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Cyclopentadienyl Ligands

Trapping of Oligomeric Cyclopentadienyllithium Cationic and Anionic Fragments by a V≡V-Bonded Ligand**

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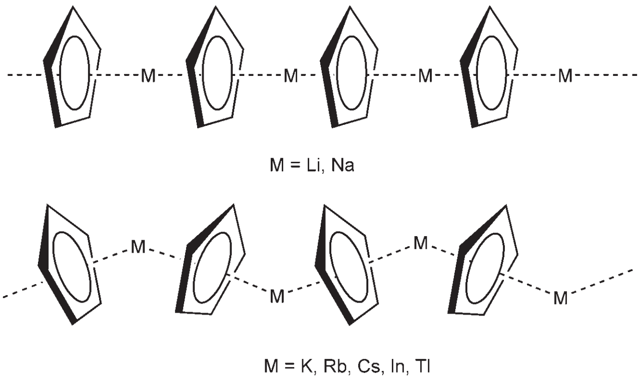
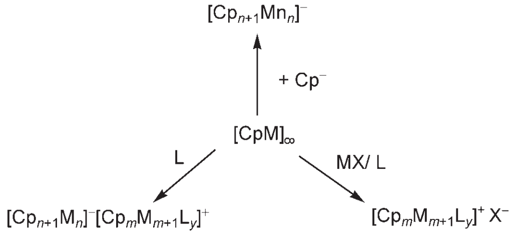
Main-group cyclopentadienyl compounds are typically far more ionic than their transition-metal relatives.[1–3] This difference is apparent not only in their reactivity patterns but also, in particular, in the frequent formation of electrostatically bonded polymeric structures for many main-group cyclopentadienyl species. Owing to the similar ionic sizes and charges of the metals, analogous infinite polymeric structures $[M(\eta^5\text{-Cp})]_\infty$ are found for the parent cylopentadienyl compounds of the alkali metals (M = Li, Na, K, Rb, Cs)[4] and for the heavier Group 13 metals (M = In, Tl).[5] As a consequence of Cp⋅⋅⋅M or M⋅⋅⋅M interactions, these polymers can be either linear or bent at the metal atoms (Scheme 1). The structures of the alkaline earth complexes and those of the heaviest Group 14 metal Pb can also be regarded as similarly related.[2]



Scheme 1. Schematic representation of the structures of $[\text{CpM}]_\infty$ (M = Li, Na, K, Rb, Cs, In, Tl).

An important focus of research in this area in recent years has been the investigation of multidecker cations and anions.[3,6] These species can be conceived of as representing fragments of the parent cyclopentadienyl lattices and are produced by a number of routes. As outlined in Scheme 2 for Group 1 and Group 13 metals, these methods include formal addition of Cp^- anions to the [CpM] lattices to give $[Cp_{n+1}M_n]^-$ anions,[2,6] addition of a metal salt to give $[Cp_mM_{m+1}L_y]^+$ cations,[7] and restricted solvation in the presence of bulky Cp ligands to give salts of the type $[Cp_{n+1}M_n]^-[Cp_mM_{m+1}L_y]^+$.[8]



Scheme 2.

Our recent interests in this field have concerned attempts to extend the ionic chemistry of main-group cyclopentadienyl compounds to the transition metals, with a particular aim of obtaining new magnetic molecules and lattices.[9,10] We have shown that manganocene $[Cp_2Mn]$, the most ionic transition-element metallocene, exhibits similar chemistry to main-group metallocenes. Herein, we report for the first time that vanadocene $[Cp_2V]$ displays similar reactivity with the lithiated amide (hpp)Li (hppH = 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine); the reaction results in substitution of the Cp ligands (as CpLi) and formation of the known V≡V-bonded compound $[V_2(\text{hpp})_4]$ (**L**).[11f] Remarkably, the product crystallizes with five units of CpLi to form the ionic species $[(\mathbf{L})\text{Li}(\mu\text{-Cp})\text{Li}(\mu\text{-Cp})\text{Li}(\mathbf{L})]^+[(\eta^5\text{-Cp})\text{Li}(\eta^5\text{-Cp})\text{Li}(\eta^5\text{-Cp})]^-$ (**1**), in which **L** intercepts formation of the polymeric lattice of $[\text{CpLi}]_\infty$ to produce an ionic arrangement (Scheme 3). The triple-decker $[(\eta^5\text{-Cp})\text{Li}(\eta^5\text{-Cp})\text{Li}(\eta^5\text{-Cp})]^-$ anion of **1** is the first such example reported for the lighter alkali metals.

