Synthesis and Solid State Structures of Sterically Crowded d⁰-Metallocenes of Magnesium, Calcium, Strontium, Barium, Samarium, and Ytterbium

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The base-free metallocenes [1,2,4-$(Me_3C)_3C_5H_2$]$_2$Ca, [1,2,4-$(Me_3C)_3C_5H_2$]$_2$Sr, and [1,2,4-$(Me_3C)_3C_5H_2$]$_2$Ba have been prepared by reaction of MI_2 and the sodium or potassium salt of the substituted cyclopentadiene anion in THF, while [1,2,4-$(Me_3C)_3C_5H_2$]$_2$Mg was prepared from the cyclopentadiene, 1,2,4-$(Me_3C)_3C_5H_3$, and dibutylmagnesium. The structures of the magnesocene and calcocene as well as those of the previously prepared ytterbium and samarium analgoues have been determined by X-ray crystallography. The metallocenes are slightly bent in the solid state with centroid−metal−centroid angles ranging from 163° to 173°. Adducts of the strontocene and samarocene with THF and of the barocene, samarocene, and ytterbocene with 2,6-$Me_2C_6H_3NC$ have also been prepared and characterized. The massive bulk of the [1,2,4-$(Me_3C)_3C_5H_2$]⁻ ligand leads to behavior quite different from that previously observed for base-free metallocenes of the alkaline earths and divalent lanthanides.

Introduction

The use of extremely bulky cyclopentadienide ligands is an active area of metallocene research in which previously unknown ligands have been prepared[1] and used to stabilize previously unknown metallocenes.[2] Reports of new base-free metallocenes of the alkaline earth metals[3] and divalent lanthanides[4−6] have recently appeared, and the structures of these relatively simple molecules continue to hold surprises. In this context and for comparison with the corresponding divalent lanthanide metallocenes,[6] we have prepared a series of main group metallocenes bearing the bulky [1,2,4-$(Me_3C)_3C_5H_2$]⁻ (Cp‡) ligand. The coordination environment of this ligand leads to structures in which the centroid−metal−centroid angle approaches 180°, but the rings are not parallel in the solid state. The origin of bending appears to be repulsive interactions between the *tert*-butyl groups in the magnesium case. For divalent metallocenes of calcium, strontium, barium, samarium, or ytterbium, bending has previously been described as the natural geometry.[5] The steric bulk of the Cp‡ ligand used in this study induces repulsion on further bending of the metallocene sandwich, and only

a few adducts have been prepared. This contrasts with the reactions of the sterically crowded $(Me_5C_5)_3Sm$, in which the steric repulsions at the metal do not inhibit reactions with incoming ligands, but the relief of these repulsions lowers the barriers to substitution reactions.[7]

We report here the synthesis and molecular structures of metallocenes of the form Cp‡$_2$M as well as some complexes with THF and xylyl isocyanide.

Results and Discussion

Stirring a THF slurry of MI_2 (M = Ca, Sr, Ba) with 2 equiv of NaCp‡ or KCp‡ results in a rapid reaction as two cyclopentadienide rings are transferred to the divalent metal center (eq 1 using sodium salt). Either the potassium or the sodium salt can be used in these reactions with equally good yields of metallocenes. This is in accord with the synthesis of many alkaline earth and lanthanide metallocenes.[5,6,8−12] However, it contrasts with the reactions of the related cyclopentadienide salts, K[1,2,4-$(Me_2CH)_3C_5H_2$] and K[1,2,3,4-$(Me_2CH)_4C_5H$], with CaI_2 in THF, studied by Hanusa.[13,14] Attempted synthesis of the corresponding calcocenes in pure THF led to the mono-ring complexes, which was attributed to kinetic stabilization due to the strong

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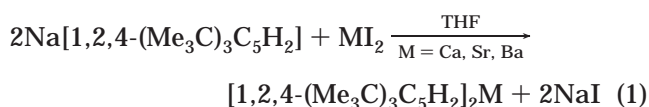
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Table 1. Physical Properties of Base-Free Metallocenes $[1,2,4\text{-}(Me_3C)_3C_5H_2]_2M$

M	color	melting point (°C)	reference
Mg	white	187–189	this work
Ca	white	123–125	this work
Sr	white	162	this work
Ba	white	115	this work
Sm	purple	125	6
Eu	red	135	6
Yb	brown-green	165	6

binding of THF to calcium, preventing substitution of the second cyclopentadienide ring. It is somewhat surprising, therefore, that the sterically even larger Cp‡ ligand leads directly to the calcocene in high yield, and no mono-ring product is observed. One explanation for this difference in reactivity is that the ligands used by Hanusa are somewhat smaller than Cp‡, which means that THF could bind more tightly to the mono-ring intermediate. Also, the rate is expected to be slower for the system studied by Hanusa as the isopropyl groups are less nucleophilic than the *tert*-butyl groups.

After removal of the solvent under reduced pressure, the base-free metallocenes are obtained and can be recrystallized from pentane.

$$2Na[1,2,4\text{-}(Me_3C)_3C_5H_2] + MI_2 \xrightarrow[\text{M = Ca, Sr, Ba}]{\text{THF}}$$

$$[1,2,4\text{-}(Me_3C)_3C_5H_2]_2M + 2NaI \quad (1)$$

This contrasts with the synthesis of metallocenes bearing less bulky cyclopentadienide ligands such as $[Me_5C_5]^-$, $[1,3\text{-}(Me_3Si)_2C_5H_3]^-$, and $[1,3\text{-}(Me_3C)_2C_5H_3]^-$. For those metallocenes, THF is not the solvent of choice for synthesis of base-free complexes because it inevitably leads to a THF adduct from which the THF cannot readily be removed.[5,8] For some strontium and barium examples, sublimation is effective to remove coordinated solvent.[10,15,16]

The magnesium analogue is prepared by heating dibutylmagnesium with the cyclopentadiene in heptane, as previously reported for $(Me_5C_5)_2Mg$[17] and $[1,3\text{-}(Me_3C)_2C_5H_3]_2Mg$.[18] The metallocenes reported here are very soluble, crystalline solids. Table 1 summarizes their physical properties and compares them to the previously reported Sm, Eu, and Yb analogues. Note that the NMR data for the paramagnetic samarium analogue previously reported[6] are incorrect as explained in detail below; the correct chemical shifts are reported in the Experimental Section.

