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Monomeric, Two-Coordinate, Univalent Chromium(I) Compounds: Steric Prevention of Metal−Metal Bond Formation

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Since the initial report on the reaction of PhMgBr with $\mathrm{CrCl_3}$ by F. Hein in 1918,[1] chromium aryls and arenes, as exemplified by bis(benzene)chromium, $\mathrm{Cr}(\eta^6\text{-}\mathrm{C_6H_6})_2$,[2] have played a leading role in the development of organometallic chemistry.[3,4] We reported recently that the aryl chromium(I) species Ar′CrCrAr′ (**1**), in which the large terphenyl ligand $\mathrm{C_6H_3\text{-}2,6\text{-}(C_6H_3\text{-}2,6\text{-}Pr^{\mathit{i}}_2)_2}$ (Ar′) stabilizes a metal−metal bonded dimer with a 5-fold bonding interaction between the metals, could be isolated and characterized.[5,6] It was prepared by the reduction of the aryl chromium halide precursor Ar′CrCl with $\mathrm{KC_8}$. Currently, we are exploring the character of this new metal−metal bond, including the effects of changes in the steric and electronic properties of the aryl ligand. We now present our results on the use of the more crowding terphenyl ligand $\mathrm{C_6H_1\text{-}2,6\text{-}(C_6H_2\text{-}2,4,6\text{-}Pr^{\mathit{i}}_3)_2\text{-}3,5\text{-}Pr^{\mathit{i}}_2}$[7] (abbreviated 3,5-$^i\mathrm{Pr_2}$−Ar*) as a chromium substituent. This has enabled the isolation of the monomeric, two-coordinate Cr(I) complexes [(3,5-$^i\mathrm{Pr_2}$-Ar*)Cr(L)] (**2**, L = THF; **3**, L = $\mathrm{PMe_3}$).

Compounds **2** and **3** were prepared via reduction of (3,5-$^i\mathrm{Pr_2}$-Ar*)CrCl[8] with $\mathrm{KC_8}$ in THF (**3** in the presence of $\mathrm{PMe_3}$) and were isolated in modest yields as air-sensitive orange (**2**) or orange-red (**3**) crystals after extraction with hexanes.[9] An X-ray crystal structure of **2**[10] revealed that no Cr−Cr bond was present. Instead, a monomeric THF complex [(3,5-$^i\mathrm{Pr_2}$-Ar*)Cr(THF)] (**2**), in which the metal atom is surrounded by an η^1-coordinate 3,5-$^i\mathrm{Pr_2}$-Ar* ligand [Cr1−C1 = 2.087(3) Å] and a THF molecule [Cr1−O1 2.062(5) Å], was observed (Figure 1).[11] The large C1−Cr1−O1 angle of 173.7(2)° shows that the Cr1 coordination geometry is nearly linear. The Cr1−C1 distance lies between the Cr−C(ipso) distance in **1** [2.131(1) Å] and the shorter Cr−C bond length in the related, quasi-four-coordinate aryl chromium(II) halide $\mathrm{[Ar'CrCl]_2}$ [Cr−C(ipso) 2.037(2) Å].[8] All other Cr−C contacts exceed 3.0 Å. Consequently, a +1 oxidation state can be assigned to chromium, which corresponds formally to a $4s^0 3d^5$ electron configuration. The solid-state molecular structure of **3**[10] displays a very similar arrangement to **2** with a slightly longer Cr−C1 distance of 2.116(2) Å and a P1−Cr1−C1 bond angle of 167.39(4)°. The Cr1−P1 distance [2.4646(5) Å] is in the expected range.[12]

The ^{1}H NMR spectrum of **2** in $\mathrm{C_6D_6}$ showed extremely broad signals near those of *n*-hexane (present in the crystal lattice) and free THF. The latter observation and a pronounced color change from orange to deep-green on dissolution indicate that $\mathrm{C_6D_6}$ can displace THF, presumably forming a complex of the composition [(3,5-$^i\mathrm{Pr_2}$-Ar*)Cr($\mathrm{C_6D_6}$)]. This species is unstable at ambient temperature since the color of the $\mathrm{C_6D_6}$ solution changed from green to yellow on standing over several days, and a multitude of signals was observed in the aliphatic and aromatic regions of the ^{1}H NMR spectrum after a week at ambient temperature. The ^{1}H NMR spectrum of **3** is also not very diagnostic due to the extreme line broadening caused by its paramagnetism.

