12H); 7.81 (m, br. 12H); elemental analysis (%) for $C_{96}H_{48}F_{102}P_2PdCl_2$ (3378.50): calcd: C 34.13, H 1.43, Cl 2.10; found: C 33.91, H 1.46, Cl 2.37.

General coupling procedure (**5a**): To a suspension of catalyst **2c** (10.1 mg, 0.003 mmol) in perfluoromethylcyclohexane (1.2 mL) was added under argon a solution of methyl 4-bromobenzoate **3a** (43.0 mg, 0.200 mmol), tributylstannylfuran **4a** (85.7 mg, 0.240 mmol), and LiCl (8.5 mg, 0.200 mmol) in DMF (1 mL). The mixture was heated at 80 °C for 3 h. After cooling to room temperature the two phases were separated and the fluorous phase was washed with DMF (3 × 1 mL). The fluorous phase containing the catalyst was removed and used as such for the next run. For isolation of product **5a** water (7.5 mL) was added to the DMF layer. After extraction with diethyl ether (4 × 2 mL), the combined diethyl ether solutions were evaporated. The residue was taken up in diethyl ether (1 mL) and aqueous KF solution (5 mL) was added. After the mixture had been stirred overnight, it was extracted with diethyl ether (4 × 2 mL), and the combined diethyl ether layers were passed through a plug consisting of Alox (2 g; neutral, Act. II-III) and silica (4 g). The filtrate was evaporated yielding the desired product **5a** (36.8 mg; 91 %).

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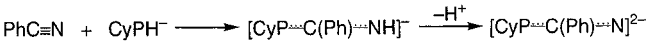
# A Li$_{10}$ Cage Containing the $[C_6H_{11}P\overset{\cdots}{-}C(Ph)\overset{\cdots}{-}N]^{2-}$ Ion: Umpolung in the Oligomerization of a Nitrile**

Neil Feeder, Yvonne G. Lawson, Paul R. Raithby, Jeremy M. Rawson, Alexander Steiner, Jody A. Wood, Anthony D. Woods, and Dominic S. Wright*

Studies of oligomeric imido alkali metal complexes $[\{(R')RC{=}NLi\}_n]$, which are readily prepared by the equimolar reactions of organoalkali metal reagents R′M (M = Li – Cs) with organic nitriles (RC≡N), have been fundamental in the development of structural models for a host of related alkali metal complexes.[1] In contrast to the wealth of knowledge concerning the reaction characteristics of organoalkali metal reagents with nitriles,[1, 2] only a few studies have investigated the analogous addition reactions with alkali metal phosphides RR′PM.[3] Surprisingly, although alkali metal complexes containing $[R^1P\overset{\cdots}{-}C(R^2)\overset{\cdots}{-}NR^3]^-$ monoanions have been prepared and structurally characterized previously, to our knowledge there are no reports of dianions of the type $[R^1P\overset{\cdots}{-}C(R^2)\overset{\cdots}{-}N]^{2-}$. Our interest in the latter stems from their potential application as precursors for the synthesis of main group heterocycles.

Accordingly, we carried out the reaction of CyPHLi (Cy = $C_6H_{11}$) with PhC≡N, followed by deprotonation of the presumed intermediate anion $[CyP\overset{\cdots}{-}C(Ph)\overset{\cdots}{-}NH]^-$[3b] with *n*BuLi (Scheme 1; see Experimental Section). The product of



Scheme 1.

this reaction, however, is the cage complex **1** containing not only the desired dianion $[CyP\overset{\cdots}{-}C(Ph)\overset{\cdots}{-}N]^{2-}$ but also the

$$[\{\{[CyPC(Ph)N]Li_2\}\{[H(PhCN)_3(CyP)_2]Li_3\}(thf)_3\}_2] \cdot 2\,C_6H_5CH_3 \cdot 2\,THF \qquad \mathbf{1}$$

trianion $[H(PhCN)_3(CyP)_2]^{3-}$, in which C–C bond formation between two PhCN molecules has occurred (Scheme 2). The observation of umpolung (polarity reversal) in the reaction forming this trianion contrasts with the normal mode of oligomerization of nitriles, which involves "head-to-tail" C–N