Addition of a donor such as THF or DME to an NMR tube containing a C_6D_6 solution of the strontium, barium, or samarium complex results in a ${}^1H$ NMR spectrum in which the separation between the two inequivalent *tert*-butyl resonances is larger than in the spectra of the corresponding base-free molecules. This

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phenomenon is most stark in the paramagnetic samarocene case, in which the separation between the *tert*-butyl groups of the base-free compound at room temperature is 5.9 ppm. With 1 equiv of THF the separation is 9 ppm, and the two resonances of the THF are observed at 2.2 ($\nu_{1/2}$ = 64 Hz) and −0.8 ($\nu_{1/2}$ = 18 Hz) ppm. The chemical shifts erroneously reported previously are for a solution containing 1 equiv of THF.[6] The shifted and broadened peaks in the proton NMR spectrum indicate clearly that the THF is bound to the paramagnetic samarium center on average, although chemical exchange is occurring in solution. Addition of more THF results in further monotonic change in the positions of the resonances of the *tert*-butyl protons of the metallocene and of the THF, so that with 3.5 equiv of THF, the spectrum consists of resonances at 16.4 (18H, CMe$_3$, $\nu_{1/2}$ = 80 Hz), 5.5 (36H, (CMe$_3$)$_2$, $\nu_{1/2}$ = 21 Hz), 2.9 (14H, THF, $\nu_{1/2}$ = 41 Hz), and 0.3 (14H, THF, $\nu_{1/2}$ = 16 Hz) ppm. With a large excess (20 equiv) of THF, the *tert*-butyl resonances are observed at 17.6 ($\nu_{1/2}$ = 54 Hz) and 5.6 ($\nu_{1/2}$ = 21 Hz) ppm and do not change further with the addition of more THF. At that concentration the THF protons resonate close to the frequencies for free THF at 3.4 ($\nu_{1/2}$ = 27 Hz) and 1.3 ($\nu_{1/2}$ = 34 Hz) ppm, but the resonances are still broader than in a diamagnetic solution.

For the diamagnetic metallocenes of barium and strontium, the changes in the ${}^1H$ NMR spectra upon addition of a donor ligand are less pronounced. Nonetheless, electron donors have the effect of increasing the separation between the two *tert*-butyl peaks (see Experimental Section for details). A similar effect, also caused by addition of THF, on the ${}^1H$ NMR spectra of alkaline earth metallocenes has been reported by Hanusa for the isopropyl-substituted complexes, $[1,2,4\text{-}(Me_2CH)_3C_5H_2]_2M$ (M = Ca, Sr, Ba).[13] This was not observed for the calcium or ytterbium complexes in our study, presumably because the metal center is too small and shielded by the *tert*-butyl groups to allow the close approach of a donor ligand.

The crystal structures of the base-free magnesium and calcium complexes have been determined, as well as those of the previously reported samarium and ytterbium analogues. Unfortunately, the magnesocene structure is the only one of high quality. This seems to be a characteristic of base-free metallocenes of Cp‡; with six *tert*-butyl groups altogether, the molecule is almost spherical within the unit cell, and the packing is not constrained to give a well-ordered structure, unless the metal atom is very small, which reduces the degrees of freedom of the molecule. In fact, all of the structures reported here are isomorphous and have two very similar independent molecules in the unit cell, as does the previously reported europocene structure.[6] Each structure other than the magnesocene has two very similar unit cell constants, which seems to be associated with their poor ordering (Table 3). The crystals therefore do not diffract well, and only low-angle data can be obtained. In the presence of an additional ligand (THF or xylyl isocyanide, see below) the ordering of the compound within the crystal is far better and the molecule packs better, giving good quality high-angle data and well-resolved structures. Despite the disorder, the overall geometry of the base-free molecules de-

Table 2. Selected Bond Distances (Å) and Angles (deg) for Base-Free Metallocenes [1,2,4-(Me₃C)₃C₅H₂]₂M

	M				
	Mg	Ca	Sm	Yb	Eu[a]
M−C (ring) (Å, range)	2.34−2.45	2.60−2.68	2.72−2.85	2.64−2.72	2.76−2.82
M−C (ring) (Å, mean)	2.39	2.64	2.79	2.67	2.78
M−centroid (Å, mean)	2.06	2.35	2.52	2.38	2.51
centroid−M −centroid (deg)	173	171	164	166	165
twist angle (deg)	3	2	1	1	2

[a] Reference 6.

Table 3. Selected Crystal Data and Data Collection Parameters for [1,2,4-(Me₃C)₃C₅H₂]₂Mg, [1,2,4-(Me₃C)₃C₅H₂]₂Ca, [1,2,4-(Me₃C)₃C₅H₂]₂Sm, and [1,2,4-(Me₃C)₃C₅H₂]₂Yb

formula	$C_{34}H_{58}Mg$	$C_{34}H_{58}Ca$	$C_{34}H_{58}Sm$	$C_{34}H_{58}Yb$
fw	491.14	506.88	617.15	639.87
space group	$P2_1/c$ (#14)	$P2_1/c$ (#14)	$P2_1/c$ (#14)	$P2_1/c$ (#14)
a (Å)	20.3699(5)	19.838(2)	19.5280(8)	19.482(1)
b (Å)	17.5802(3)	18.220(1)	18.3913(9)	18.066(1)
c (Å)	19.2997(4)	19.694(2)	19.8608(5)	19.526(1)
β (deg)	112.774(1)	110.41(1)	109.895(2)	109.819(2)
V (Å³)	6372.5(2)	6671(1)	6707.2(5)	6465.4(7)
Z	8	8	8	8
d_{calc} (g/cm³)	1.024	1.01	1.222	1.31
μ(Mo Kα)$_{calc}$ (cm⁻¹)	0.7	2.06	17.69	29.11
size (mm)	0.32 × 0.28 × 0.14	0.21 × 0.19 × 0.12	0.35 × 0.25 × 0.20	0.19 × 0.14 × 0.08
temperature (K)	149	293	293	136
diffractometer[a]	SMART	Stoe IPDS	Enraf-Nonius	SMART
scan type	ω	ϕ	ϕ	ω
2θ range (deg)	4−46	4.3−52.1	3.1−55.1	4−52
no. of reflns collected	25 981	23 297	22 324	26 407
no. of unique reflns	9451	7943	13 936	9617
no. of obsd reflns	5342 ($I > 3\sigma I$)	2954 ($I > 2\sigma I$)	7537 ($I > 2\sigma I$)	2707 ($I > 3\sigma I$)
variables	631	671	667	291
abs corr	XPREP	XPREP	none	SADABS
transmn range	0.978−0.947	0.964−0.854		0.962−0.786
R_1[b]	0.0447	0.095	0.15	0.035
wR_2[c]	0.0511	0.24	0.36	0.033
wR_{all}	0.0615	0.20	0.42	0.057
GOF	1.58	0.94	1.34	0.88
min. and max. RED (e⁻/Å³)	−0.19 and 0.25	−0.38 and 0.75	−2.02 and 4.04	−0.50 and 0.70

