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A Novel Coordination Mode for Pentalene in Trinuclear Chromium Complexes

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The first chromium pentalene complexes have been characterized; in these the ligand displays a hitherto-unknown bonding mode whereby a dimeric $[Cr(Cp^*)]_2(\mu\text{-}OR)$ unit is bound $(\mu{:}\eta^2{:}\eta^2)$- to one face, and Cp*Cr is bound η^5- to the other. The magnetic properties of these compounds can be understood as the superposition of those of a chromocene and an antiferromagnetically coupled Cr–Cr bonded unit.

The pentalene ligand has been used to form organometallic complexes featuring a wide range of coordination geometries; contemporary interest has been invigorated by the discovery that the ligand can bind by folding all eight carbon atoms toward a single metal atom.[1] Previous reports have described dinuclear metal−pentalene species, where the ligand is complexed to two metal atoms in an η^5/η^5-mode, as seen for homoleptic, "double-sandwich" molecules[2] and in *syn*- or *anti*-pentalene bridged complexes.[3] Binding of pentalene that is fluxional between two and three metal fragments has also been observed for a series of *syn*-trinuclear ruthenium carbonyl cluster molecules.[4] We report here the existence of a new coordination mode whereby pentalene binds three metal atoms in an *anti*-arrangement.

Reaction of $Li_2Pn\cdot x$DME (Pn = pentalene, C_8H_6; DME = 1,2-dimethoxyethane) with one equivalent of $[Cr(Cp^*)(\mu{-}Cl)]_2$ (Cp* = η^5-pentamethylcyclopentadienyl)[5] afforded a dark red, highly air-sensitive crystalline compound, **1**; a single-crystal X-ray diffraction study[6a] revealed that **1** was not the anticipated bimetallic species (*i.e.* $[Cr(Cp^*)]_2Pn$), but instead had the novel trimetallic constitution shown in Figure 1.

1 is the first characterized chromium−pentalene complex.[7] The structure shows it to be formed from two discrete metal-containing units bridged by a planar pentalene group. One unit consists of a $(Cp^*)Cr^{II}$ fragment bound η^5- to one face of the ligand; Cr(1) is coordinated by five carbons in the pentalene ring (C(1)−C(3), C(7), C(8)) with bond lengths in this chromocene part unexceptional for $S = 1$ Cr^{II} metallocene species.[8] The other consists of a pentalene- and methoxy-bridged $[(Cp^*)Cr^{II}]_2$ dimer on the opposite face. Cr(2) and Cr(3) lie further than 2.90 Å from the pentalene ring-junction carbon atoms, and therefore this unit is coordinated only by the three terminal atoms C(4)−C(6); this geometry is similar to the "butterfly"-like arrangement of chromium atoms in dinuclear $(\mu{:}\eta^2{:}\eta^2)$-allyl complexes[9] and in the structures of tris(indenyl)dichromium chloride and bis-

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(6) (a) Crystal data for **1**: dark red, $C_{39}H_{54}Cr_3O$, $M = 694.82$, monoclinic, space group $P2_1/n$ (No. 14), $a = 12.1885(2)$ Å, $b = 20.5648(3)$ Å, $c = 14.6298(2)$ Å, $\beta = 97.0320(10)°$, $V = 3639.44(9)$ Å^3, $T = 150(2)$ K, $Z = 4$, $F(000) = 1472$, $\mu = 0.907$ mm^{-1}. Data were collected in the θ range 3.42−27.49°, 15067 reflections, 8257 unique ($R_{int} = 0.0203$), $R_1 = 0.0401$, w$R_2 = 0.0989$ for $I > 2\sigma(I)$ with allowance for thermal anisotropy of all non-hydrogen atoms. (b) Crystal data for **2**: dark red, $C_{40}H_{56}Cr_3O$, $M = 708.87$, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.6702(2)$ Å, $b = 12.2604(2)$ Å, $c = 16.0714(3)$ Å, $\alpha = 86.511(1)°$, $\beta = 77.575(1)°$, $\gamma = 65.0582(8)°$, $V = 1860.7(6)$ Å^3, $T = 150(2)$ K, $Z = 2$, $F(000) = 752$, $\mu = 0.889$ mm^{-1}. Data were collected in the θ range 5.10−27.35°, 15634 reflections, 8298 unique ($R_{int} = 0.0245$), $R_1 = 0.0586$, w$R_2 = 0.1490$ for $I > 3\sigma(I)$ with allowance for thermal anisotropy of all non-hydrogen atoms.