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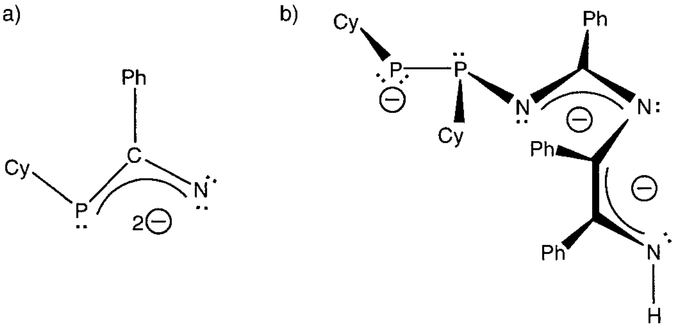

Scheme 2. The bonding within a) the dianion, and b) the trianion present in **1**.

bond formation (as occurs in the cyclotrimerization of PhCN to triazines or lithiotriazines in the presence of organolithium reagents[2b,c]). The formation of a C–C bond in the trianion prompted us to investigate whether a single-electron transfer (SET) mechanism is involved, which competes with the anion mechanism responsible for the formation of the $[\mathrm{CyP}\overset{\cdots}{-}\mathrm{C(Ph)}\overset{\cdots}{-}\mathrm{N}]^{2-}$ ion. Similar competition is well known in reactions of ketones with Grignard reagents,[4] and the reactions of $\mathrm{Ph_2C{=}O}$ with a range of lithium amides occur through the $[\mathrm{Ph_2\dot{C}{-}O}]^{-}$ radical anion (with the formation of C–C coupled by-products).[5] A further clue to the participation of radicals in the reaction forming **1** is the rapid development of a sustained (>2 h), deep green color upon addition of *n*BuLi to the mixture of PhCN and CyPHLi. Prior to the addition of *n*BuLi, the orange mixture of PhCN and CyPHLi was ESR silent. However, on addition of *n*BuLi the ESR spectrum of the green reaction mixture indicated the possibility of a P-centered radical in low concentration (doublet, $g = 2.00$ G, $a_p = 33$ G). This radical (or others too short-lived to be observed) could be involved in single-electron reduction of PhCN, with the combination of two $[\mathrm{Ph\dot{C}{=}N^{-}}]$ radicals resulting in the observed C–C coupling in the trianion of **1**.[6] The room-temperature $^{31}$P NMR spectrum of the initial mixture of PhCN and CyPHLi shows the presence of unreacted CyPHLi ($\delta = -111.9$) and $[\mathrm{CyP}]_4$ ($\delta = -68.3$). However, the major product is the monoanion $[\mathrm{CyP}\overset{\cdots}{-}\mathrm{C(Ph)}\overset{\cdots}{-}\mathrm{NH}]^{-}$,[3b] the chemical shift involved ($\delta = 59.4$) being similar to that found for related anions (e.g., $\delta = 34.3$ for $[\mathrm{PhP}\overset{\cdots}{-}\mathrm{C(Me)}\overset{\cdots}{-}\mathrm{NH}]^{-}$ [3b] and as high as 65.2 in similarly substituted 1-phosphallyl anions[7]). Interestingly, the $[\mathrm{CyP}\overset{\cdots}{-}\mathrm{C(Ph)}\overset{\cdots}{-}\mathrm{N}]^{2-}$ ion is also a minor product at the initial stage of the reaction ($\delta = 192.8$). After the second stage of the reaction is complete (i.e., the green paramagnetic intermediate has faded) the resonance signal of the monoanion has almost disappeared and the resonance signal of the dianion dominates the spectrum; additional resonances ($\delta = 38.4$ and 19.4 (ratio 1:1)) are tenatively assigned to the P–P portion of the trianion of **1**. Unfortunately, owing to the very low solubility of **1** once isolated, full confirmation of these $^{31}$P NMR assignments has not been possible. However, the appearance of a singlet resonance at $\delta = 200.0$ for **1** in DMSO confirms our assignment for the dianion.