[a] Radiation: graphite monochromated Mo Kα (λ = 0.71073 Å). [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

scribed here, including the centroid−metal−centroid angles and relative arrangement of the cyclopentadienide rings, is clear. All of these metallocenes crystallize as slightly bent sandwiches. Unsubstituted magnesocene is linear,[19] as is decamethylmagnesocene,[20] while [(Me₃Si)₃C₅H₂]₂Mg is also slightly bent.[21] Thus, it appears that the steric bulk of the Cp‡ groups forces the rings to bend back in the case of the small metal magnesium. For Ca, Ba, Sm, Eu, and Yb, the cyclopentadienide rings are closer to parallel in the structures determined here than in those of their less-substituted base-free metallocenes.[5,12,22−24] Again, the steric bulk of the Cp‡ groups seems to be responsible, in these cases by not allowing the rings to bend back as much as their natural geometry would require, due to an increase in repulsion at the backside of the wedge. A similar effect was noticed for the smaller ligand [(Me₂CH)₃C₅H₂]⁻.[25,26]

The arrangement of the cyclopentadienide rings in the solid state is found to be eclipsed, so that, viewed

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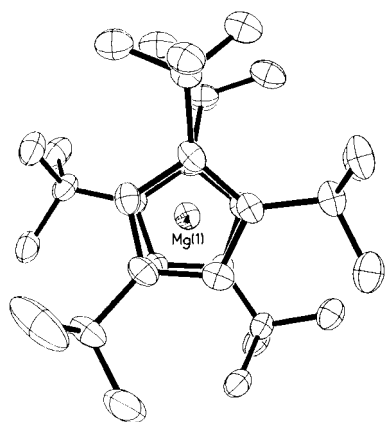
Figure 1. Schematic representation of eclipsed (A, D) and staggered (B, C) conformations of metallocenes in which the cyclopentadienide rings each bear three substituents. U represents a substituent on the upper ring; L represents a substituent on the lower ring.

down the centroid−centroid axis, exactly one *tert*-butyl group on one ring is directly over one on the other ring (Figure 1A). Although the metallocenes are almost linear (centroid−metal−centroid angles 163−173°), in every case the two *tert*-butyl groups that are directly over one another are located at the slightly open side of the wedge (at the top of the diagram in the view shown; Figure 1A). This geometry was also found for

Figure 2. ORTEP diagram (50% probability ellipsoids) of Cp‡₂Mg. Only one of the two independent molecules in the asymmetric unit is shown. Hydrogen atoms have been omitted for clarity.

the corresponding europocene,[6] as well as the bismocenium and stibocenium cations of Cp‡.[27,28] It has also been observed for hexa(trimethylsilyl)metallocenes of tin, germanium, magnesium, and iron and for the corresponding ferrocenium cation.[21,29−32] In this arrangement, the other four *tert*-butyl (or trimethylsilyl) groups are far apart from one another. This arrangement (which can be achieved in two different ways) is apparently energetically favored in the solid state over the alternative, staggered arrangements, in which no group lies directly over another, but each *tert*-butyl group has a minimum of one near neighbor on the opposite ring (Figure 1B,C). Two of the five possible staggered positions lead to three of these interactions (Figure 1B), while three of these arrangements result in four near neighbors on the opposite ring (Figure 1C). The latter staggered geometry has been observed in structures in which an additional ligand is present (see the THF adducts below). The other three possible eclipsed arrangements involve two or all three substituents being located directly over each other and are presumably much higher in energy. Nonetheless, the chloride Cp‡₂-BiCl adopts an arrangement with two sets of *tert*-butyl groups directly over one another, Figure 1D.[33] The chloride ligand in that structure is located in the position with no *tert*-butyl groups at the top, as shown in Figure 1D. A similar eclipsed geometry was found for isocyanide adducts in this work (see below).

An ORTEP diagram of Cp‡₂Mg is shown in Figure 2, while Table 2 gives selected bond distances and angles of these structures (the mean of the two independent molecules is given). The corresponding data for the reported Eu structure are included for comparison.[6] As the calcium, samarium, and ytterbium compounds are isostructural to the magnesocene, ORTEP diagrams of

these metallocenes are not given and can be found in the Supporting Information. Important data collection and structure solution parameters are provided in Table 3, and full details of the crystallography are included in the Supporting Information.

Despite the crowded environment, the mean metal−ring carbon distances in the crystal structures of these complexes are not elongated from the corresponding values in the respective decamethylmetallocenes (2.64 for Ca,[24] 2.80 for Sm and Eu,[23] and 2.67 for Yb[5]) (Table 2), other than for magnesium. The mean Mg−C distance in both independent molecules of Cp‡₂Mg, at 2.39(6) Å, is slightly longer than in decamethylmagnesocene, whose structure has been determined both in the solid state (mean Mg−C 2.30 Å[20]) and in the gas phase (mean Mg−C 2.34 Å[17]). Comparison with the reported structure of [1,2,4-(Me₃Si)₃C₅H₂]₂Mg indicates that the steric bulk of the tris(trimethylsilyl)cyclopentadienide ligand is similar to that of Cp‡; as in the trimethylsilyl-substituted case, the metal−ring carbon distances for both molecules in the asymmetric unit lie between 2.32 and 2.40 Å (mean 2.37 Å).[31] The *tert*-butyl groups are expected to cause slightly more steric pressure due to the shorter and less flexible C−C bond compared with the C−Si bond. This is consistent with the bending in these two magnesocenes being caused by steric pressure as described above.

