3324 *Organometallics* **1994,** *13,* 3324−3329

Synthesis and Structural Characterization of Dicyclopentadienylaluminum Alkyl and Tricyclopentadienylaluminum Compounds: Crystal Structure of a Bis(η^2-cyclopentadienyl)aluminum Alkyl Compound

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The reaction of magnesocene with an alkylaluminum dichloride compound offers a convenient route to the corresponding dicyclopentadienylaluminum alkyl species. This method was used to prepare $(C_5H_5)_2AlCH_3$ (**1**) and $(C_5H_5)_2AlCH_2CH_3$ (**2**). The X-ray crystal structure of **1** was determined. The compound crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 6.899(2)$ Å, $b = 9.152(2)$ Å, $c = 16.224(3)$ Å, $Z = 4$, $V = 1024.4(4)$ Å^3, and $d_{calc} = 1.117$ g cm^{-3}. Full-matrix least-squares refinement converged with $R = 0.0559$ for 768 reflections having $|F| > 3\sigma$. Surprisingly, **1** is monomeric in the solid state, with *both* cyclopentadienyl rings coordinated in an η^2 fashion to the aluminum. Treatment of **1** with ethyl ether affords the ethyl ether complex $Cp_2AlMe{\cdot}Et_2O$ (**3**) as a white, microcrystalline solid. The ^{1}H NMR spectrum of **3** reveals small amounts of the ligand redistribution species $CpAlMe_2$ and Cp_3Al in the sample. Minor amounts of these species are apparent whenever **1** is in the presence of a Lewis base. When **1** or **3** is combined with *tert*-butyl isocyanide in petroleum ether, the ligand redistribution product $(C_5H_5)_3Al(C{\equiv}NC(CH_3)_3)$ **4** precipitates selectively from solution. Tricyclopentadienylaluminum complexes such as **4** and the trimethylacetonitrile adduct $(C_5H_5)_3Al(N{\equiv}CC(CH_3)_3)$ (**5**) can be prepared more directly in higher yields from $AlCl_3$ and magnesocene. Single crystals of **4** were obtained from a dichloromethane solution cooled to −60 °C, and the X-ray crystal structure was determined. Complex **4** crystallizes in the rhombohedral space group $R3$ with $a = 10.162(2)$ Å, $c = 30.529(6)$ Å, $Z = 3$, $V = 2730.2(9)$ Å^3, and $d_{calc} = 1.114$ g cm^{-3}. Full-matrix least-squares refinement converged with $R = 0.0497$ for 586 reflections having $|F| > 4\sigma$. The complex is a monomer with C_3 symmetry and the cyclopentadienyl rings coordinated in an η^1 fashion to the aluminum.

Introduction

Cyclopentadienyl compounds of the main group elements are intriguing structurally due to the variety of cyclopentadienyl ring bonding modes which they display. Unlike transition metals and the f-block metals, which typically adopt an η^5-cyclopentadienyl geometry, main group metals and metalloids often display "ring-slipped" η^2 and η^3 geometries in addition to the η^1 and η^5 coordination modes.[1] Aluminum in particular appears to be quite flexible in its manner of coordinating a cyclopentadienyl ring, in that examples of cyclopentadienylaluminum compounds with η^1, η^2, η^3, and η^5 geometries have all been characterized.[2] The majority of these structural characterizations have involved monocyclopentadienylaluminum compounds. There have been surprisingly few reports of the synthesis of di-[3] and tricyclopentadienylaluminum[4] compounds and, until recently,[2h] no structurally characterized examples of these species. We report here the facile synthesis of some di- and tricyclopentadienylaluminum compounds along with the first X-ray structural characterizations of these types of compounds. The molecular structure of Cp_2AlCH_3 (**1**; Cp = C_5H_5), in addition to providing the first solid-state structural confirmation of an η^2-Cp geometry on aluminum, is remarkable for the η^2 coordination of *both* cyclopentadienyl rings by the aluminum atom.

Results and Discussion

Synthesis of Cp_2AlR Complexes. Cyclopentadienylaluminum compounds have been prepared by the

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[†] University of Idaho.

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[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1994.

(1) For reviews on main-group cyclopentadienyl compounds see: (a) Jutzi, P. *Adv. Organomet. Chem.* **1986**, *26*, 217. (b) Jutzi, P. *J. Organomet. Chem.* **1990**, *400*, 1.

(2) (a) Drew, D. A.; Haaland, A. *Acta Chem. Scand.* **1973**, *27*, 3735. (b) Teclé, B.; Corfield, P. W. R.; Oliver, J. P. *J. Am. Chem. Soc.* **1982**, *21*, 458. (c) Schonberg, P. R.; Paine, R. T.; Campana, C. F. *J. Am. Chem. Soc.* **1979**, *101*(26), 7726. (d) Schonberg, P. R.; Paine, R. T.; Campana, C. F.; Duesler, E. N. *Organometallics* **1982**, *1*, 799. Dohmeier, C.; Robl, C.; Tacke, M.; Schnöckel, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*(5), 564. (e) Koch, H. J.; Schulz, S.; Roesky, H. W.; et al. *Chem. Ber.* **1992**, *125*, 1107. (f) Jutzi, P.; Dahlhaus, J.; Bangel, M. *J. Organomet. Chem.* **1993**, *460*, C13. (g) Dohmeier, C.; Robl, C.; Tacke, M.; Schnöckel, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 564. (h) Dohmeier, C.; Schnöckel, H.; Robl, C.; Schneider, U.; Ahlrichs, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*(11), 1655.