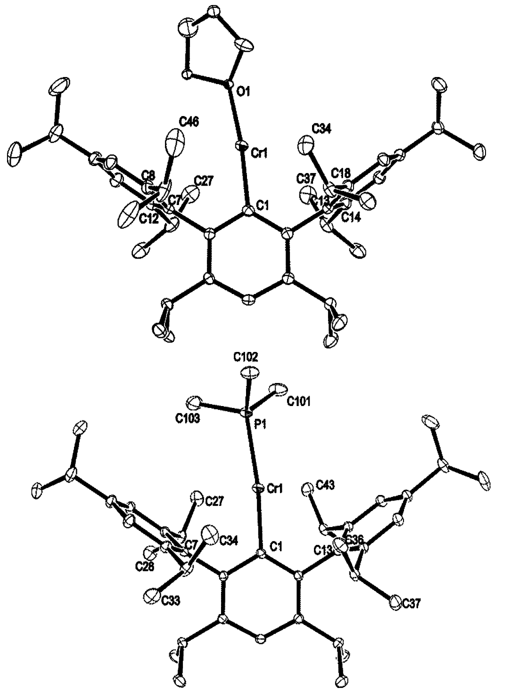

Figure 1. Solid-state molecular structures of **2** (top) and **3** (bottom), 30% thermal ellipsoid level, H-atoms are not shown. Hexane solvent molecules in the structures of **2** and **3** and the disorder in the THF molecule of **2** are omitted.

Like **2**, **3** decomposes in $\mathrm{C_6D_6}$, albeit more slowly than in the case of **2**. A singlet at +34 ppm in the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum may be assigned to the coordinated $\mathrm{PMe_3}$ ligand. The UV−vis spectra of both compounds were rather similar, displaying moderately intense bands at 430 nm (**2**) and 442 nm (**3**) as well as additional, weak absorptions at 628 nm (**2**) and ca. 500 nm (**3**).

Geometry optimizations of model species [ArCr(L)] (L = $\mathrm{PMe_3}$ or THF, Ar = $\mathrm{C_6H_3\text{-}2,6\text{-}Ph_2}$) in the high-spin sextet state reproduced the core structural parameters of **2** and **3** fairly well at the B3LYP/6-31g* level of theory.[13] Calculations on various spin states for both [ArCr($\mathrm{PMe_3}$)] and [ArCr(THF)] showed that the ground state was a sextet with the quartet state significantly higher in energy (L = THF, +70.6 kJ/mol; L = $\mathrm{PMe_3}$, +162.7 kJ/mol).[14] MO analysis[15] showed a congruent picture for both species in that five half-occupied d-orbitals of chromium form the frontier orbitals with $d_{x^2-y^2}$ being the HOMO (Figure 2).[16] Preliminary time-dependent DFT (TD-DFT) results indicate that the absorption close to 420 nm could be associated with transitions from half-occupied d-orbitals to the LUMO orbital which has some contribution from

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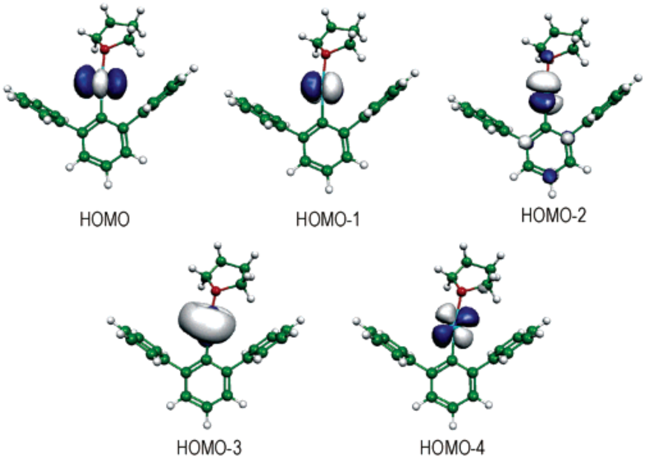

Figure 2. The five highest singly occupied molecular orbitals of [ArCr(THF)] (Ar = C_6H_3-2,6-Ph_2) calculated at the B3LYP/6-31g* level of theory.

the p_z-orbital of ligand C(ipso) for [ArCr(THF)], and a much greater p-orbital contribution in the phosphine complexed [ArCr(PMe_3)].