Crystallization of the strontium, barium, and samarium complexes from THF leads to the formation of the corresponding THF adducts, but the THF is easily lost upon exposure of the crystals to vacuum. This is in stark contrast to several previously reported soluble metallocenes, which must be subjected to heating under vacuum in order to remove coordinated ethers.[5,13] For the calcium and ytterbium metallocenes, THF coordination has not been observed, even when the compound was crystallized from neat THF. Clearly the metal center is shielded from incoming ligands by the bulky *tert*-butyl groups. However, unlike the heavily shielded complexes [(Me₂CH)₄C₅H]₂Ca[26] and [(Me₂CH)₅C₅]₂M (M = Ca, Sr, Ba),[2] the base-free metallocenes reported here are nonetheless extremely moisture sensitive.

The THF adducts of the strontocene and samarocene were characterized by X-ray crystallography in order to determine the structural changes upon adduct formation. The strontocene adduct contains two disordered *tert*-butyl groups, which are the isolated *tert*-butyl groups (in the 4-position) on each cyclopentadienide ring. Figure 3 shows an ORTEP diagram of the strontocene THF adduct Cp‡₂Sr(THF), while important bond distances and angles for both compounds are given in Table 4. The complexes are isomorphous and isostructural, so no ORTEP diagram of the THF adduct of the samarocene is given here; it can be found in the Supporting Information. Table 5 contains relevant data collection and structure solution parameters, and full crystallographic details are given in the Supporting Information.

It can be seen that the cyclopentadienide rings are staggered; the twist angle is 26°.[34] This is presumably a consequence of the position in the middle of the open wedge being occupied by the THF molecule, so it is no longer energetically feasible for two *tert*-butyl groups to lie above one another in that position. Instead the

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Table 4. Selected Bond Distances (Å) and Angles (deg) of [1,2,4-(Me₃C)₃C₅H₂]₂Sr(THF), [1,2,4-(Me₃C)₃C₅H₂]₂Sm(THF), [1,2,4-(Me₃C)₃C₅H₂]₂Sm(2,6-Me₂C₆H₃NC)·Toluene, [1,2,4-(Me₃C)₃C₅H₂]₂Yb(2,6-Me₂C₆H₃NC)·Toluene, and [1,3-(Me₃C)₂C₅H₃]₂Yb(2,6-Me₂C₆H₃NC)₂

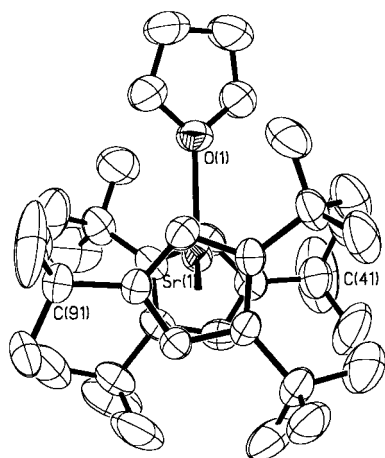|	Cp‡₂Sr(THF)	Cp‡₂Sm(THF)	Cp‡₂Sm(2,6-Me₂C₆H₃NC)·toluene	Cp‡₂Yb(2,6-Me₂C₆H₃NC)·toluene	[1,3-(Me₃C)₂C₅H₃]₂Yb(2,6-Me₂C₆H₃NC)₂[a]
M−C (ring) (Å, mean)	2.87	2.86	2.86	2.75	2.72
M−centroid (Å, mean)	2.61	2.60	2.59	2.47	2.44
centroid−M−centroid (deg)	150	149	155	154	133
twist angle (deg)	26	26	3	3	1
M−O or M−C$_{CNR}$ (Å)	2.587(3)	2.605(3)	2.749(4)	2.588(5)	2.61
C$_{CNR}$−N (Å)			1.142(5)	1.150(6)	1.15
N−C$_R$ (Å)			1.399(5)	1.393(6)	1.40
M−C$_{CNR}$−N (deg)			180	180	172

[a] Reference 36.

Figure 3. ORTEP diagram (50% probability ellipsoids) of Cp‡₂Sr(THF). Hydrogen atoms have been omitted for clarity. Only one set of methyl atoms from each of the two disordered *tert*-butyl groups (on C41 and C91) is shown.

molecule has adopted a staggered conformation similar to that shown in Figure 1C, with somewhat elongated metal−ring carbon distances due to the higher coordination number and therefore greater ionic radius.[35] The THF ligand is twisted so as to minimize steric interactions between it and the neighboring *tert*-butyl groups.

The reaction of the ytterbium complex with carbon monoxide was attempted, as carbonyl complexes of three slightly less bulky ytterbocenes have recently been reported.[36] However, no change in the infrared spectrum was observed in methylcyclohexane at room temperature. As mentioned above, this contrasts with the reaction of the sterically encumbered complex (Me₅C₅)₃-Sm, which couples two CO groups to one of the cyclopentadienide ligands.[7]

To compare the new metallocenes with the well-studied (Me₅C₅)₂Yb, 2 equiv of the isocyanide 2,6-Me₂C₆H₃NC was added to toluene solutions of the base-free metallocenes of Ba, Sm, and Yb. Instead of forming the 2:1 compounds that have been reported for several ytterbocenes with a series of isocyanides,[36] 1:1 products were formed. The infrared spectra of Cp‡₂M(2,6-Me₂C₆H₃-NC) (M = Sm, Yb) both contain a sharp CN stretch at

2140 cm⁻¹ (the barium analogue was characterized only by NMR spectroscopy, which shows that the adducts have identical stoichiometry). This value compares with the single stretch at 2129 cm⁻¹ observed for the 2:1 ytterbium analogue [1,3-(Me₃C)₂C₅H₃]₂Yb(2,6-Me₂C₆H₃-NC)₂, which has only two *tert*-butyl groups per cyclopentadienide ligand and two isocyanide ligands. The trimethylsilyl-substituted compound [1,3-(Me₃Si)₂C₅H₃]₂-Yb(2,6-Me₂C₆H₃NC)₂ has a single stretch at 2142 cm⁻¹, so the electronic nature of the Cp‡₂M (M = Sm, Yb) fragment bound to one xylylisocyanide ligand is similar to that of [1,3-(Me₃Si)₂C₅H₃]₂Yb bound to two such ligands. These metallocenes do not engage in back-donation of electron density in a manner similar to the fragment [1,3-(Me₃C)₂C₅H₃]₂Yb.[36]