(3) (a) Hamprecht, G.; Tittel, M.; Rother, E.; Schwarzmann, M. Belg. Patent 635,856; *Chem. Abstr.* **1965**, *62*, 1688c. (b) Stadelhofer, J.; Weidlein, J. *J. Organomet. Chem.* **1975**, *84*, C1−C4.

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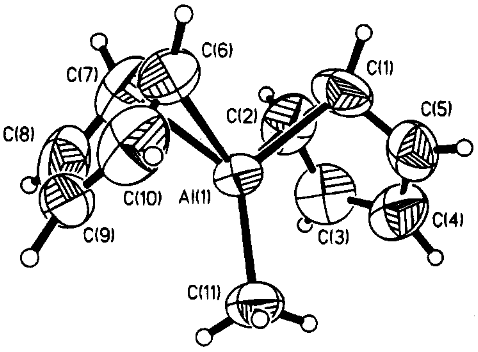

Figure 1. ORTEP drawing of the molecular structure of $(C_5H_5)_2AlCH_3$. Thermal ellipsoids are shown at the 50% probability level.

metathesis of alkylchloroaluminum compounds with alkali-metal cyclopentadienide salts[5] or a cyclopentadienyl Grignard reagent[2c,d] and by the metathesis of trichloroaluminum with trimethylsilylcyclopentadiene[2e] as well as by the direct metalation of cyclopentadiene by an aluminum alkyl.[2b,6] We found magnesocene to be a convenient, general reagent for the substitution of a cyclopentadienyl ligand for a chloride on aluminum.[7] The solubility of magnesocene in hydrocarbon solvents such as toluene and methylcyclohexane allows the reaction to be carried out at room temperature and in the absence of an etherial solvent. In this way we have prepared Cp_2AlMe and Cp_2AlEt from the corresponding alkyldichloroaluminum compounds. Both compounds are isolated as oils; however, careful recrystallization of the methyl derivative from petroleum ether does afford low-melting crystals (m.p. 34−35 °C).[8] Crystals of Cp_2AlMe also formed from the oil upon storage in the dry-box. From these a single crystal was isolated and its X-ray structure was determined.

Table 1. Crystal and Intensity Data for the X-ray Diffraction Study of $(C_5H_5)_2AlMe$ (1)

Crystal Parameters

cryst syst:	orthorhombic	$V = 1024.4(4)$ Å^3	
space group:	$P2_12_12_1$	$Z = 4$	
$a = 6.899(2)$ Å		$d_{calc} = 1.17$ mg/m^3	
$b = 9.152(2)$ Å		abs coeff:	0.142 mm^{-1}
$c = 16.224(3)$ Å			

Measurement of Intensity Data

diffractometer	Siemens R3m/V
radiation	Mo Kα ($\lambda = 0.710\,73$ Å)
temp	294 K
monochromator	highly oriented graphite crystal
2θ range	3.0−45.0°
scan type	ω
scan speed	variable; 3.00−60.0°/min in ω
scan range (ω)	1.00°
bkgd measurement	stationary cryst and stationary counter at beginning and end of scan, each for 50.0% of total scan time
std rflns	3 measd every 97 rflns
index ranges	$-1 \le h \le 6$, $-1 \le k \le 9$, $-1 \le l \le 20$
no. of rflns collected	1312
no. of indep rflns	1295
no. of obsd rflns	768 ($\|F\| > 3.0\sigma(F)$)
abs cor	none applied

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for Non-Hydrogen Atoms in $(C_5H_5)_2AlMe$ (1)

	x	*y*	*z*	*U*(eq)[a]
Al(1)	7509(3)	1053(2)	8821(1)	51(1)
C(1)	5679(9)	2793(7)	8365(4)	78(3)
C(2)	6325(11)	1937(7)	7675(4)	76(3)
C(3)	7939(11)	2616(9)	7374(3)	85(3)
C(4)	8304(10)	3830(8)	7825(4)	87(3)
C(5)	6940(9)	3954(7)	8437(4)	76(3)
C(6)	5585(10)	−35(7)	9695(5)	78(3)
C(7)	5753(12)	−820(8)	8967(4)	85(3)
C(8)	7317(15)	−1701(8)	9046(6)	116(4)
C(9)	8100(11)	−1504(9)	9811(8)	131(5)
C(10)	7011(13)	−488(9)	10197(4)	94(4)
C(11)	10241(7)	1353(6)	9059(3)	63(2)

[a] Equivalent isotropic *U*, defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Selected Bond Lengths (Å) for $(C_5H_5)_2AlMe$ (1)

Al(1)—C(1)	2.163(7)	C(3)—C(4)	1.3753(10)
Al(1)—C(2)	2.186(7)	C(4)—C(5)	1.373(10)
Al(1)—C(6)	2.182(7)	C(6)—C(7)	1.386(10)
Al(1)—C(7)	2.113(8)	C(7)—C(8)	1.353(12)
Al(1)—C(11)	1.943(5)	C(8)—C(9)	1.365(15)
C(1)—C(2)	1.437(9)	C(9)—C(10)	1.350(12)
C(1)—C(5)	1.378(9)	C(8)—C(11)	1.366(10)
C(2)—C(3)	1.366(10)		
Al(1)—C(3)	2.766(6)	Al(1)—C(4)	3.061(8)
Al(1)—C(5)	2.756(7)	Al(1)—C(8)	2.550(7)
Al(1)—C(9)	2.868(10)	Al(1)—C(10)	2.664(7)