The absence of paramagnetic broadening or shifting of the resonances outside the normal region in the room-temperature ^{1}H NMR spectrum of **1** in THF gave an initial indication of the diamagnetic nature of this compound and of the formation of V≡V bonds in which the d^3 electrons of the V^{II} ions are paired.[11,12] The spectrum shows a series of poorly resolved multiplets for the hpp ligand in the region $\delta = 3.57$–1.74 ppm and a singlet C_5H_5 resonance ($\delta = 5.70$ ppm). The complicated appearance of the spectrum and its temperature- and concentration-dependent behavior can be attributed to the presence of dynamic equilibria in solution. On changing from 300 to 190 K, the ^{1}H NMR spectrum exhibits several changes, including the appearance of an additional Cp resonance ($\delta = 6.20$ ppm). The temperature-dependent ^{7}Li NMR

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$$4[\mathrm{Cp_2V}] \quad + \quad 8[(\mathrm{hpp})\mathrm{Li}] \xrightarrow{-3\mathrm{CpLi}} [(\mathbf{L})\mathrm{Li}(\mu\text{-Cp})\mathrm{Li}(\mu\text{-Cp})\mathrm{Li}(\mathbf{L})]^{+}[(\eta^5\text{-Cp})\mathrm{Li}(\mu\text{-Cp})\mathrm{Li}(\eta^5\text{-Cp})]^{-}$$

$\mathbf{L} = [\mathrm{V_2(hpp)_4}]$

1

Scheme 3.

spectrum also supports this behavior. It displays a singlet at 300 K ($\delta = -9.24$ ppm relative to saturated $LiCl/D_2O$), but two other resonances [$\delta = -7.50$ ppm (major) and $\delta = -1.34$ ppm (minor)] appear as the temperature is reduced to 250 K. These resonances can be assigned tentatively to the three Li environments present in the solid-state structure. As noted by Cotton et al., one of "the major problems in the development of the chemistry of V^{II}" has been "the lack of good [amine-free] starting materials."[11c] Previously, studies have used $VCl_3 \cdot 3THF$, which can be reduced to V^{II} prior to or during reaction.[11] $[Cp_2V]$ is not only a readily prepared precursor to V^{II}, but, to our knowledge, it is the only stable V^{II} precursor of this type reported to date.

The solid-state structure of **1**·2 THF[13] consists of [(**L**)Li(μ-Cp)Li(μ-Cp)Li(**L**)]$^+$ cations and $[CpLi(\mu\text{-}Cp)LiCp]^-$ anions (Figure 1), in which the neutral V≡V-bonded $[V_2(hpp)_4]$ molecules (**L**) function as N ligands, effectively terminating the growth of the infinite polymeric chain of $[CpLi]_\infty$ (Figure 1 a). Furthermore, there are two molecules of THF in the crystal lattice. The coordination of the Li^+ ions in **1** within the cleft of the hpp ligands is similar to that seen in $[K(thf)_3]^+[V_2(dPhf)_4]^-$ (dPhf = *N*,*N'*-diphenylformaminato), which has a metal–metal bond order of 3.5 in the anion.[11f] However, the trapping of a multidecker sandwich cation and a multidecker sandwich anion in this manner is highly unusual and has only one precedent, which is found in the structure of $[(thf)Li(\mu\text{-}Cp^{Ar})Li(\mu\text{-}Cp^{Ar})Li(thf)]^+[(\eta^5\text{-}Cp^{Ar})_2Li]^-$ ($Cp^{Ar} = 3,5\text{-}(Me_2C_6H_3)_5C_5$),[8] which contains a similar $[Li(\mu\text{-}Cp)Li(\mu\text{-}Cp)Li]^+$ core to **1**. This fragment represents the next homologue of the series of alkali metal cations of the type $[M(\mu\text{-}Cp)M]^+$ which have been reported.[7] In addition, apart from the Cs-based anion $[CpCs(\mu\text{-}Cp)Cs(\mu\text{-}Cp)CsCp]^-$,[14] no other related triple-decker anions of any of the other alkali metals have been observed.[15]