The Sm and Yb isocyanide adducts have been characterized by X-ray crystallography (with a toluene of crystallization), which confirms that the single isocyanide ligand is bound in the middle of the open side of the metallocene wedge. They are isostructural, so only the ORTEP diagram for the samarium complex is shown in Figure 4. Selected bond lengths and angles are presented in Table 4 and compared with the corresponding data for the reported structure of [1,3-(Me₃C)₂C₅H₃]₂Yb(2,6-Me₂C₆H₃NC)₂, an ORTEP diagram of which is provided in Figure 5.[36] Important data collection and structure solution parameters are provided in Table 5, and full details of the crystallography are included in the Supporting Information.

The metal atom in both the samarium and ytterbium complexes lies on a crystallographic C_2 axis, along with the *ipso*-CNC part of the isocyanide ligand and its *para* ring carbon atom, so the asymmetric unit consists of half the molecule. Thus, the isocyanide ligand is crystallographically in the center of the wedge. The two cyclopentadienide rings are eclipsed, and in two positions *tert*-butyl groups are directly above one another, similar to the geometry observed for Cp‡₂BiCl and depicted in Figure 1D.[33] Note that the centroid−metal−centroid angle of the bismuth complex is 145°, compared with 155° in these complexes, so the steric hindrance of the eclipsed *tert*-butyl groups is less in that case than in these complexes.

The most dramatic difference between Cp‡₂Yb(2,6-Me₂C₆H₃NC) and [1,3-(Me₃C)₂C₅H₃]₂Yb(2,6-Me₂C₆H₃-NC)₂ is the number of isocyanide ligands that each fragment binds. In the case of [1,3-(Me₃C)₂C₅H₃]₂Yb, in the presence of 1 or 2 equiv of isocyanide, only the bis-isocyanide adduct can be isolated, with the remainder of the ytterbocene remaining base-free if a deficiency of isocyanide ligand is present.[36] In stark contrast, Cp‡₂-

(34) The twist angle of a metallocene is measured by first creating 10 planes, each through the two calculated centroids and one of the 10 ring carbon atoms of the molecule. The smallest 5 angles of intersection of pairs of planes, each pair having one plane with a ring carbon on the top ring and one plane with a ring carbon on the bottom ring, are summed, and the mean of these 5 angles is the twist angle.

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**Table 5. Selected Crystal Data and Data Collection Parameters for [1,2,4-(Me₃C)₃C₅H₂]₂Sr(THF),
[1,2,4-(Me₃C)₃C₅H₂]₂Sm(THF), [1,2,4-(Me₃C)₃C₅H₂]₂Sm(2,6-Me₂C₆H₃NC)·Toluene, and
[1,2,4-(Me₃C)₃C₅H₂]₂Yb(2,6-Me₂C₆H₃NC)·Toluene**

	$Cp^‡_2Sr(THF)$	$Cp^‡_2 Sm(THF)$	$Cp^‡_2Sm$ (2,6-Me₂C₆H₃NC)·toluene	$Cp^‡_2Yb$ (2,6-Me₂C₆H₃NC)·toluene
formula	$C_{38}H_{66}OSr$	$C_{38}H_{66}OSm$	$C_{50}H_{75}NSm$	$C_{50}H_{75}NYb$
fw	626.53	689.26	840.46	863.15
color	white	purple	dark green-blue	dark blue
space group	$P2_1/n$ (#14)	$P2_1/n$ (#14)	Pbcn (#60)	Pbcn (#60)
a (Å)	10.3389(6)	10.3387(9)	16.3115(6)	16.2302(4)
b (Å)	16.0479(8)	16.0316(9)	15.0697(6)	14.8966(4)
c (Å)	23.471(1)	23.435(2)	19.2592(6)	19.2822(4)
β (deg)	94.595(7)	94.63(1)	90	90
V (Å³)	3881.8(4)	3871.5(5)	4734.1(3)	4662.0(2)
Z	4	4	4	4
d_{calc} (g/cm³)	1.072	1.183	1.179	1.230
μ (mm⁻¹)	1.413	1.541	1.271	2.037
size	0.60 × 0.45 × 0.42	0.42 × 0.31 × 0.18	0.43 × 0.40 × 0.33	0.40 × 0.30 × 0.20
temp (K)	293	293	200	200
diffractometer[a]	Stoe IPDS	Stoe IPDS	SMART	SMART
scan type	ϕ rotation	ϕ rotation	ω	ω
2θ range (deg)	5.7–50.7	5.7–51.4	3.6–54.8	3.7–54.9
no. of reflns collected	51 812	46 948	14 968	15 124
unique	6937	7345	5279	5110
obsd ($I > 2\sigma I$)	5274	5612	3561	3104
no. of variables	410	379	233	233
abs corr	numeric (XRED/STOE)	numeric (XRED/STOE)	SADABS[43]	SADABS[43]
transmn range	0.34–0.42	0.54–0.79	0.67–0.73	0.63–0.72
R_1^b	0.051	0.042	0.027	0.027
wR_2^c	0.105	0.097	0.063	0.066
wR_{all}	0.119	0.101	0.074	0.077
GOF	1.13	1.076	1.07	1.04
min. and max. RED (e⁻/Å³)	−0.350 and 0.458	−0.427 and 0.646	−0.51 and 0.51	−0.61 and 0.58

[a] Radiation: graphite-monochromated Mo Kα (λ = 0.71073 Å). [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.
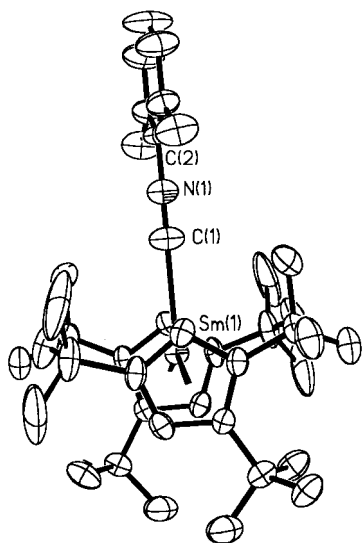

Figure 4. ORTEP diagram (50% probability ellipsoids) of Cp$^‡_2$Sm(2,6-Me₂C₆H₃NC)·toluene. The whole molecule, consisting of two asymmetric units, is shown. Hydrogen atoms and the toluene of crystallization have been omitted for clarity.