The unambiguous characterization of **1** by NMR and elemental analysis was hindered by extensive desolvation of the complex once isolated under vacuum. The true nature and complexity of this species only became apparent following the structural characterization. Although crystals of **1** are relatively weakly diffracting, the essential structural features of the complex are determined unambiguously.[8] Centrosymmetric molecules of **1** are composed of two $[\mathrm{CyP{:}C(Ph){:}N}]^{2-}$ ions and two $[\mathrm{H(PhCN)_3(CyP)_2}]^{3-}$ ions associated by ten $\mathrm{Li^+}$ ions into an elaborate cage structure (Figure 1 a). In addition, there are two THF molecules and two toluene molecules present in the lattice. The bond lengths found in the $[\mathrm{CyP}\overset{\cdots}{-}\mathrm{C(Ph)}\overset{\cdots}{-}\mathrm{N}]^{2-}$ ion of **1** (P(1)–C(1) 1.83(1), C(1)–N(1) 1.27(1) Å) are similar to those observed previously in $[\mathrm{R^1P}\overset{\cdots}{-}\mathrm{C(R^2)}\overset{\cdots}{-}\mathrm{NR^3}]^{-}$ monoanions (P–C ca. 1.75–1.79, C–N 1.30–1.35 Å[3b–d]). The N-C-P angle in the dianion (122.0(7)°) is significantly smaller than that observed for the most closely related $[\mathrm{PhP}\overset{\cdots}{-}\mathrm{C(Me)}\overset{\cdots}{-}\mathrm{NH}]^{-}$ monoanion (132.0(3)°),[3b] but similar to that observed for silylated monoanions chelated to Group 2 ions.[3d] The bond lengths within the $[\mathrm{H(PhCN)_3(CyP)_2}]^{3-}$ ion indicate that the charge is located essentially in three distinct regions of the chain (Scheme 2). Although shorter than the value expected for a P–P single bond (ca. 2.21 Å[9]), the P–P bond length in the $[\mathrm{CyP}]_2$ unit [2.170(4) Å] is similar to that in the $[t\mathrm{BuPP}t\mathrm{Bu(H)}]^{-}$ ion (2.150(5) Å),[10] suggesting that the negative charge is more or less concentrated on the terminal P atom. A further negative charge is delocalized over the N(2)-C(2)-N(3) fragment of the chain; the C–N bond lengths within this unit (C(2)–N(2) 1.32(1), C(2)–N(3) 1.35(1) Å) are typical of those found in amidines.[11] The final negative charge is found within the C(3)-C(4)-N(4) unit; the C–C (1.40(1) Å) and C–N (1.38(1) Å) bonds involved are similar to those present in aza-allyl complexes.[12] There appears to be little additional delocalization between the amidine and aza-allyl units, judging by the large C(3)–N(3) bond length (1.45(1) Å; cf mean 1.35 Å for the other $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ bonds in the trianion) and the acute angle at N(3) (115.8(7)°). In addition, the nonplanar geometry of the chain precludes alignment of the p orbitals between these units.

Each of the five $\mathrm{Li^+}$ ions of the asymmetric unit of **1** has a distinct coordination environment (Figure 1 b). Overall, the connectivities of the three- and four-coordinate $\mathrm{Li^+}$ ions present reflect the charge distributions found in the dianion and trianion (Scheme 2). The coordination of Li(1) is particularly noteworthy. In addition to its bonding to the P(1) center of a dianion (2.45(2) Å[13]) and the amidine N(2) center (1.93(2) Å) of a trianion, there is an allylic interaction with C(3) (2.41(2) Å) and the *ipso*- (C(61)) and *ortho*-C (C(66)) centers of the attached phenyl ring (each ca. 2.52 Å).