Solid-State Structure of Cp_2AlMe (1). The ORTEP drawing of the structure is shown in Figure 1. Bond lengths and bond angles are listed in Table 3 and 4, respectively. Surprisingly, the compound is monomeric in the solid state, not dimeric as is Al_2Me_6[9] or polymeric as is $CpAlMe_2$.[2b] Rather, η^2 coordination of both cyclopentadienyl rings is sufficient to satisfy the electronic requirements of the aluminum center. As can be seen from the crystal-packing structure of 1 shown in Figure 2, there are no unusually short intermolecular interactions which might impose the η^2 geometry of both cyclopentadienyl rings. While C(1), C(2), C(6), and C(7) clearly coordinate the aluminum, these atoms are not related by symmetry; their corresponding Al—C distances range from 2.113 to 2.186 Å, considerably shorter than the distances of the remaining cyclopentadienyl carbons from aluminum, which range from 2.550 to 3.061 Å. The aluminum−methyl carbon distance of 1.943(5) Å is comparable to other terminal Al—C bond distances.[2b−d,9] The methyl substituent is slightly off-center in the molecule, with an angle of 147.3° between the Al—C(11) bond and the Al—C(1)—C(2) plane *vs* an angle of 139.5° between the Al—C(11) bond and the Al—C(6)—C(7) plane. Nevertheless, the degree of distortion is not substantial enough to suggest an agostic interaction between the methyl group and the aluminum. The coordinated C—C bonds are only slightly lengthened relative to the noncoordinated C—C bonds of the cyclopentadienyl rings. These C—C bond lengths, though they are nonuniform, are intermediate in length between single and double bonds, indicating considerable π-electron delocalization in the rings. In contrast, in the molecular structure of $Cp_3Al(C{\equiv}NtBu)$ (*vide*

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[5] (a) Giannini, N.; Cesca, S. *Gazz. Chim. Ital.* **1961**, *91*, 597. (b) Reference 3b. (c) Kroll, W. R.; McDivitt, J. R.; Naegele, W. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 973. (d) Kroll, W. R.; Naegele, W. *J. Chem. Soc. D* **1969**, 246.

[6] Kroll, W. R.; Hudson, B. E., Jr. *J. Organomet. Chem.* **1971**, *28*, 205.

[7] $Mg(C_5Me_5)_2$ has been used to prepare $\{Al(C_5Me_5)\}_4$ from AlCl.[2g]

[8] In ref 3b analytical data for Cp_2AlMe are reported, although the synthesis of this compound is not described. The authors report a melting point of 80−85 °C and a sublimation temperature of 65 °C. The material we isolate exhibits much lower sublimation and melting temperatures (see Experimental Section).

[9] Coates, G. E.; Green, M. L. H.; Wade, K. *Organometallic Compounds*; Methuen: London, 1967; Vol. 1, Chapter 3, p 301.

Table 4. Selected Bond Angles (deg) for $(C_5H_5)_2AlMe$ (1)

C(1)—Al(1)—C(3)	107.5(3)	Al(1)—C(3)—C(5)	73.9(4)
C(1)—Al(1)—C(5)	101.7(3)	Al(1)—C(3)—C(12)	92.1(5)
C(1)—Al(1)—C(7)	122.0(2)	C(5)—C(3)—C(12)	107.2(7)
C(1)—Al(1)—C(11)	38.6(2)	C(2)—C(4)—C(8)	109.3(6)
C(3)—Al(1)—C(5)	37.6(3)	Al(1)—C(5)—C(3)	68.5(4)
C(3)—Al(1)—C(7)	130.4(3)	Al(1)—C(5)—C(10)	95.1(5)
C(3)—Al(1)—C(11)	100.4(3)	C(3)—C(5)—C(10)	107.2(6)
C(5)—Al(1)—C(7)	121.7(2)	C(4)—C(8)—C(11)	109.4(6)
C(5)—Al(1)—C(11)	119.6(3)	C(10)—C(9)—C(12)	107.1(8)
C(7)—Al(1)—C(11)	118.7(3)	C(5)—C(10)—C(9)	109.8(7)
Al(1)—C(1)—C(2)	99.8(4)	Al(1)—C(11)—C(1)	69.8(4)
Al(1)—C(1)—C(11)	71.6(4)	Al(1)—C(11)—C(8)	99.7(5)
C(2)—C(1)—C(11)	106.9(6)	C(1)—C(11)—C(8)	106.4(6)
C(1)—C(2)—C(4)	107.9(6)	C(3)—C(12)—C(9)	108.8(7)

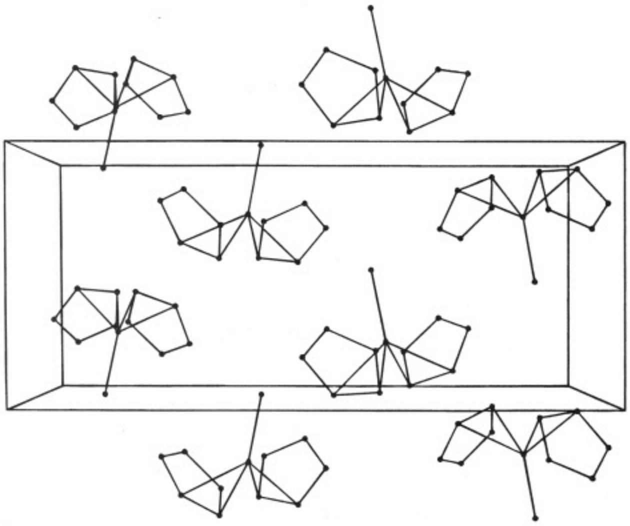

Figure 2. Drawing of the unit cell of Cp_2AlMe crystal, illustrating the molecular packing.

infra) the π-bonds of the η^1-cyclopentadienyl rings appear to be fairly localized.