The V≡V bond length within the $\{V_2(hpp)_4\}$ (**L**) unit of the [(**L**)Li(μ-Cp)Li(μ-Cp)Li(**L**)]$^+$ ion of **1** (1.933(1) Å) is identical to that observed in the previously reported structure of $[V_2(hpp)_4]$ (1.932(1) Å).[11e] The chelation to Li(3) of both of the V-bonded N centers of two of the hpp ligands results in some elongation of the V–N bonds in **1** (range 2.057(4)–2.116(4) Å) compared to the free $[V_2(hpp)_4]$ complex (2.058(4)–2.076(3) Å);[11e] the longest of V–N bonds in **1** are found at the Li-bonded atoms N(41) and N(12) (2.111(4) and 2.116(4) Å, respectively). This coordination, together with the η^5-coordination by a Cp ligand, produces a distorted square-based pyramidal geometry for Li(3). The result of this coordination is the elongation of the Cp–Li bonds at the termini [C···Li(3) 2.41(1)–2.51(1) Å ($Cp_{centroid}$···Li(3) 2.15 Å)] compared to the other Cp–Li bonds [C···Li(2) 2.280(5)–2.336(5) Å ($Cp_{centroid}$···Li(2) 1.96 Å)]. This pattern is reversed in the $[(\eta^5\text{-}Cp)Li(\mu\text{-}Cp)Li(\eta^5\text{-}Cp)]^-$ multidecker anion of **1**, with $C_{terminal}$···Li(1) in the range 2.24(1)–2.33(1) Å ($Cp_{centroid}$···Li 1.93 Å) and $C_{bridging}$···Li(1) in the range 2.33(2)–2.40(2) Å ($Cp_{centroid}$···Li 2.04 Å). Like the arrangement of $[CpLi]_\infty$ itself, the $[(\eta^5\text{-}Cp)Li(\mu\text{-}Cp)Li(\eta^5\text{-}Cp)]^-$ ion adopts a linear arrangement in the solid state, while the structure of the related ion $[(\eta^5\text{-}Cp)Cs(\mu\text{-}Cp)Cs(\eta^5\text{-}Cp)]^-$,[14] like the parent $[CpCs]_\infty$, is bent at the metal atoms and adopts a zig-zag arrangement. Presumably, the small size of the Li^+ ion results in the interring separation (Cp···Cp) in the anion being too short to allow Cp···M intermolecular interactions between the cations and anions of **1**.

In summary, the use of $[Cp_2V]$ as a new precursor to V^{II} has been demonstrated. The V≡V-bonded compound $[V_2(hpp)_4]$ that is formed from this precursor reveals its ability to stabilize the rare $[Cp_2Li_3]^+$ cation, acting as a bulky ligand in the coordination of the terminal Li^+ ions. Our study provides a new direction in regard to the preparation of multidecker sandwich arrangements and in the formation of bimetallic lattices. The simplest triple-decker sandwich anion $[Cp_3Li_2]^-$ of the lightest alkali metal has been obtained.

Experimental Section

1: *n*BuLi (2.62 mL, 1.60 M in hexanes, 4.20 mmol) was added to a solution of hppH (0.56 g, 4.00 mmol) in THF (7.0 mL) at −78 °C. The solution was warmed to room temperature and stirred for 1 h. The faint yellow solution that was obtained was transferred to a