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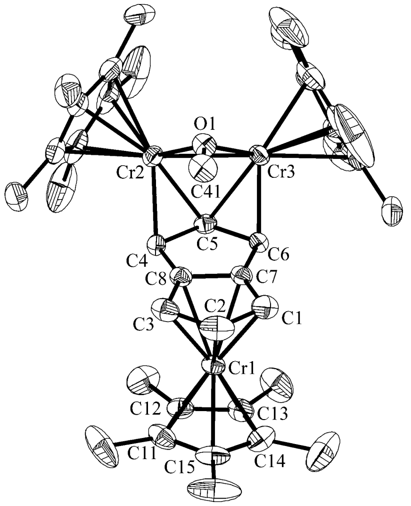

Figure 1. Molecular structure of **1** with thermal ellipsoids at 50% probability and all H atoms omitted for clarity. Selected bond distances [Å] and angles [deg]: Cr(2)−Cr(3) 2.4895(5), Cr(2)−O−Cr(3) 79.66(6), Cr(2)−C(4) 2.085(2), Cr(2)−C(5) 2.243(2), Cr(3)−C(5) 2.301(2), Cr(3)−C(6) 2.081(2), Cr(2)−O(1) 1.9373(15), Cr(3)−O(1) 1.9494(15), Cr(1)−Cp* centroid 1.782, Cr(1)−Pn five-membered ring centroid 1.778.

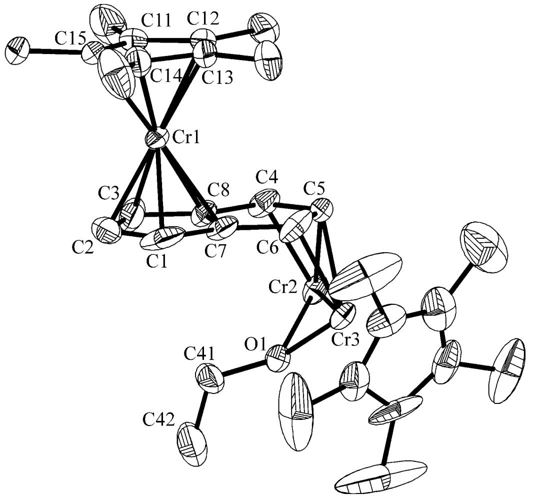

Figure 2. "Cutaway" view of the molecular structure of **2** with one Cp* ring and all Cr(3)−Cp* bonds removed, allowing the bridging OEt group clearly to be seen. Thermal ellipsoids are at 50% probability, and all H atoms have been omitted. Selected bond distances [Å] and angles [deg]: Cr(2)−Cr(3) 2.4800(12), Cr(2)−O−Cr(3) 79.03(11), Cr(2)−C(4) 2.089(6), Cr(2)−C(5) 2.225(6), Cr(3)−C(5) 2.267(6), Cr(3)−C(6) 2.079(6), Cr(2)−O(1) 1.944(4), Cr(3)−O(1) 1.954(4), Cr(1)−Cp* centroid 1.786, Cr(1)−Pn five-membered ring centroid 1.783.

(indenyl)chromium (which is dimeric in the solid state),[10] while the bridging alkoxy motif echoes that found for $[\mathrm{Cr(Cp)}(\mu\text{-OCMe}_3)]_2$ and related complexes.[11] The eight-electron pentalene ligand may thus be considered as binding to Cr(1) as a five-electron donor cyclopentadienyl-like unit while acting as a three-electron bridging-allyl-like fragment toward Cr(2) and Cr(3). This clear separation by pentalene into two distinct ligand modes in the same complex is unprecedented. It may be noted, however, that intermediates such as $[\mathrm{(PnH)Fe(Pn)}]^-$ presumably contain (η^5-Pn)−Fe coordination along with a reactive, unbound allyl anion center;[12] hence **1** may be viewed as the product of reaction between a $[\mathrm{(Cp^*)Cr(Pn)}]^-$-like intermediate with $[\mathrm{Cr(Cp^*)}(\mu\text{-X})]_2$ (where X is potentially either Cl or OMe). Similar reactivity of $[\mathrm{Cr(Cp)}(\mu\text{-OCMe}_3)]_2$ with nucleophiles to give ligand-bridged, dichromium cluster-like species has previously been observed.[13]