Haaland and co-workers have invoked η^2-Cp coordination as the structure most consistent with the gas-phase electron diffraction pattern for $CpAlMe_2$.[2a,10] In the solid state, however, the compound forms an infinite polymeric chain in which the Cp—Al—Cp—Al backbone displays η^1 coordination by the aluminums at 1,3-positions on opposite sides of each ring.[2b] The structure of Cp_2AlMe reported here represents, to our knowledge, the first X-ray structural characterization of a Cp_2AlX complex and the first solid-state structural confirmation of a η^2 mode of Cp coordination by aluminum. While η^2-Cp coordination to As,[11] Sn,[12,13] Ge,[13,14] and, notably, Ti[15] has been characterized, the η^2 coordination of *both* cyclopentadienyl rings by the aluminum in **1** is unique.

Preliminary INDO calculations on Cp_2AlMe based on the crystal structure coordinates support the η^2 nature of the bonding between the cyclopentadienyl rings and the aluminum. The Mulliken bond order between Al and the methyl carbon is 1, as expected. By comparison, the Mulliken bond orders between Al and C(2), C(1), C(6), and C(7) are all approximately 0.4. The next closest contact is between Al and C(8) with a bond order of 0.18, followed by C(3), C(5), C(8), and C(10) with bond orders of approximately 0.1. Bonding between Al and C(4) and C(9) is minimal with Mulliken bond orders of 0.05. These calculations also reveal that the the lowest unoccupied molecular orbital of the molecule is primarily Al 3s (*ca.* 50%) in character and that the formal charge on aluminum is +0.6. This is consistent with chemical intuition concerning the electrophilicity of the aluminum center in the molecule.

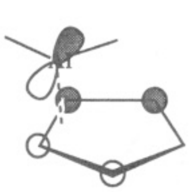

Figure 3. Stabilizing interaction between the 3p orbital on aluminum and one of the e_1 π orbitals on the cyclopentadienyl ring in an η^2 geometry.

In their intrepretation of CNDO/2 calculations performed on η^2-$CpAlMe_2$,[10] Gropen and Haaland attribute the preference for η^2-Cp coordination by the aluminum to a weak interaction between the formally vacant Al 3p orbital with the e_1 π orbital of the Cp ring (Figure 3). Extended Hückel calculations performed by Hoffman and co-workers on isoelectronic $CpCH_2^+$ [16] corroborate this interpretation. The orbital interactions responsible for stabilizing the η^2 coordination geometries of both cyclopentadienyl rings in Cp_2AlMe is less obvious, however, since our INDO calculations reveal that the overlap of the corresponding, formally vacant p orbital with C(1), C(2), C(6), and C(7) is comparable to its overlap with C(3), C(5), C(8), and C(10). Significantly, there is negligible interaction between this same p orbital and C(4) and C(9).

Solution Properties and Ligand Redistribution Chemistry of 1. Rapid migration of the aluminum about the cyclopentadienyl rings produces a single resonance for the cyclopentadienyl carbons and hydrogens in the solution ^{13}C and ^1H NMR spectra. This fluxionality was not frozen out in the ^1H spectrum of a toluene-d_8 solution of the sample on cooling down to −90 °C. This behavior is consistent with the calculated barrier of less than 3 kcal/mol for the 1,2-migration of the aluminum about a cyclopentadienyl ring.[10]

When **1** is treated with ethyl ether, $Cp_2AlMe{\cdot}Et_2O$ (**3**) precipitates as a white, microcrystalline solid. The ^1H NMR spectrum of the material reveals the presence of small amounts (*ca.* 10%) of Cp_3Al and $CpAlMe_2$ redistribution products. Similar amounts of these ligand redistribution products were apparent int the C_6D_6 and toluene-d_8 solution ^1H NMR spectra of **1** treated with other Lewis bases such as *tert*-butyl isocyanide, trimethylacetonitrile, and tetrahydrofuran. Ligand redistribution species were also observed in the ^1H NMR spectrum of a sample of Cp_2AlEt (**2**) treated with 1 equiv of *tert*-butyl isocyanide.

When either **1** or **3** is combined with an equivalent amount of *tert*-butyl isocyanide in petroleum ether, $[(C_5H_5)_3Al(C{\equiv}NtBu)]$ (**4**) precipitates selectively from

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[10] Gropen, T.; Haaland, A. *J. Organomet. Chem.* **1975**, *92*, 157.

[11] Jutzi, P.; Wippermann, T.; Kruger, C.; Kraus, H. J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 250.

[12] Bos, K. D.; Bulten, E. J.; Noltes, J. G. *J. Organomet. Chem.* **1975**, *99*, 71.

[13] (a) Jutzi, P.; Hampel, B.; Stroppel, K.; Kruger, C.; Angermund, K. Hofmann, P. *Chem. Ber.* **1985**, *118*, 2789. (b) Kohl, F. X.; Dickbreder, R.; Jutzi, P. Muller, G.; Huber, B. *Chem. Ber.* **1989**, *122*, 871.

[14] (a) Jutzi, P.; Hampel, B.; Hursthouse, M. B.; Howes, A. J. *J. Organomet. Chem.* **1986**, *299*, 19. (b) Jutzi, P.; Hampel, B. *Organometallics* **1986**, *5*, 1944.

[15] Lucas, C. R.; Green, M.; Forder, R. A.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1973**, 97.