The magnetic properties of **2** and **3** are fully consistent with the presence of paramagnetic high-spin Cr^I with a $3d^5$ electronic configuration, as predicted by the theoretical calculations, and a nominal $^6A_1$ ground state in a distorted environment. A plot of the inverse molar magnetic susceptibilities versus temperature is linear in the range of 10−320 K, and the effective magnetic moments, μ_{eff}, of 5.95 μ_B (for **2**) and 6.17 μ_B (for **3**) are in reasonable agreement with the expected moment of 5.92 μ_B.

In conclusion, the unprecedented monomeric, two-coordinate Cr(I) species **2** and **3** have been isolated and characterized. The results suggest that, although steric bulk is necessary for the stabilization of the Cr−Cr bond in Ar′CrCrAr′ (**1**), an extremely bulky ligand such as 3,5-$^iPr_2$-Ar* creates sufficient steric pressure that coordination of THF or PMe_3 is preferred to dimerization (cf. the Cr−Cr bond energy calculated for PhCrCrPh = 318 kJ/mol).[6] Also, it is noteworthy that **2** and **3** are rare examples of two-coordinate chromium compounds.[17] The only previously known examples involve chromium(II) and have bent geometries with secondary metal−ligand interactions.[17,18] In contrast, **2** and **3** have almost linear geometries and are the first examples of two-coordinate, open shell transition metal complexes of a metal in a +1 oxidation state. Organometallic Cr(I) complexes are normally only found with π-acid ligands. For **2** and **3**, however, the low coordination number apparently limits charge build up at the metal and renders π-acidity of the ligands unnecessary to maintain electroneutrality.[19]