The formation of trimetallic **1**, rather than a bimetallic species, was unexpected considering the reaction stoichiometry; presumably steric repulsion between methyl groups on the Cp* rings is too great to permit formation of a metal−metal bonded *syn*-bimetallic analogous to *syn*-$[\mathrm{Cr(Cp)}]_2(\mu$:η^5:η^5-cyclooctatetraene)[14] while a possible *anti*-bimetallic is perhaps too electron-poor for stability in the absence of such a metal−metal bond. The trimetallic structure of **1** allows a greater electron count at each Cr atom to be achieved with two distinct Cr coordination environments. **1** is stable in refluxing THF; prolonged heating does not result in thermolysis of the dimeric Cr unit to give a bimetallic species. Attempted reaction of $[\mathrm{Cr(Cp^*)}(\mu\text{-Cl})]_2$ with donor ligand-free $\mathrm{Li_2Pn}$ in THF does not produce a tractable product, suggesting that the alkoxy group is necessary to stabilize the structure and that the source of this bridging group is DME. Accordingly, reaction of $[\mathrm{Cr(Cp^*)}(\mu\text{-Cl})]_2$ with the 1,2-di*ethoxy*ethane adduct of $\mathrm{Li_2Pn}$, $\mathrm{Li_2Pn}\cdot x\mathrm{DEE}$, gives dark red, very air-sensitive crystals of **2**, the OEt-bridged analogue of **1** (Figure 2). The coordination of the metal atoms by pentalene in **2** is essentially identical to that observed for **1**.[6b]

The Cr(2)−Cr(3) distances found in **1** and **2** are significantly shorter than in the dimeric starting material $[\mathrm{Cr(Cp^*)}(\mu\text{-Cl})]_2$ (2.642(2) Å),[15] despite the greater ligand bulk around the central metal atoms, suggesting a stronger Cr−Cr bonding interaction in **1** and **2**.[16] Similarly, the bonds in **1** and **2** are shorter than in $[\mathrm{Cr(Cp)}(\mu\text{-OCMe}_3)]_2$ (2.651 Å, mean value);[11] the considerably reduced Cr(2)−O−Cr(3) bond angles in these complexes are also indicative of stronger metal−metal bonding than in the bis(alkoxy) complex (∠Cr−O−Cr = 85.2°, mean value). A double bond would give every

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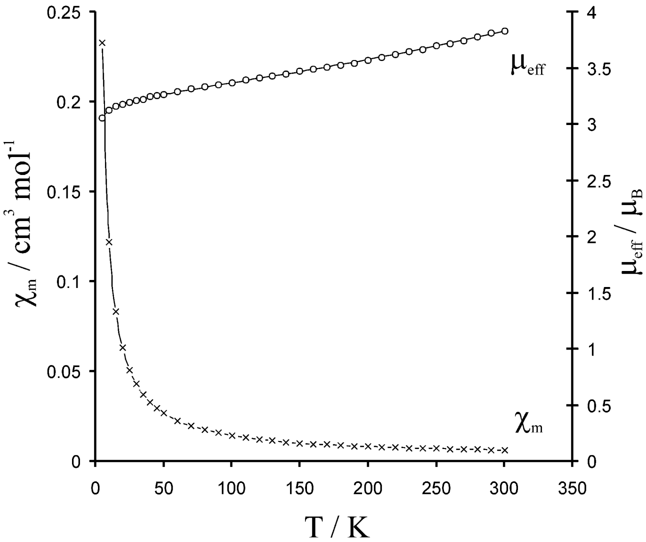

Figure 3. Plots of χ_m (×) and μ_{eff} (○) vs T for **1**. The solid lines represent the calculated values from a fit of the data using the expression in the text; least-squares analysis affords $J = -356$ cm^{-1}, $g_1 = 2.25$, $\theta = -0.48$ K with $g_2 = 2.00$, TIP = 0.00159 cm^3 mol^{-1}. For **2** a similar fit gives parameters $J = -382$ cm^{-1}, $g_1 = 2.21$, $\theta = -0.86$ K with $g_2 = 2.00$, TIP = 0.00128 cm^3 mol^{-1}.