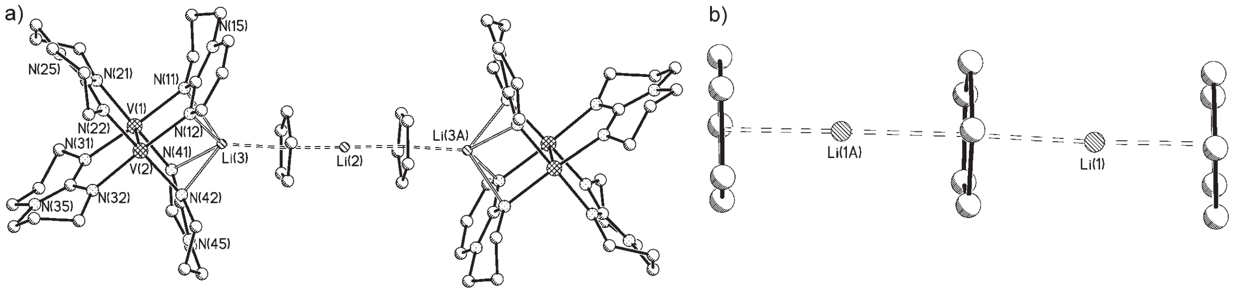

Figure 1. a) The centrosymmetric cation, and b) the centrosymmetric anion of **1** (showing one orientation of the disordered central Cp ligand). H atoms and lattice-bound THF molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: V(1)-V(2) 1.933(1), V-N 2.057(4)–2.116(4), N(11)-Li(3) 2.23(1), N(12)-Li(3) 2.34(1), N(41)-Li(3) 2.33(1), N(42)-Li(3) 2.24(11), Li(3)···C 2.41(1)–2.51(1) ($Cp_{centroid}$···Li(3) 2.15), Li(2)···C 2.280(5)–2.336(5) ($Cp_{centroid}$···Li(2) 1.96), Li(1)···$C_{terminal}$ 2.24(1)–2.33(1) ($Cp_{centroid}$···Li(1) 1.93), Li(1)-$C_{bridging}$ 2.33(2)–2.40(2), ($Cp_{centroid}$···Li(1) 2.04); N-V-N 88.3(2)–91.0(2), N-V-V 93.5(1)–96.3(1).

suspension of [Cp_2V][16] (0.36 g, 2.00 mmol) in THF (8.0 mL) at room temperature. The mixture was stirred overnight, and the solid that formed was filtered off. The deep brown filtrate was concentrated to about 10 mL to afford brown crystals of **1**·2 THF at −25 °C in 5 d. Spectroscopic and elemental analysis shows that once isolated under vacuum (ca. 10^{-3} torr), all of the THF in the lattice is removed. The following analysis refers to this THF-free material. Yield of crystalline **1** 0.25 g (30 % with respect to vanadium); m.p. 220 °C; elemental analysis (%) calcd for $C_{81}H_{121}N_{24}Li_5V_4$: C 58.3, H 7.3, N 20.1; found: C 57.4, H 7.6, N 19.7; IR (Nujol, NaCl windows): $\tilde{\nu} = 3065$(w; C-H stretch Cp), 1618(w), 1139(s), 1112(w), 1071(m), 1024(m), 1007(m), 916(w), 799(w), 725 cm^{-1} (vs). ^1H NMR (400 MHz, [D_8]THF, 300 K): $\delta = 5.70$ (s, 25 H; Cp), 3.57–3.37 (t and br sh, 32 H; NCH_2CH_2), 3.01–2.65 (br mult, 32 H; CH_2CH_2N), 1.97–1.74 ppm (br mult and quint, 32 H; $CH_2CH_2CH_2$): ^7Li NMR (194.39 MHz, [D_8]THF, 300 K): $\delta = -9.24$ ppm; ^7Li NMR (194.39 MHz, [D_8]THF, 250 K): $\delta = -9.24, -7.50, -1.34$ ppm (minor).

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[13] Crystallographic data for **1**·2 THF ($C_{89}H_{137}Li_5N_{24}O_2V_4$): $M_r = 1813.69$, triclinic, space group $P\bar{1}$, $a = 10.868(2)$, $b = 13.783(3)$, $c = 16.716(3)$ Å, $\alpha = 105.75(3)$, $\beta = 103.41(3)$, $\gamma = 94.80(3)°$, $Z = 1$, $V = 2315.3(8)$ Å^3, $\rho_{calcd} = 1.301$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 0.542$ mm^{-1}, $T = 180(2)$ K. Data were collected on a Nonius Kappa CCD diffractometer. Of a total of 18 930 reflections collected, 7222 were unique ($R_{int} = 0.065$). The refinement was made by full-matrix least squares on F^2 with anisotropic displacement parameters assigned to all full-occupancy non-hydrogen atoms (G. M. Sheldrick, SHELX-97, Göttingen, Germany, **1997**). Final $R1 = 0.077$ [$I > 2\sigma(I)$] and $wR2 = 0.212$ (all data). CCDC-637966 contains 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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