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Supporting Information Available: Computational details, graphical representations of the magnetic data of **2** and **3**, crystallographic data in cif format, and a complete ref 13. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) [(3,5-$^iPr_2$-Ar*)Cr(THF)] (**2**): Under anaerobic and anhydrous conditions, a blue solution of (3,5-$^iPr_2$-Ar*)CrCl (0.95 g, 1.46 mmol), prepared analogously to $[Ar'CrCl]_2$[8] from (3,5-$^iPr_2$-Ar*)Li[6a] and $CrCl_2(THF)_2$, in ca. 30 mL of THF, was added to a suspension of KC_8 (0.25 g, 1.8 mmol) at 0 °C in ca. 10 mL of THF. A dark, yellow-orange suspension formed immediately on addition. After stirring for ca. 24 h, the solvent was evaporated completely, and the dark residue was extracted with ca. 60 mL of hexanes. The dark-orange extract was concentrated to ca. 2 mL. Storage at −20 °C for several days gave large, orange crystals of **2**•*n*-hexane. Yield: 0.22 g [20%]. Mp 117−119 °C (black oil). ^1H NMR (300.08 MHz, C_6D_6, 21 °C): $\delta = 0.5-4$ (br), 0.8−1.4 (overlapping m, *n*-hexane), 1.42 (br s, CH_2-CH_2O of THF), 3.59 (br s, CH_2-CH_2O of THF). IR (Nujol) ν (cm^{-1}): 1763 (w), 1724 (w), 1604 (m), 1561 (m), 1361 (s), 1311 (s), 1165 (m), 1083 (s), 1069 (s), 1051 (s), 943 (w), 917 (w), 875 (s), 643 (m). UV/vis (hexanes; λ_{max}, nm {ϵ, $L \cdot mol^{-1} \cdot cm^{-1}$}): 430 (1140), 628 (400). $\mu_{eff} = 5.96\ \mu_B$. [(3,5-$^iPr_2$-Ar*)Cr(PMe_3)] (**3**): A cooled, deep blue solution of (3,5-$^iPr_2$-Ar*)CrCl (0.95 g, 1.46 mmol) and PMe_3 (0.5 mL, 4.8 mmol) in ca. 40 mL of THF was added to a stirred suspension of KC_8 (0.25 g, 1.8 mmol) at 0 °C in ca. 10 mL of THF. The mixture assumed a deep orange color upon stirring overnight. The solvent was evaporated, and the dark residue was extracted with 60 mL of hexanes. Concentration of the dark-orange extract to ca. 5 mL and subsequent storage at −20 °C for 2 days gave orange-red crystals of **3**. Yield: 0.20 g [17%]. Mp 140−141 °C (black oil). ^1H NMR (300.08 MHz, C_6D_6, 21 °C): $\delta = -1$ to 4 (br), 1.23 (br d, $^2J_{PH} = 33$ Hz), 6.5 to 10 (br). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, 21 °C): $\delta = 34.3$ (s). IR (Nujol) ν (cm^{-1}): 1761 (w), 1749 (w), 1602 (m), 1560 (m), 1421 (m), 1381 (m), 1309 (m), 1291 (m), 1283 (m), 1076 (s), 1048 (s), 952 (m), 876 (m), 664 (w), 653 (w), 469 (w). UV/vis (hexanes; λ_{max}, nm {ϵ, $L \cdot mol^{-1} \cdot cm^{-1}$}): 442 (1000), ca. 500 (shoulder). $\mu_{eff} = 6.17\ \mu_B$.
(10) Crystal data for **2**•*n*-hexane and **3**•*n*-hexane at 90 K with Mo Kα (λ = 0.71073 Å). **2**•*n*-Hexane: $a = 9.7312(9)$ Å, $b = 27.140(2)$ Å, $c = 18.507(2)$ Å, $\beta = 90.610(1)°$, $V = 4887.5(8)$ Å^3, $M = 776.18$ $g \cdot mol^{-1}$, monoclinic, space group $P2_1/c$, $Z = 4$, $R1 = 0.0668$ ($I > 2\sigma(I)$ data), $wR2 = 0.1877$ for all 8795 data. **3**•*n*-Hexane: $a = 9.414(2)$ Å, $b = 18.655(3)$ Å, $c = 28.054(4)$ Å, $\beta = 98.097(2)°$, $V = 4878(2)$ Å^3, $M = 780.15$ $g \cdot mol^{-1}$, monoclinic, space group $P2_1/c$, $Z = 4$, $R1 = 0.0434$ ($I > 2\sigma(I)$ data), $wR2 = 0.1417$ for all 12074 data.
(11) The Cr−O distances of 88 Cr−THF complexes in the Cambridge Crystal Structure Database (version 5.27, Aug 2006) range from 1.994 to 2.449 Å, median 2.097 Å.
(12) The Cr−P distances of 53 Cr−PMe_3 complexes in the Cambridge Crystal Structure Database (version 5.27, Aug 2006) range from 2.288 to 2.525 Å, median 2.383 Å.
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(14) These values refer to geometries obtained from the X-ray crystal structures of **2** and **3**. The values for the optimized geometries are 160.2 kJ/mol for [ArCr(PMe_3)] and 64.0 kJ/mol for [ArCr(THF)].
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(16) While for [ArCr(THF)] these are almost pure d-type orbitals, this is not the case for [ArCr(PMe_3)]. In the latter, the HOMO-3 and HOMO-4 exhibit a net overlap of the Cr d_{xz}- and d_{yz}-orbitals with p-orbitals of the P atom. The ordering of the frontier d-orbitals is also affected. For [ArCr(THF)] (HOMO = $d_{x^2-y^2}$, d_{xy}, d_{xz}, d_{z^2}, d_{yz}) the d_{z^2}-orbital lies lower in energy than in ArCrP(Me_3) (HOMO = $d_{x^2-y^2}$, d_{xy}, d_{z^2}, d_{xz}, d_{yz}). See Supporting Information for details.
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