, or the widely differing spin states of **3** and **5** (i.e., a dramatic example of "spin blocking").[13] These questions, as well as the further exploration of molecules akin to **3** and **5**, are the subject of current research.

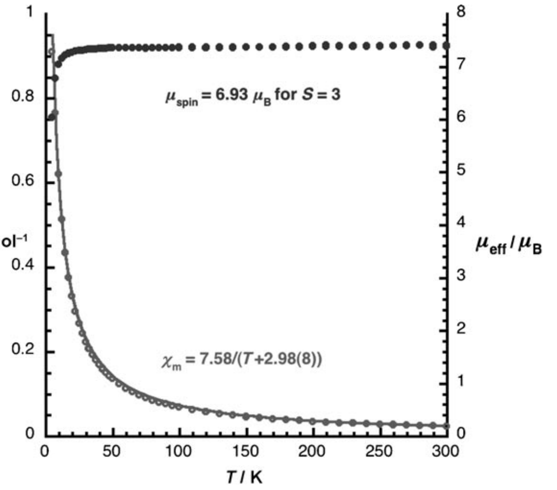

Figure 2. Temperature dependence of the molar magnetic susceptibility (χ_M, open circles, line is the fit with a Curie–Weiss expression) and the effective magnetic moment (μ_{eff}, filled circles) of **5**.

Experimental Section

3: $[(\{i\text{Pr}_2(\text{C}_6\text{H}_3)\}_2\text{nacnac})\text{Cr}(\text{Ph})(\text{thf})]$ (500 mg, 0.808 mmol) was dissolved in pentane (50 mL) and placed in an ampule. The ampule was evacuated and filled with H_2 (1 atm), and the solution was allowed to stir 10 h, during which time the solution became cloudy. The hydrogen and pentane were removed in vacuo. The product was extracted with pentane (25 mL) to give a brown solution. The byproduct filtered off was identified as $[\{(\{i\text{Pr}_2(\text{C}_6\text{H}_3)\}_2\text{nacnac})\text{Cr}\}_2(\mu\text{-H})_2]$ (**2**). The solution was concentrated and cooled to −30 °C to yield brown crystals of **3** (142 mg, 17 % yield). ^{1}H NMR (400 MHz, $[\text{D}_8]$THF, 295 K): $\delta = 23.2$ (br), 7.05 (br), 6.41 (br), 2.69 (br), 0.30 ppm (br). IR (KBr): $\tilde{\nu} = 3058$ (w), 2959 (s), 2929 (s), 2867 (m), 1526 (s), 1461 (s), 1435 (s), 1392 (s), 1314 (s), 1524 (m), 1174 (m), 1098 (w), 1020 (w), 932 (w), 796 (m), 760 cm^{-1} (w). UV/Vis (pentane): $\lambda_{\max}$ (ε) = 622 (236 $\text{M}^{-1}\text{cm}^{-1}$), 689 nm (259 $\text{M}^{-1}\text{cm}^{-1}$). $\mu_{\text{eff}} = 2.4(1)\mu_\text{B}$ (293 K); m.p. 224 °C (decomp); LIFDI-MS m/z (%): 1016.6 (100) $[M^+]$.[5] Elemental anal. calcd (%) for $\text{C}_{64}\text{H}_{88}\text{N}_4\text{Cr}_2$: C 75.55, H 8.72, N 5.51; found: C 74.09, H 8.26, N 5.25.