In summary, the results reported here show that nucleophile-induced oligomerization of organic nitriles does not always occur by head-to-tail C–N bond formation. The presence of the two different anions in **1** can be ascribed to competing nucleophilic and SET mechanisms. However, clearly further mechanistic studies will be required to elucidate the exact mechanism and the extent to which radicals are involved. The $[\mathrm{CyP}\overset{\cdots}{-}\mathrm{C(Ph)}\overset{\cdots}{-}\mathrm{N}]^{2-}$ ion in **1** is the first example of such a dianion to be structurally characterized.

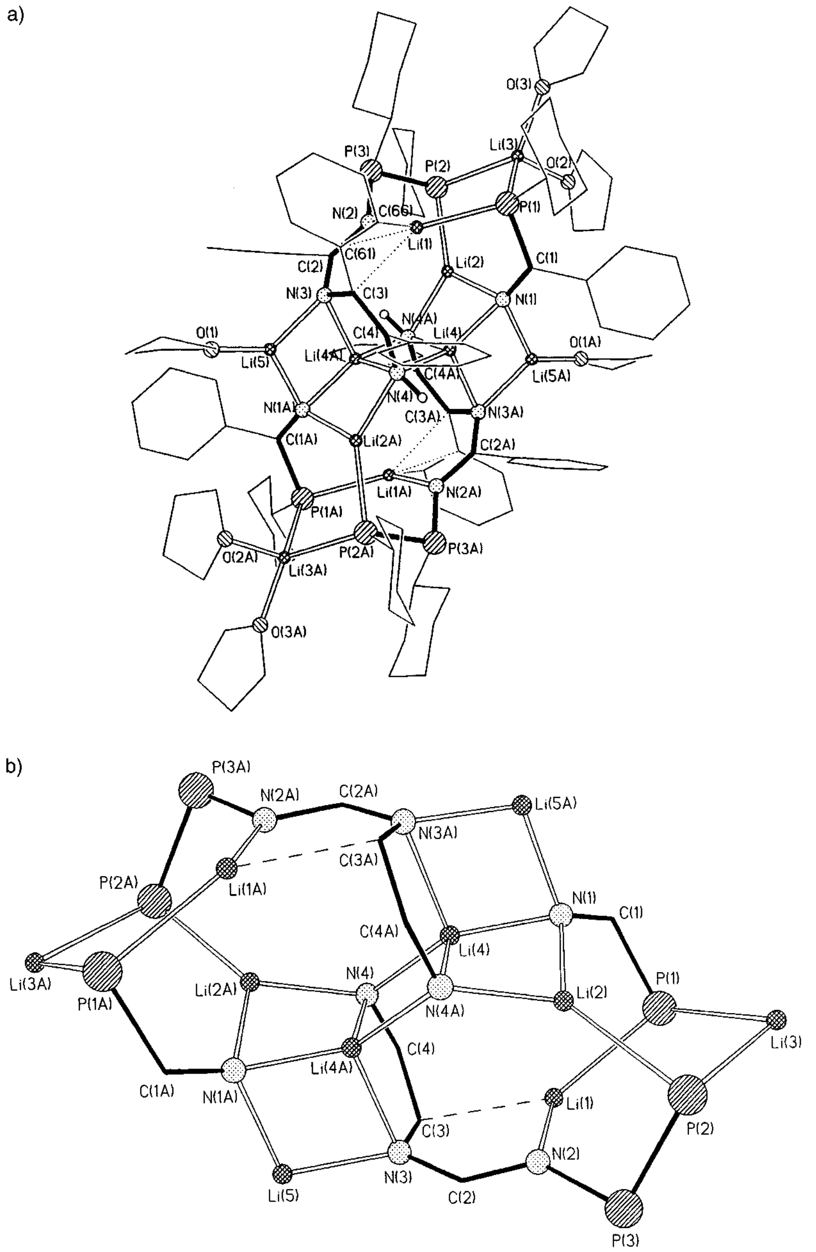

Figure 1. a) Molecular structure of **1**. Hydrogen atoms (except those terminating the trianion chain) and lattice-bound THF and toluene molecules have been omitted for clarity. Key bond lengths [Å] and angles [°]: Li(1)-P(1) 2.45(2), Li(1)-N(2) 1.93(2), Li(1)-C(3) 2.41(2) Li(1)-C(61,66) 2.52Å (av), Li(2)-N(1) 2.03(2), Li(2)-P(2) 2.50(2), Li(2)-N(4A) 2.11(2), Li(3)-P(1) 2.62(2), Li(3)-P(2) 2.58(2), Li(3)-O(2,3) 1.96 (av), Li(4)-N(4) 2.09(2), Li(4)-N(4A) 2.06(2), Li(4)-N(1) 1.94(2), Li(4)-N(3A) 2.14(2), Li(5)-N(1A) 2.03(2), Li(5)-N(3) 2.01(2), Li(5)-O(1) 1.92(2), P(1)-C(1) 1.83(1), N(1)-C(1) 1.27(1), N(4)-C(4) 1.38(1), C(4)-C(3) 1.40(1), C(3)-N(3) 1.45(1), N(3)-C(2) 1.35(1), C(2)-N(2) 1.32(1), N(2)-P(3) 1.750(8), P(3)-P(2) 2.170(4); P(1)-C(1)-N(1) 122.0(7), N(4)-C(4)-C(3) 122.7(8), C(4)-C(3)-N(3) 118.9(8), C(3)-N(3)-C(2) 115.8(7), N(3)-C(2)-N(2) 125.2(8), C(2)-N(2)-P(3) 121.9(7), N(2)-P(3)-P(2) 102.3(3). b) Core structure of **1** showing the connectivities of the $Li^+$ ions.