Yb binds only one isocyanide ligand even when the isocyanide ligand is present in excess. Figure 5 shows, for comparison, an ORTEP diagram of the published structure of [1,3-(Me₃C)₂C₅H₃]₂Yb(2,6-Me₂C₆H₃NC)₂, and it can be seen that the cyclopentadienide rings in that molecule are also eclipsed, but no *tert*-butyl groups are forced to lie above one another due to the lower degree of substitution. The difference in structure between these two compounds is presumably the result of steric pressure; in each case the compounds adopt the
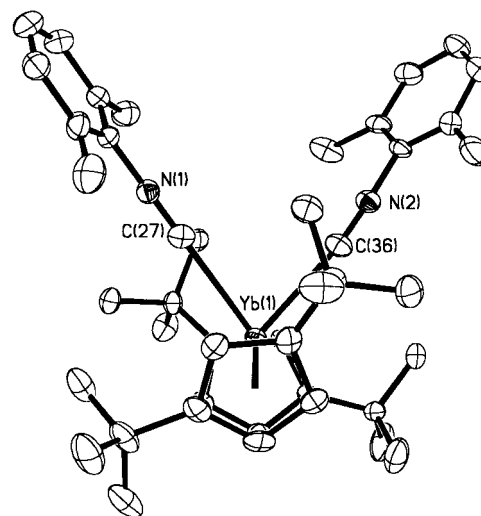

Figure 5. ORTEP diagram of the published structure of [1,3-(Me₃C)₂C₅H₃]₂Yb(2,6-Me₂C₆H₃NC)₂.[36]

lowest energy geometry consistent with their ring substitutions. The less-heavily substituted compound can bend the metallocene wedge more easily, as no *tert*-butyl groups are at the backside of the wedge. The resulting smaller centroid−metal−centroid angle (133° rather than 155°) allows the approach of two rather than only one isocyanide ligand. The controlling factor appears to be the reorganization energy on bending the metallocene sandwich. The metal−ring carbon bonds are the same length in all the ytterbocene structures; variations in structure occur to maintain these distances.[37]

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It has been reported that alkyl isocyanides are reductively cleaved by decamethylsamarocene, with cyanide-bridged trimers of Sm(III) being produced;[38] the same products were reportedly formed by reaction of the isocyanides with $(Me_5C_5)_3Sm$.[7] In both of these reports, the isocyanides were used without distillation. In our experience, the purity of the isocyanide is crucial. For example, addition of "old" ^tBuNC to decamethylytterbocene in toluene led to the formation of a cyanide-bridged dimer in which one of the Yb centers has been oxidized to Yb(III).[39] However, when freshly distilled isocyanide was used, the simple adduct $(Me_5C_5)_2Yb$-$(^tBuNC)_2$ was isolated.[36] Thus, it seems possible that impurities, not the alkyl isocyanides themselves, may be responsible for the formation of the products observed by Evans. The isocyanide used in this work, 2,6-$Me_2C_6H_3NC$, is a solid that is readiliy purified by sublimation. Using this pure isocyanide gave simple adducts without the formation of the oxidized metallocene cyanide compounds.

Conclusions

Use of the bulky cyclopentadienide $[1,2,4-(Me_3C)_2-C_5H_2]^-$ yields base-free metallocenes of s and f metals upon removal of THF solvent under reduced pressure. Base-free metallocenes bearing this ligand are crystallographically problematic, presumably because the bulky ligand leads to a molecule that is almost spherical, so the packing is not well-ordered. The only exception is the magnesocene, in which the extremely small metal leads to a tight packing arrangement of the ligands. In the solid state the base-free compounds are isostructural, with eclipsed cyclopentadienide rings in a slightly bent metallocene; two *tert*-butyl groups lie above one another at the open side of the metallocene wedge. Enough space remains in the coordination environment of Sm, Sr, Yb, and Ba to coordinate one more ligand, but this is weakly bound compared with adducts of the corresponding decamethylmetallocenes. With an additional ligand, different ring conformations are observed in the molecular structures; both staggered and eclipsed, with *two* sets of eclipsed *tert*-butyl groups, geometries have been found. The steric bulk of the $[1,2,4-(Me_3C)_2C_5H_2]^-$ ligand is starkly illustrated by the ytterbocene, which binds only a single isocyanide ligand, in contrast to less-substituted ytterbocenes, which always bind two.

Experimental Section

All reactions and product manipulations were carried out under dry nitrogen using standard Schlenk and drybox techniques. Dry, oxygen-free solvents were employed throughout. The elemental analyses and mass spectra were performed at the analytical facility at the University of Kaiserslautern. The following compounds were prepared as previously described: $NaNH_2$,[40] SmI_2,[41] YbI_2,[11] $1,2,4-Me_3C_5H_3$.[42] The alka-

line salts $Cp^‡Na$ and $Cp^‡K$ were prepared from $NaNH_2$ and KH, in THF solvent, respectively. BaI_2 was prepared in an analogous manner to YbI_2. CaI_2 and SrI_2 were purchased from Strem and used without further purification. Bu_2Mg was purchased as a heptane solution from Aldrich, and its concentration was determined by titration. All NMR spectra were recorded at ambient temperature in C_6D_6 solution.

$[1,2,4-(Me_3C)_3C_5H_2]_2Mg$. Tri-*tert*-butylcyclopentadiene $(1,2,4-(Me_3C)_3C_5H_3)$ (12.8 g, 55 mmol) was added to dibutylmagnesium (31 mL, 0.87 M in heptane, 27 mmol), and the mixture was heated to a vigorous reflux with stirring for 7 days. The solution was cooled slowly to -20 °C, and colorless crystals formed (2.0 g, 32% yield). The yield is low; additional crops of crystals cannot be obtained from the oily mother liquor. Mp: 187−189 °C. The compound sublimes at 100−120 °C and 10^{-3} Torr. Anal. Calcd for $C_{34}H_{58}Mg$: C, 83.1; H, 11.9. Found: C, 82.9; H, 12.1. ^1H NMR: δ 6.12 (4H), 1.51 (36H), 1.38 (18H).