chromium atom in **1** and **2** a sixteen-electron configuration (as in a chromocene).[17] The existence of strong metal−metal interaction between Cr(2) and Cr(3) here is supported by variable-temperature SQUID magnetometry, the results of which are shown for **1** in Figure 3 (the magnetic behavior of **2** is very similar). For both species χ_m does not obey the Curie law, the effective magnetic moment ($\mu_{eff} = \sqrt{(8\chi_m T)}\,\mu_B$) steadily increasing with temperature from a value of ca. 3 μ_B at 5 K. The magnetic moment of chromocene is essentially temperature-independent between 12 and 300 K, and has a value of 3.00 μ_B at 300 K.[18] The magnetism of **1** and **2** can be modeled successfully as the superposition of a chromocene species and an antiferromagnetically coupled Cr^{II}_2 dimer unit; the experimental molar susceptibilities were fitted to an expression combining a Curie−Weiss term for an $S = 1$ chromocene, together with a term describing two antiferromagnetically coupled $S = 1$ centers (for which the temperature dependence of the molar susceptibility may be derived from the Heisenberg−Dirac−van Vleck model with spin Hamiltonian $\hat{\mathbf{H}} = -2J{\cdot}\mathbf{S}_1{\cdot}\mathbf{S}_2$)[19] and a correction for temperature-independent paramagnetism (TIP), shown below. Satisfactory fits were obtained by least-squares analysis.

$$\chi_m = \left(\frac{2N_A g_1{}^2 \mu_B{}^2}{3k(T-\theta)}\right) + \left(\frac{2N_A g_2{}^2 \mu_B{}^2}{kT}\right)\left(\frac{e^{2J/kT} + 5e^{6J/kT}}{1 + 3e^{2J/kT} + 5e^{6J/kT}}\right) + \text{TIP}$$

The g-values for the Cr dimer units (g_2) were held constant at 2.00; g-values for the chromocene fragment (g_1) were fitted and are consistent with those found for other chromocenes,[20] reflecting the large orbital contribution to the magnetic moment from a degenerate ^{3}E configuration. The magnitude of the antiferromagnetic coupling between chromium atoms is very similar for compounds **1** and **2** and is indicative of significant metal−metal interaction. The starting material and its closely related alkyl analogue $[Cr(Cp^*)(\mu\text{-Me})]_2$ (where $r_{Cr-Cr} = 2.263(3)$ Å) also display magnetic behavior attributed to antiferromagnetically coupled $S = 1$ Cr centers;[15] $[Cr(Cp)(\mu\text{-OCMe}_3)]_2$ has been determined likewise to be an antiferromagnetic complex.[13a] The values of the exchange constants, J, obtained for **1** and **2** lie between those found for $[Cr(Cp^*)(\mu\text{-Cl})]_2$ and $[Cr(Cp^*)(\mu\text{-Me})]_2$ (−212 cm^{-1} and −471 cm^{-1}, respectively), consistent with the Cr−Cr distances observed which are intermediate between the chloro and methyl complexes. The values for **1** and **2** similarly are compatible with the smaller J-value determined for $[Cr(Cp)(\mu\text{-OCMe}_3)]_2$ (−246 cm^{-1}). The magnetic behavior of these pentalene-bridged *anti*-trimetallics is therefore well-described as the sum of that due to a chromocene and a pair of antiferromagnetically coupled chromium(II) fragments, entirely consistent with the coordination environments observed in the crystal structures.

We have shown by the formation of these chromium complexes that pentalene can behave unusually as a bridging species between three metal atoms in an *anti*-geometry, resulting in the division of this ligand into η^5-cyclopentadienyl and (μ:η^2:η^2)-allyl functionalities. Potentially, these complexes may display interesting reactivity arising through cooperative interactions between the chromium atoms, and investigations into this are in progress.

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Supporting Information Available: Details of the synthesis and magnetic measurement of **1** and **2** along with X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) A search of the compounds listed in the Cambridge Structural Database uncovers a mean Cr−Cr double bond distance of 2.478 Å.

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