[16] Anh, N. T.; Elian, M.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*(1), 110.

the reaction mixture (occasionally contaminated with *ca.* 10% $Cp_2AlMe(C{\equiv}NtBu)$). The oily residue left behind upon stripping away the petroleum ether from the filtrate was found by ^1H NMR to contain Cp_2AlMe and $CpAlMe_2$ along with some Cp_3Al. The precipitation of **4** from the petroleum ether appears to be a thermodynamic driving force for its formation, since **4** can generally be isolated in this manner in 30–40% yields based on total aluminum while, as mentioned above, only *ca.* 10% redistribution to Cp_3Al and $CpAlMe_2$ is apparent in the ^1H NMR spectra of benzene and toluene solutions of Cp_2AlMe treated with a Lewis base.

Analogous ligand redistribution chemistry has been reported for $CpAlMe_2$, which was found to decompose to Cp_2AlMe and $AlMe_3$ in the presence of tetrahydrofuran.[17] Ligand redistribution has also been observed among the heavier group 13 analogs $CpGaMe_2$ and Cp_2GaMe.[18] We were puzzled by the fact that small amounts of the ligand redistribution species Cp_3Al and $CpAlMe_2$ appear upon treating Cp_2AlMe with a Lewis base but were not apparent in a toluene-d_8 solution ^1H spectrum of Cp_2AlMe in the absence of a Lewis base, even when the sample was cooled to −90 °C. A 1:1 mixture of Cp_3Al and $CpAlMe_2$ in toluene-d_8 produced an ^1H NMR spectrum corresponding exactly to Cp_2AlMe, indicating that both Me and Cp ligand exchange occur readily in the absence of a Lewis base. To determine if we could detect the presence of $CpAlMe_2$ in a sample of Lewis-base-free Cp_2AlMe by ^1H NMR, we examined a mixture of the two species in toluene-d_8 solution. The Cp proton chemical shifts of the two Lewis-base-free species were indistinguishable by ^1H NMR. At room temperature the methyl peaks were broad and overlapping due to methyl group exchange between the aluminums near the slow exchange limit. Cooling the sample resulted in further decoalescence of the methyl peaks. Nevertheless, when we monitored the ^1H NMR spectra of a toluene-d_8 sample of Cp_2AlMe in 5 °C increments down to −90 °C, while broadening of the methyl resonance was observed, a methyl peak assignable to $CpAlMe_2$ was not detected.

Upon addition of Et_2O to a solution of Cp_2AlMe in C_6D_6 toluene-d_8, minor amounts (~10%) of Cp_3Al and $CpAlMe_2$ appeared in the ^1H NMR spectrum of the sample. The dynamic nature of the ligand exchange was apparent from the coalescence behavior of the Cp resonances and the methyl resonances by ^1H NMR as the sample was heated. Increasing the amount of Et_2O in the sample from 1/2 to 1 to 2 equiv relative to Cp_2AlMe did not alter perceptibly the amount of the minor species present but did increase the temperatures at which the methyl peaks as well as the Cp peaks coalesced. Slowing of the ligand exchange rate by a Lewis base is common in organoaluminum chemistry and may be attributed to the effect of coordinated Lewis base in reducing the Lewis acidity of the aluminum and in blocking coordination sites on the aluminum necessary for ligand exchange.[19]

Synthesis and Structural Characterization of $Cp_3Al(L)$ (L = :C≡NtBu, :N≡CtBu). The tricyclopentadienylaluminum complexes $Cp_3Al(C{\equiv}NtBu)$ (**4**) and $Cp_3Al(N{\equiv}CtBu)$ (**5**) can be prepared more directly in higher yield based on aluminum by reacting Cp_2Mg with $AlCl_3$ in a 1.5:1 ratio in toluene and treating the resulting yellow oil with *tert*-butyl isocyanide and trimethylacetonitrile, respectively, to afford the corresponding Lewis-base-coordinated tricyclopentadienylaluminum complexes as tan solids. The reaction of bis(cyclopentadienyl)mercury with elemental aluminum to afford Cp_3Al as a solid (mp 55–60 °C) has been reported previously in the patent literature.[4] We consistently isolate this material as an oil.

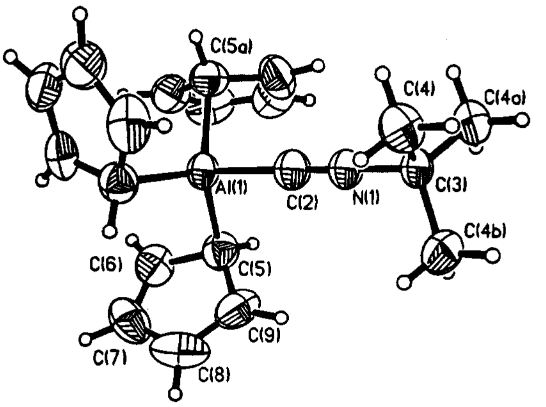

Figure 4. ORTEP drawing of the molecular structure of $(C_5H_5)_3Al(C{\equiv}NCMe_3)$. Thermal ellipsoids are shown at the 50% probability level.