5: $[(\{i\text{Pr}_2(\text{C}_6\text{H}_3)\}_2\text{nacnac})\text{Cr}(\mu\text{-Cl})]_2$ (2.00 g, 1.96 mmol) was dissolved in THF (75 mL). Excess Mg (500 mg, 20.6 mmol), excess benzene (1 mL, 11.3 mmol), and a catalytic amount of napthalene (5 mg, 0.04 mmol) were added, and the solution was allowed to stir overnight. The color gradually changed from deep green to black. The solvent was removed in vacuo and the product was extracted with cold THF (25 mL). Concentration and cooling to −30 °C yielded black crystals of **5** (1.23 g, 58 % yield). ^{1}H NMR (400 MHz, $[\text{D}_8]$THF, 295 K): $\delta = 98.2$ (br), 12.0 (br), 8.88 (br), 2.59 ppm (br). IR (KBr): $\tilde{\nu} = 3052$ (w), 2953 (s), 2925 (m), 2865 (m), 1537 (s), 1520 (s), 1457 (s), 1433 (s), 1407 (s), 1360 (m), 1312 (s), 1258 (w), 1226 (w), 1173 (m), 1103 (w), 1023 (w), 932 (w), 791 (m), 758 (m), 724 cm^{-1} (w). UV/Vis (pentane): $\lambda_{\max}$ (ε) = 485 (4392 $\text{M}^{-1}\text{cm}^{-1}$), 865 nm (991 $\text{M}^{-1}\text{cm}^{-1}$); m.p. 290 °C (decomp). MS m/z (%): 469.3 (100) $[(M^+-\text{C}_6\text{H}_6)/2]$, 954.5

(11) $[M^+-C_5H_3]$, 1016.5 (4) $[M^+]$. Elemental anal. calcd (%) for $C_{64}H_{88}N_4Cr_2$: C 75.55, H 8.72, N 5.51; found: C 75.15, H 8.60, N 5.73.

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[4] Crystal data for **3**·1.5 pentane: $C_{71.5}H_{106}Cr_2N_4$, $M_r = 1125.60$, $0.35\times0.25\times0.15$ mm^3, triclinic, space group $P\bar{1}$, $a = 13.308(7)$, $b = 13.368(7)$, $c = 19.253(10)$ Å, $\alpha = 102.741(5)$, $\beta = 105.688(5)$, $\gamma = 89.970(5)$°, $V = 3210(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.165$ g cm^{-3}, $\mu = 0.382$ mm^{-1}, Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $T = 120(2)$ K, $2\theta_{max} = 56.56$°, 35508 reflections, 14514 independent, $R_{int} = 0.0777$, $R = 0.0552$, $wR = 0.1434$, largest difference peak and hole: 0.753 and −0.380 e Å^{-3}. Hydrogen atom H1 was the largest peak in the penultimate difference map and yielded computationally stable results of isotropic refinement. The data set was treated with SQUEEZE (A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7–13) to model the 1.5 molecules of cocrystallized pentane as bulk solvent. Crystal data for **5**·benzene: $C_{70}H_{94}Cr_2N_4$, $M_r = 1095.49$, $0.26\times0.21\times0.18$ mm^3, triclinic, space group $P\bar{1}$, $a = 9.5649(16)$, $b = 13.372(2)$, $c = 13.549(2)$ Å, $\alpha = 86.983(2)$, $\beta = 72.575(2)$, $\gamma = 82.523(3)$°, $V = 1639.3(5)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.110$ g cm^{-3}, $\mu = 0.372$ mm^{-1}, Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $T = 120(2)$ K, $2\theta_{max} = 56.58$°, 14033 reflections, 7269 independent, $R_{int} = 0.0262$, $R = 0.0735$, $wR = 0.2278$, largest difference peak and hole: 1.683 and −0.773 e Å^{-3}. Data sets were treated with SADABS absorption corrections. No symmetry higher than triclinic was observed in the diffraction data, and the structural solution in the centrosymmetric space group option yielded chemically reasonable and computationally stable results of refinement. The compound molecule is located at an inversion center in **5**. A large range of nonsolvent, equivalent isotropic parameters, $CU_{eq}(\text{max/min}^{-1}) = 6.23$, are observed in **5** because of irresolvable, continuous oscillation disorder of isopropyl fragments. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. Structure factors are contained in SHELXTL 6.12 program library (G. Sheldrick, Siemens XRD, Madison, WI, **2001**). CCDC-644369 (**3**) and CCDC-644366 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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