## *Experimental Section*

**1**: *n*BuLi (4.70 mL, 7.0 mmol, 1.5 mol$L^{-1}$ in hexanes) was added to a solution of $CyPH_2$ (0.93 mL, 7.0 mmol) in toluene (10 mL) at −78 °C. A light yellow precipitate of [CyPHLi] was produced by stirring the mixture at room temperature (ca. 30 min). Addition of PhCN (0.72 mL, 7.0 mL) to the mixture at −78 °C gave an immediate red coloration. Stirring at room temperature (ca. 40 min) gave a red-brown solution with a brown suspension, which was completely dissolved by the addition of THF (2.0 mL). Addition of *n*BuLi (4.70 mL, 7.0 mmol, 1.5 mol$L^{-1}$ in hexanes) to this solution at −78 °C gave a deep orange-red solution. As the temperature was allowed to increase to about 0 °C, a deep green coloration began to develop. Stirring for about 2 h at room temperature led to gradual fading of the green intermediate and finally a deep red solution was obtained. The solvent was removed under vacuum and the glassy red oil was dissolved in toluene (5 mL) and THF (0.5 mL). Storage of the red solution (5 °C, up to two weeks) gave small light orange crystals of **1**. Elemental analysis and the $^1H$ NMR spectrum reveal that only traces of THF and toluene are present in the complex once isolated under vacuum (15 min, $10^{-1}$ atm). Yield 0.16–0.23 g (12–17 %, based on PhCN consumed, for unsolvated complex). M.p. 225–230 °C (decomp). IR (NaCl, Nujol): $\tilde{\nu}$ = 3374 (vw; =N–H str.), 3050–3023 (w; aryl C-H), 1599 (w.,sh), 1594 (m), 1570 (w; C$\overset{\cdots}{-}$N str.), 1480 (s; C$\overset{\cdots}{-}$C str.), other bands at 1203 (w), 1069 (m), 1037 (s), 885 (m), 831 (m), 782 (s), 764 (vs), 719 (vs) $cm^{-1}$ (air-exposure led to an increase in intensity of the =N–H band and the appearance of Li-OH stretching frequency at 3678 $cm^{-1}$). $^1H$ NMR (400.13 MHz, $[D_6]$DMSO, +25 °C): $\delta$ = 8.0–7.0 (overlapping m, 20 H; Ph), 1.70–0.90 (overlapping m, 33 H; Cy). elemental analysis: calcd for unsolvated **1**: C 70.0, H 6.7, N 7.1; found: C 68.5, H, 6.2, N, 8.0. **Caution**: ignites extremely violently in acids, therefore no P analysis could be obtained.