Table 5. Crystal and Intensity Data for the X-ray Diffraction Study of $(C_5H_5)_3Al(C{\equiv}NtBu)$ (4)

Crystal Parameters	
cryst syst: rhombohedral (hexagonal setting)	$V = 2730.2(9)$ Å^3
space group: $R3$	$Z = 3$
$a = 10.162(2)$ Å	$d_{calc} = 1.103$ Mg/m^3
$c = 30.529(6)$ Å	abs coeff: 0.924 mm^{-1}

Measurement of Intensity Data	
diffractomer	Siemens R3m/V
radiation	Cu Kα ($\lambda = 1.541$ 84 Å)
temp	294 K
monochromator	highly oriented graphite cryst
2θ range	3.0–110.0°
scan type	ω
scan speed	variable; 3.00–60.0°/min in ω
scan range (ω)	1.20°
bkgd measurement	stationary cryst and stationary counter at beginning and end of scan, each for 50.0% of total scan time
std rflns	3 measd every 97 rflns
index ranges	$-1 \le h \le 10, -10 \le k \le 1, -1 \le l \le 32$
no. of rflns collected	1087
no. of indep rflns	776 ($R_{int} = 2.37\%$)
no. of obsd rflns	586 ($\lvert F\rvert > 4.0\sigma(F)$)
abs cor	empirical

The molecular structure of **4**, shown in Figure 4, represents the first crystal structure determination of a tricyclopentadienylaluminum species. In the solid state, the cyclopentadienyl rings of **4** are symmetry related by a 3-fold rotational axis with each ring η^1 to the aluminum. As can be seen from Table 7, the cyclopentadienyl rings in **4** contain localized carbon–carbon double and single bonds with the aluminum occupying the allylic position of each cyclopentadienyl ring. The sp^3 hybridization of the allylic carbon is revealed by the 106.3° angle between the Cp plane and the Al–C(5) vector.

As in the mono- and dicyclopentadienylaluminum compounds, the ^1H and ^{13}C NMR spectra of **4** and **5** display equivalent cyclopentadienyl carbons and hydro-

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Table 6. Atomic Coordinates ($\times 10^4$) and Isotropic Displacement Coefficients (Å$^2 \times 10^3$) for $(C_5H_5)_3Al(C{\equiv}NtBu)$ (4)

	x	*y*	*z*	*U*(eq)[a]
Al(1)	3333	6667	476(1)	45(1)
N(1)	3333	6667	−579(1)	47(2)
C(2)	3333	6667	−201(2)	52(2)
C(3)	3333	6667	−1058(2)	42(2)
C(4)	2715(4)	7688(4)	−1204(1)	59(2)
C(5)	1235(4)	4971(4)	621(1)	56(2)
C(6)	1438(4)	4594(5)	1060(1)	62(2)
C(7)	1533(5)	3338(5)	1054(1)	75(2)
C(8)	1299(6)	2776(5)	623(2)	84(2)
C(9)	1062(4)	3704(5)	358(1)	72(2)

[a] Equivalent isotropic *U*, defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 7. Selected Bond Lengths (Å) for $(C_5H_5)_3Al(C{\equiv}NtBu)$ (4)

Al(1)—C(2)	2.067(6)	C(5)—C(6)	1.437(5)
Al(1)—C(5)	2.010(3)	C(5)—C(9)	1.452(6)
N(1)—C(2)	1.152(7)	C(6)—C(7)	1.327(8)
N(1)—C(3)	1.463(6)	C(7)—C(8)	1.407(6)
C(3)—C(4)	1.524(5)	C(8)—C(9)	1.351(7)

Table 8. Selected Bond Angles (deg) for $(C_5H_5)_3Al(C{\equiv}NtBu)$ (4)

C(2)—Al(1)—C(5)	102.8(1)	C(4)—C(3)—C(4a)	111.8(2)
C(5)—Al(1)—C(5a)	115.2(1)	C(5)—C(9)—C(8)	107.7(4)
Al(1)—C(5a)—C(6)	101.7(2)	C(5)—C(6)—C(7)	109.4(4)
Al(1)—C(5)—C(9)	104.1(3)	C(7)—C(8)—C(9)	109.2(5)
N(1)—C(3)—C(4)	107.0(2)	C(6)—C(5)—C(9)	104.4(4)
		C(6)—C(7)—C(8)	109.0(4)

gens due to the rapid migration of the aluminum about the cyclopentadienyl rings. Predictably, the C≡N stretching frequencies of the nitrile and isonitrile ligands increase upon coordination to aluminum. The C≡N stretching frequency of *tert*-butyl isocyanide increases from 2140 to 2218 cm^{-1} upon coordination to aluminum in **4**, while in **5** $\nu_{C\equiv N}$ increases only slightly from 2230 cm^{-1} in the free nitrile to 2240 cm^{-1} in the complexed molecule. This shifting of $\nu_{C\equiv N}$ to higher frequency is common for nitriles and isonitriles bound to metals offering little or no back-donation of π electrons.[20]

In conclusion, we have found magnesocene to be a particularly convenient reagent for transferring cyclopentadienyl rings to aluminum. We are presently using this method to prepare other di- and tricyclopentadienylaluminum compounds in order to explore the effects of varying ligands on the aluminum as well as substituents on the cyclopentadienyl rings on the chemistry and structural properties of these compounds.

Experimental Section

General Considerations. All manipulations were performed using a combination of glovebox, high-vacuum, and Schlenk techniques. All solvents were distilled under nitrogen over sodium benzophenone ketyl (toluene, ethyl ether, THF) or CaH_2 (petroleum ether, methylene chloride). The solvents were then stored in line-pots, from which they were either vacuum-transferred from sodium benzophenone ketyl or cannulated directly. The NMR solvents benzene-d_6 and chloroform-d_3 were dried over activated 4-Å molecular sieves. Argon was purified by passage over oxy tower BASF catalyst (Aldrich) and 4-Å molecular sieves. Aluminum trichloride (Aldrich) was sublimed prior to use. Methylaluminum dichloride, purchased as a 1.0 M solution in hexanes from Aldrich, was dried to a solid and stored in the glovebox prior to use. Ethylaluminum dichloride, trimethylacetonitrile, and *tert*-butyl isocyanide were all used as received from Aldrich. Magnesocene was prepared as described in the literature.[21]

NMR spectra were recorded on an IBM NR-300 (300.13 MHz, ^{1}H; 74.43 MHz, ^{13}C; 78.206 MHz, ^{27}Al) and an IBM NR-200 (200.13 MHz, ^{1}H; 50.327 MHz, ^{13}C; 52.148 MHz, ^{27}Al). All chemical shifts are reported in ppm and referenced to solvent (^{13}C, ^{1}H) or $Al(OH)_3$ (^{27}Al, external reference, δ 0 ppm). Elemental analyses were determined by Desert Analytics and the University of Idaho analytical facilities.