$[1,2,4-(Me_3C)_3C_5H_2]_2Ca$. A 1.08 g (4.21 mmol) sample of $[1,2,4-(Me_3C)_3C_5H_2]Na$ and 0.59 g (2.01 mmol) of CaI_2 were stirred in 20 mL of tetrahydrofuran for 2 days. After complete evaporation of the solvent, the residue was extracted with petroleum ether (3 × 10 mL) and the combined extracts were filtered and evaporated to dryness to yield 0.99 g (1.95 mmol, 97%) of the white product. Mp: 123−125 °C. Anal. Calcd for $C_{34}H_{58}Ca$: C, 80.6; H, 11.5. Found: C, 79.3; H, 11.4. ^1H NMR: δ 6.03 (4H), 1.48 (36H), 1.41 (18H). ^{13}C NMR: δ 133.8 (m, 2C, ring $C(CMe_3)$), 131.1 (m, 4C, ring $C(CMe_3)_2$), 107.9 (dd, 4C, ring CH, $^1J_{C,H} = 158$ Hz, $^3J_{C,H} = 5$ Hz), 34.5 (q, 12C, CH_3 of $(CMe_3)_2$, $^1J_{C,H} = 125$ Hz), 33.8 (m, 4C, $(CMe_3)_2$), 33.8 (q, 6C, CH_3, $^1J_{C,H} = 125$ Hz), 32.2 (m, 2C, CMe_3). EI-MS: m/z 506 (81, M⁺), 273 (100, M⁺ − $C_5H_2(CMe_3)_3$), 234 (48, $C_5H_2(CMe_3)_3$), each with correct isotope pattern.

$[1,2,4-(Me_3C)_3C_5H_2]_2Sr$. A 1.18 g (4.33 mmol) sample of $[1,2,4-(Me_3C)_3C_5H_2]K$ was stirred with 0.70 g (2.05 mmol) of SrI_2 in THF (25 mL) overnight at room temperature. Workup similar to that for the calcium analogue led to the isolation of 0.84 g of the white product (1.52 mmol, 74%). Mp: 162 °C. Anal. Calcd for $C_{34}H_{58}Sr$: C, 73.6; H, 10.5. Found: C, 72.2; H, 10.7. ^1H NMR: δ 5.96 (4H), 1.43 (36H), 1.39 (18H). ^{13}C NMR: δ 133.0 (m, 2C, ring $C(CMe_3)$), 129.9 (m, 4C, ring $C(CMe_3)$), 107.2 (dd, 4C, ring CH, $^1J_{C,H} = 155$ Hz, $^3J_{C,H} = 7$ Hz), 34.5 (q, 12 C, CH_3 of $(CMe_3)_2$, $^1J_{C,H} = 125$ Hz), 33.6 (m, 4C, $(CMe_3)_2$), 33.2 (q, 6C, CH_3, $^1J_{C,H} = 125$ Hz), 32.1 (m, 2C, CMe_3). EI-MS: m/z 554 (17, M⁺), 321 (100, M⁺ − $C_5H_2(CMe_3)_3$), 234 (32, C_5H_2-$(CMe_3)_3$)), each with correct isotope pattern.

$[1,2,4-(Me_3C)_3C_5H_2]_2Sr(THF)$. Crystallization of $[1,2,4-(Me_3C)_3C_5H_2]_2Sr$ from a minimum volume of THF leads to isolation of the colorless mono-THF adduct. Upon heating in a melting point capillary, THF is lost and the compound melts at the same temperature as the base-free adduct (162 °C). Anal. Calcd for $C_{38}H_{64}SrO$: C, 72.8; H, 10.6. Found: C, 70.7; H, 10.7. ^1H NMR: δ 6.01 (4H), 3.59 (m, 4H, O(CH_2CH_2)₂), 1.56 (36H), 1.41 (m, 4H, O(CH₂CH_2)₂), 1.34 (18H). $^{13}C\{^1H\}$ NMR: δ 130.6 (2C, ring $C(CMe_3)$), 130.0 (4C, ring $C(CMe_3)_2$), 106.5 (4C, ring CH), 68.3 (2C, O(CH_2CH_2)₂), 35.1 (12 C, CH_3 of $(CMe_3)_2$), 33.8 (4C, $(CMe_3)_2$), 33.2 (6C, CH_3), 32.2 (2C, CMe_3), 25.6 (2C, O(CH_2CH_2)₂).

$[1,2,4-(Me_3C)_3C_5H_2]_2Ba$. In a manner similar to the synthesis of the calcium analogue, 0.52 g (2.03 mmol) of $[1,2,4-(Me_3C)_3C_5H_2]Na$ was stirred with 0.39 g (1.00 mmol) of BaI_2 in THF overnight at room temperature. An analogous workup led to 0.60 g (0.99 mmol, 99%) of the white product. Mp: 115 °C. Anal. Calcd for $C_{34}H_{58}Ba$: C, 67.6; H, 9.68. Found: C, 67.6; H, 9.63. ^1H NMR: δ 5.85 (4H), 1.42 (36H), 1.36 (18H). ^{13}C NMR: δ 132.9 (m, 2C, ring $C(CMe_3)$), 130.4 (m, 4C, ring $C(CMe_3)$), 108.5 (dd, 4C, ring CH, $^1J_{C,H} = 156$ Hz, $^3J_{C,H} = 8$ Hz), 34.5 (q, 12 C, CH_3 of $(CMe_3)_2$, $^1J_{C,H} = 124$ Hz), 33.5 (m, 4C, $(CMe_3)_2$), 33.0 (q, 6C, CH_3, $^1J_{C,H} = 124$ Hz), 32.0 (m, 2C,

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*C*Me$_3$). EI-MS: *m/z* 604 (4, M$^+$), 371 (54, M$^+$ − C$_5$H$_2$(CMe$_3$)$_3$), 234 (10, C$_5$H$_2$(CMe$_3$)$_3$), 57 (100, CMe$_3$), each with correct isotope pattern.