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weakly and the data is relatively poor). Final $R1 = 0.096$ $[I > 2\sigma(I)]$ and $wR2 = 0.265$ (all data).[14] All four of the C atoms of the THF molecule bonded to Li(5) are disordered over 50:50 sites. The H atom attached to N(4), which is inferred from the IR spectrum of **1**, was located in the final difference map. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-144824. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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# Stabilization of a Pentastibacyclopentadienyl Ligand in the Triple-Decker Sandwich Complexes $[\{(\eta^5\text{-}1,2,4\text{-}t\mathrm{Bu}_3\mathrm{C}_5\mathrm{H}_2)\mathrm{Mo}\}_2(\mu,\eta^5\text{-}\mathrm{Sb}_5)]$ and $[(\eta^5\text{-}1,2,4\text{-}t\mathrm{Bu}_3\mathrm{C}_5\mathrm{H}_2)\mathrm{Mo}(\mu,\eta^5\text{-}\mathrm{Sb}_5)\mathrm{Mo}(\eta^5\text{-}1,4\text{-}t\mathrm{Bu}_2\text{-}2\text{-}\mathrm{MeC}_5\mathrm{H}_2)]$**

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Triple-decker sandwich complexes containing *cyclo*-$(\eta^n\text{-E}_n)$ ligands ($n = 5$, 6) are well known for E = P, As.[1–3] Although elemental pnictogens (white phosphorus, $\mathrm{P_4}$, and yellow arsenic, $\mathrm{As_4}$) are the most obvious reagents and have been used in many cases, organophosphorus[4] and organoarsenic[1] rings, and $[(\mathrm{CO})_5\mathrm{CrPCl_3}]$[5] are also viable sources of phosphorus and arsenic elemental ligands. Since an $\mathrm{Sb_4}$ molecule is not available for synthetic purposes, other starting materials have been used for the preparation of complexes with substituent-free antimony ligands: both metallic antimony[6a] and *cyclo*-$\mathrm{Cp^*_4Sb_4}$[6b] ($\mathrm{Cp^* = Me_5C_5}$) gave complexes containing $\mathrm{Sb_2}$ fragments. *cyclo*-$t\mathrm{Bu_4Sb_4}$[7] proved to be a versatile reagent in the synthesis of complexes containing both $\mathrm{Sb_2}$ and *cyclo*-$\mathrm{Sb_3}$ ligands.[8] Compounds containing *cyclo*-$\mathrm{Sb_5}$ ligands were observed as decomposition products in the mass spectra of clusters containing $\mathrm{Sb_2}$ and $\mathrm{Sb_3}$ fragments but have not yet been identified in the condensed phase.[8b] We report here on the stabilization of the pentastibacyclopentadienyl ligand *cyclo*-$(\eta^5\text{-}\mathrm{Sb}_5)$ as the middle-deck in the triple-decker sandwich complexes **1** and **2**.