Procedures. Cp_2AlMe (1). Solid methylaluminum dichloride (3.0 g, 27 mmol) was added to a solution of magnesocene (4.1 g, 27 mmol) in 70 mL of methylcyclohexane cooled to −78°C. The reaction mixture was warmed to room temperature and stirred overnight. The reaction mixture was filtered to remove the $MgCl_2$, and methylcyclohexane was removed under reduced pressure. $MgCl_2$ was washed repeatedly with petroleum ether, and the combined filtrates were dried *in vacuo* to afford **1** as a yellow oil. Yield: 2.40 g, 52%. Recrystallization of **1** from petroleum ether or sublimation at 65 °C (*ca.* 10^{-2} Torr) affords low-melting crystals (mp 34−35 °C). ^{1}H NMR (C_6D_6): δ 6.09 (s, 10, C_5H_5), −1.47 (s, 3, CH_3). ^{13}C NMR (C_6D_6): δ 111.95 (C_5H_5), 14.05 (CH_3). ^{27}Al NMR (C_6D_6): δ 72.7. Anal. Calcd for $C_{11}H_{13}Al$: C, 76.7; H, 7.6. Found: C, 76.7; H, 7.1.

Cp_2AlEt (2). A 4.3-mL portion (41 mmol) of ethylaluminum dichloride was added by syringe to a solution of 6.34 g (41.1 mmol) of magnesocene in 150 mL of toluene at −78 °C. The reaction mixture was then stirred for 1 $^1/_2$ h at room temperature. A reaction workup similar to the one described above for **1** afforded 5.74 g (77.2%) of **2** as a clear, yellow oil. ^{1}H NMR (C_6D_6): δ 6.09 (s, 10, C_5H_5), 0.82 (br, 2, CH_2), −0.60 (br, 3, CH_3). ^{13}C NMR (C_6D_6): δ 111.8 (C_5H_5), 12.2 (CH_3). ^{27}Al NMR (C_6D_6): δ 67.2. Anal. Calcd for $C_{12}H_{15}Al$: C, 77.4; H, 8.1. Found: C, 77.0; H, 8.0.

$Cp_2AlMe{\cdot}Et_2O$ (3). Solid methylaluminum dichloride (3.6 g, 32 mmol) was added to a solution of magnesocene (5.0 g, 32 mmol) in 100 mL of toluene cooled to −78 °C. The reaction mixture was warmed to 25 °C and was stirred overnight. A reaction workup similar to the one described above afforded **1** as a clear, yellow oil. Upon addition of 50 mL of Et_2O to the oil, **3** precipitated as a white, microcrystalline solid which was isolated by filtration and dried. Yield: 3.8 g, 63%. ^{1}H NMR (toluene-d_8): δ 6.39 (s, 10, C_5H_5), 3.45 (q, 5.2, $(CH_3CH_2)_2O$), 1.23 (t, 7.8, $(CH_3CH_2)_2O$), −1.07 (s, 3, CH_3). The sample reveals peaks due to contamination by *ca.* 10% $CpAlMe_2$ (δ 6.50 (s, C_5H_5), −0.62, (s, CH_3)) and *ca.* 10% Cp_3Al (δ 6.27 (s, C_5H_5)). Anal. Calcd for $C_{16.2}H_{26}O_{1.3}Al$: C, 72.4; H, 9.8. Calcd for $C_{15}H_{23}OAl$: C, 73.1; H, 9.4. Found: C, 73.3; H, 9.1.

$Cp_3Al(C{\equiv}NCMe_3)$ (4). (a) By Ligand Redistribution. *tert*-Butyl isocyanide (1.45 mL, 12.8 mmol) was distilled into a flask containing **3** (5.00 g, 12.7 mmol) in 70 mL of petroleum ether cooled to −78 °C. When the reaction mixture was warmed to room temperature, an insoluble, gummy, white material formed. Upon further stirring of the reaction mixture overnight, an off-white precipitate formed, which was collected by filtration. Recrystallization of the powder in methylene chloride at −60 °C afforded **4** as clear, colorless crystals. Yield: 1.32 g, 34% based on total aluminum.

(b) By Direct Synthesis from $AlCl_3$. Toluene (50 mL) was added to a mixture of magnesocene (1.7 g, 17 mmol) and $AlCl_3$ (1.5 g, 11 mmol), and the reaction mixture was heated to 60 °C overnight. The reaction mixture was then filtered to remove the $MgCl_2$ byproduct, which was washed repeatedly with toluene. The combined toluene filtrates were dried under reduced pressure to leave a yellow oil, which was redissolved

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in 30 mL of petroleum ether. Upon addition of 1.3 mL (11 mmol) of *tert*-butyl isocyanide to the petroleum ether solution, **4** precipitated from solution and was isolated by filtration as a tan solid (mp 103 °C). Yield: 2.5 g, 74%. ^{1}H NMR (C_6D_6): δ 6.23 (s, 10, C_5H_5), 0.64 (s, 9, $(CH_3)_3CN{\equiv}C$). ^{13}C NMR (C_6D_6): δ 113.6 (C_5H_5), 28.7 ($(CH_3)_3CN{\equiv}C$). ^{27}Al NMR (C_6D_6): δ 59. Anal. Calcd for $C_{20}H_{24}AlN$: C, 78.6; H, 7.9; N, 4.6. Found: C, 77.5; H, 7.9; N, 4.31. Elemental analyses of this compound were consistently low in carbon, although the hydrogen analysis was consistently close to the theoretical value. The error of 1.1% in the carbon analysis involves a deviation of less than one carbon atom in the molecular formula. We suspect incomplete combustion of the isonitrile carbon to be the culprit, perhaps due to the formation of aluminum carbide. The addition of tungsten oxide to the analysis sample to aid in burning did not improve our results.