[1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Ba(2,6-Me$_2$C$_6$H$_3$NC). Two equivalents of 2,6-Me$_2$C$_6$H$_3$NC was stirred with the base-free compound in the minimum volume of toluene for 2 h at room temperature. Colorless crystals were collected after reducing the volume of the solution and cooling to −20 °C. Single crystals suitable for X-ray diffraction were grown from pentane at ambient temperature. ^{1}H NMR: δ 6.74 (t, 1H, *p*-C$_6$H$_3$, $^3J_{H,H}$ = 7.80 Hz), 6.57 (d, 2H, *m*-C$_6$H$_3$, $^3J_{H,H}$ = 7.56 Hz), 6.10 (s, 4H, ring *H*), 2.15 (s, 6H, (C*H*$_3$)$_2$C$_6$H$_3$NC), 1.59 (s, 36H, C*H*$_3$ of (CMe$_3$)$_2$), 1.41 (s, 18H, C*H*$_3$ of (CMe$_3$)).

[1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Sm.[6] Samarium iodide was generated in situ by stirring 0.55 g (3.66 mmol) of Sm with 0.80 g (2.84 mmol) of ICH$_2$CH$_2$I in THF for 2 days. To the green slurry was added 1.60 g (6.24 mmol) of Na(C$_5$H$_2$(CMe$_3$)$_3$), and the mixture was stirred for a further day. A workup similar to that of the calcium analogue led to the isolation of purple crystals. Yield: 1.39 g (2.25 mmol, 79%), mp 125 °C. Anal. Calcd for C$_{34}$H$_{58}$Sm: C 66.2; H 9.47. Found: C 66.2; H 9.81. ^{1}H NMR: δ 10.59 (18H, $\nu_{1/2}$ = 75 Hz), 10.15 (4H, $\nu_{1/2}$ = 45 Hz), 4.72 (36H, $\nu_{1/2}$ = 67 Hz). EI-MS: *m/z* 618 (75, M$^+$), 385 (29, M$^+$ − C$_5$H$_2$(CMe$_3$)$_3$), 234 (12, C$_5$H$_2$(CMe$_3$)$_3$), 57 (100, CMe$_3$), each with correct isotope pattern.

[1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Sm(THF). Crystallization of the base-free compound at −20 °C from a minimum of THF led to the isolation of the THF adduct. ^{1}H NMR: δ 14.16 (18H, $\nu_{1/2}$ = 29 Hz), 5.21 (36H, $\nu_{1/2}$ = 15 Hz), 2.15 (s, 4H, O(C*H*$_2$CH$_2$)$_2$, $\nu_{1/2}$ = 64 Hz), −0.79 (s, 4H, O(CH$_2$C*H*$_2$)$_2$, $\nu_{1/2}$ = 18 Hz). The cyclopentadienide ring protons were not observed.

[1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Sm(2,6-Me$_2$C$_6$H$_3$NC). A 0.40 g (0.65 mmol) sample of the base-free (C$_5$H$_2$(CMe$_3$)$_3$)$_2$Sm was stirred with 0.17 g (1.30 mmol) of 2,6-Me$_2$C$_6$H$_3$NC in toluene. Cooling to −35 °C led to the isolation of dark green-blue crystals, 0.37 g (0.44 mmol, 68%) yield. The ^{1}H NMR spectrum indicates that no toluene is present after the product was dried under vacuum, although a toluene of crystallization is observed in the crystal structure, the crystal for which was mounted without exposure to vacuum. ^{1}H NMR: δ 10.38 (18H, $\nu_{1/2}$ = 17 Hz), 7.48 (br, 2H, *m*-C$_6$H$_3$), 5.98 (br, 1H, *p*-C$_6$H$_3$), 5.80 (36H, $\nu_{1/2}$ = 19 Hz), 3.80 (s, 6H, (C*H*$_3$)$_2$C$_6$H$_3$NC, $\nu_{1/2}$ = 14 Hz). The cyclopentadienide ring protons were not observed.

[1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Yb.[6] A 0.95 g (3.71 mmol) sample of Na(C$_5$H$_2$(CMe$_3$)$_3$) was stirred with 0.78 g (1.83 mmol) of YbI$_2$

in THF. Workup analogous to the calcium analogue led to the collection of 0.89 g (1.39 mmol, 76%) of the dark green-brown product. Mp: 165 °C. Anal. Calcd for C$_{34}$H$_{58}$Yb: C, 63.8; H, 9.13. Found: C, 63.0; H, 9.14. The NMR data were in agreement with those reported previously.[6]

[1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Yb(2,6-Me$_2$C$_6$H$_3$NC). A 0.32 g (0.50 mmol) sample of the base-free [1,2,4-(Me$_3$C)$_3$C$_5$H$_2$]$_2$Yb was stirred in toluene with 0.13 g (0.99 mmol) of the isocyanide. Cooling to −35 °C led to the formation of dark blue crystals, yield 0.30 g (0.35 mmol, 70%). The compound did not melt, but a colorless liquid appeared at 65 °C (presumably free isocyanide) and the solid did not melt on further heating. The ^{1}H NMR spectrum indicates that no toluene is present after the product was dried under vacuum, although a toluene of crystallization is observed in the crystal structure, the crystal for which was mounted without exposure to vacuum. ^{1}H NMR: δ 6.77 (t, 1H, *p*-C$_6$H$_3$, $^3J_{H,H}$ = 7.42 Hz), 6.60 (d, 2H, *m*-C$_6$H$_3$, $^3J_{H,H}$ = 7.45 Hz), 6.27 (s, 4H, ring *H*), 2.20 (s, 6H, (C*H*$_3$)$_2$C$_6$H$_3$NC), 1.66 (36H), 1.41 (18H).

Crystallographic Studies. Details of the crystallographic studies are included in the Supporting Information. Selected crystal data and data collection parameters are in Tables 3 and 5, while selected bond lengths and angles are in Tables 2 and 4.

Supporting Information Available: Details of crystallographic studies, atomic positions and anisotropic thermal parameters, tables of bond lengths and angles, and an ORTEP diagram showing the atom labeling scheme for each structure are available. This material is available free of charge via the Internet at http://pubs.acs.org. Structure factor tables are available from the authors.

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