$[(\eta^5\text{-}1,2,4\text{-}t\mathrm{Bu}_3\mathrm{C}_5\mathrm{H}_2)\mathrm{Mo}(\mu,\eta^5\text{-}\mathrm{Sb}_5)\mathrm{Mo}(\eta^5\text{-}1,2,4\text{-}t\mathrm{Bu}_3\mathrm{C}_5\mathrm{H}_2)]$ **1**

$[(\eta^5\text{-}1,2,4\text{-}t\mathrm{Bu}_3\mathrm{C}_5\mathrm{H}_2)\mathrm{Mo}(\mu,\eta^5\text{-}\mathrm{Sb}_5)\mathrm{Mo}(\eta^5\text{-}1,4\text{-}t\mathrm{Bu}_2\text{-}2\text{-}\mathrm{MeC}_5\mathrm{H}_2)]$ **2**

Complexes **1** and **2** are formed when a mixture of *cyclo*-$t\mathrm{Bu_4Sb_4}$ and $[\mathrm{Cp'''(CO)_3MoCH_3}]$ ($\mathrm{Cp'''} = \eta^5\text{-}1,2,4\text{-}t\mathrm{Bu}_3\mathrm{C}_5\mathrm{H}_2$)[9] is heated in decaline. It is not surprising that a by-product of the thermal reaction is $[\{\mathrm{Cp'''Mo(CO)_2}\}_2]$ (*Mo*≡*Mo*) (**3**). Unexpected, however, is the formation of the complex **2** by replacement of one of the *tert*-butyl groups in position 1 or 2 on one of the cyclopentadienyl rings in the compound **1** by a methyl group. The triple-decker sandwich complexes **1** and **2** could not be separated by chromatography. After chromatographic separation from the reaction mixture an air-sensitive, dark green, microcrystalline solid containing both **1** and **2** was obtained in about 18% overall yield. The two complexes are very soluble in hydrocarbons, giving emerald-green solutions that are air-sensitive. These solutions immediately change color to brown when exposed to air. A few relatively large single crystals of **2** were grown from a solution of the mixture in hexane. The identity of the compounds was confirmed by elemental analysis and by $^1$H NMR and IR (**3**) spectroscopy and mass spectrometry. The mass spectra suggested a mole ratio of 4:1 (**1**:**2**) in the mixture. The complexes **1** and **2** have a remarkable thermal stability, the mixture melting without significant decomposition at 331–333 °C and subliming at 260 °C/$10^{-3}$ Torr.

The crystal structure of **2** was determined by X-ray crystallography.[10] The molecule has a typical triple-decker sandwich structure (Figure 1), with the bulky cyclopentadienyl rings almost parallel to each other (dihedral angle 5.3°) and to the $\mathrm{Sb_5}$ ring (3.2° each). The $\mathrm{Sb_5}$ middle deck is very slightly folded towards Mo(2), with Sb(2) lying 20 pm out of the plane formed by the other four antimony atoms. The Sb–Sb bonds (275.59(11) and 276.56(9) pm) involving Sb(2) are shorter than the single bonds in *cyclo*-$t\mathrm{Bu_4Sb_4}$ (Sb–Sb 281.7(2)–282.1(2) pm)[11a] or *cyclo*-$((\mathrm{Me_3Si})_2\mathrm{CH})_4\mathrm{Sb_4}$ (282.1(1)–287.8(1) pm),[11b] and similar to those in the clusters $[\mathrm{Cp(CO)_2MoSb_3}]$ (273.45(10)–278.05(11) pm) and $[\mathrm{Cp^*(CO)_2MoSb_3}]$ (273.97(9)–276.82(8) pm).[8a] They are considerably longer than an Sb–Sb double bond (264.2(1) pm in $\{2,4,6\text{-}[(\mathrm{Me_3Si})_2\mathrm{CH}]_3\mathrm{C_6H_2}\}_2\mathrm{Sb_2}$).[12] The Sb–Sb bonds involving Sb(5) are longer (284.24(9) and 285.04(9) pm), their lengths falling in the normal range for Sb–Sb single bonds. The Sb(3)–Sb(4) bond length has an intermediate value (279.78(8) pm). A

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