$Cp_3Al(N{\equiv}CCMe_3)$ (5). The reaction is carried out in a manner similar to preparation b of compound **4**. Magnesocene (10.4 g, 67.3 mmol) and $AlCl_3$ (6.0 g, 45 mmol) were combined in 300 mL of toluene. The reaction mixture was heated to 60 °C with stirring overnight. A workup similar to that for **4** afforded a yellow oil, which was redissolved in *ca.* 100 mL of petroleum ether. Upon addition of 5.0 mL (45 mmol) of trimethylacetonitrile to the petroleum ether solution, **5** precipitated from solution and was isolated by filtration as an off-white powder. Yield: 9.3 g, 67%. The compound decomposes with melting between 154 and 163 °C. ^{1}H NMR (C_6D_6): δ 6.21 (s, 10, C_5H_5), 0.44 (s, 9, $(CH_3)_3CC{\equiv}N$). ^{13}C NMR (C_6D_6): δ 113.2 (C_5H_5), 26.2 ($(CH_3)_3CC{\equiv}N$). ^{27}Al NMR (C_6D_6): δ 64. Anal. Calcd for $C_{20}H_{24}AlN$: C, 78.6; H, 7.9; N, 4.6. Found: C, 78.1; H, 8.1; N, 4.4.

Crystal Structure Determination of Cp_2AlMe (1). Low-melting crystals of **1** formed from the oil while it was stored in the drybox. A single, pale yellow crystal with dimensions 0.12 × 0.34 × 0.2 mm was mounted in a glass capillary. The X-ray diffraction data were collected on a Syntex $P2_1$ diffractometer upgraded to Siemens P4 specifications. Graphite-monochromatized Mo Kα (λ = 0.710 69 Å) radiation was used. The orientation matrix and lattice parameters were optimized from a least-squares calculation on 25 carefully centered reflections. Data were collected in the ω scan mode. The intensities of 3 standard reflections measured every 97 scans revealed no significant changes during the data collection.

All calculations were performed using the SHELXTL PLUS program packages.[22] Data reductions were done by applying Lorentz and polarization corrections. No absorption correction was applied.

All non-H atoms were refined with isotropic thermal parameters. Hydrogen atoms were added at calculated positions, assuming sp^2 hybridization for all C atoms in the cyclopentadienyl rings. The refinement converged to R = 0.0599 and R_w = 0.0577 for $|F| \geq 3\sigma$. A goodness of fit of 1.26 was obtained with a maximum residual of 0.22 e Å^{-3} in the final difference map.

Refinement was also attempted using sp^3 hybridization for the cyclopentadienyl carbon atoms bonded to the aluminum. However, this led to a substantial increase in the R values (R = 0.0630 and R_w = 0.0708) and residual electron density remained at the sp^2 type sites. Hence, the diffraction data are consistent with the retention of conjugation for the full cyclopentadienyl rings.

The absolute configuration of the molecules in the crystal could not be determined because the esd for the η value calculated was too high, −1.72(1.39).

Crystal Structure Determination of $Cp_3Al(C{\equiv}NCMe_3)$ (4). Crystals of **4** were grown from a methylene chloride solution at −60 °C. A single, colorless crystal with dimensions 0.2 × 0.35 × 0.55 mm was mounted in a glass capillary. The X-ray diffraction data were collected on a Nicolet P3 diffractometer upgraded to Siemens P4 specifications. Graphite-monochromatized Cu Kα (λ = 1.541 84 Å) radiation was used. The orientation matrix and lattice parameters were optimized from a least-squares calculation on 25 carefully centered reflections. Data were collected in the ω-scan mode. The intensities of 3 standard reflections measured every 97 scans revealed no significant changes during the data collection.

All calculations were performed using the SHELXTL PLUS program packages. Data reductions were done by applying Lorentz and polarization corrections. Empirical absorption corrections were applied.

All non-H atoms were refined with isotropic thermal parameters. Hydrogen atoms were added at calculated positions, assuming sp^3 hybridization at the cyclopentadienyl carbons bonded to aluminum and sp^2 hybridization for the remaining Cp carbons. The refinement converged to R = 0.0497 and R_w = 0.0574 for $|F| > 4\sigma$. A goodness of fit of 1.48 was obtained with a maximum residual of 0.26 e Å^{-3} in the final difference map.

Theoretical Calculations for Cp_2AlMe (1). Electronic structure calculations on **1** were of the INDO type, based on the methods of Zerner et al.[23] using the original Pople, Santry, and Segal parametrization (geometry parameters).[24] The starting geometries were derived from the X-ray crystal structure.

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Supplementary Material Available: Tables of crystallographic data collection, solution, and refinement details, anisotropic displacement coefficients, and calculated hydrogen atom coordinates for **1** and **4** (10 pages). Ordering information is given on any current masthead page.

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