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Synthesis and Structure of the Sterically Crowded Trimesitylaluminum–Tetrahydrofuran Adduct

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The trimesitylaluminum–tetrahydrofuran adduct, $Mes_3Al{\cdot}THF$, was prepared by the reaction of mesitylmagnesium bromide with a $AlCl_3$/THF solution. The structure of the $Mes_3Al{\cdot}THF$ has been determined by single-crystal X-ray diffraction techniques. It crystallizes in the monoclinic lattice system, space group $P2_1/c$, with unit cell dimensions of a = 8.457 (1) Å, b = 14.318 (2) Å, c = 22.234 (3) Å, β = 98.271 (9)°, V = 2264.5 (5) Å^3, and Z = 4. The final full-matrix least-squares refinement on 2062 data gave R = 7.5% and R_w = 4.5%. The compound is similar to other organoaluminum adducts yielding a four-coordinate aluminum atom with relatively long Al–C distances of 2.011 (7), 2.021 (6), and 2.020 (6) Å and an Al–O distance of 1.969 (5) Å which is slightly longer than the Al–O distance observed in the known THF adducts but lies in the range observed for other ether complexes.

Introduction

The only reported solid-state structure for a simple tricoordinate organoaluminum compound is that of trimesitylaluminum, 1 (Mes = mesityl = 2,4,6-trimethylphenyl).[1] Other monomeric aluminum derivatives have been reported in solution such as trineopentylaluminum,[2] and many other compounds are known to exist with an equilibrium between monomer and dimer in solution[3,4] and in the gas phase.[5] Other monomeric aluminum compounds for which structures have been determined in the solid state are $Al[N(SiMe_3)_2]_3$[6] and bis(2,6-di-*tert*-butylphenoxy)methylaluminum.[7] In each of these cases, it was concluded that the electronic stabilization that would be gained by dimerization, observed for other triorganoaluminum compounds,[8] was not sufficient to overcome the steric requirements the mesityl group placed on such a geometry. The ability of these monomeric derivatives to form addition compounds has not been explored extensively. Beachley et al.[9] have reported that $Al(CH_2SiMe_3)_3$ forms adducts but that $Al(CH_2CMe_3)_3$ does not coordinate strongly with ethers. In fact these workers have suggested that the neopentyl group is among the most bulky groups and interferes with the bridge formation due to the steric hindrance at the bridging site.[2,9] The mesityl group also affords a very bulky unit with the ortho methyl groups providing significant steric hindrance/protection of the metal center.

In one of the initial reports of the synthesis of 1,[10] the author described the ability of this compound to reversibly coordinate a molecule of THF according to eq 1. These

$$\underset{\mathbf{1}}{Mes_3Al} \xrightleftharpoons[\text{vacuum, -THF}]{\text{+THF}} \underset{\mathbf{2}}{Mes_3Al{\cdot}THF} \qquad (1)$$

results and our determination of the structure of 1, which shows that there is hindered access to the metal center, led us to think that this system would provide an excellent model for the exploration of the interaction between hindered organometallic compounds and Lewis bases. In our first step to explore this, we have examined the structure of the $Mes_3Al{\cdot}THF$ by single-crystal X-ray diffraction techniques to determine how the trimesitylaluminum monomer had to be distorted in order to accept the donor THF molecule.

Experimental Section

Preparation of Trimesitylaluminum–Tetrahydrofuran. The trimesitylaluminum–tetrahyrofuran adduct was prepared by the reaction of mesitylmagnesium bromide with a $AlCl_3$/THF solution. The compound is both air- and water-sensitive so standard drybox and Schlenk line techniques were employed. Mesityl Grignard reagent was prepared from mesityl bromide (32 mL, 206 mmol) and magnesium metal (5 g, 206 mmol) in THF. Then a solution of 7.3 g of $AlCl_3$ dissolved in THF at –78 °C was added to the Grignard at 0 °C. The reaction mixture was stirred overnight at room temperature and filtered and the THF removed under vacuum. The resulting product was recrystallized several times from toluene. Physical and chemical properties were compared with the known compound. NMR (C_6D_6): ^1H $\delta_{p\text{-Me}}$ = 2.24, s, 9; $\delta_{o\text{-Me}}$ = 2.45, s, 18; δ_{THF} = 3.58, broad line, 4; δ_{THF} = 1.06, broad line, 4; $\delta_{aromatic}$ = 6.85, m, 6; $^{13}C\{^1H\}$ $\delta_{p\text{-Me}}$ = 21.18, $^1J_{C-H}$ = 125 Hz; δ_{C2-THF} = 24.91, $^1J_{C-H}$ = 148 Hz; $\delta_{m\text{-Me}}$ = 25.41, $^1J_{C-H}$ = 124 Hz; δ_{C1-THF} = 70.61, $^1J_{C-H}$ = 148 Hz; $\delta_{m\text{-C}}$ = 128.06, $^1J_{C-H}$ = 155 Hz; $\delta_{p\text{-C}}$ = 136.51; $\delta_{o\text{-C}}$ = 145.80; $\delta_{ipso\text{-C}}$ = 147.86 ppm.

Structure Determination and Refinement of $Mes_3Al{\cdot}THF$. Crystals of trimesitylaluminum–tetrahydrofuran were grown from a toluene solution by slow evaporation on the vacuum system. A crystal suitable for X-ray diffraction was mounted in a thin-walled capillary tube in the drybox, plugged with grease, removed from the drybox, flame sealed, mounted on a goniometer head, and placed on a Syntex $P2_1$ diffractometer for data collection. Crystal and X-ray data collection parameters are listed in Table I.

The trimesitylaluminum–tetrahydrofuran adduct was found to be monoclinic and was assigned to the space group $P2_1/c$ on the basis of systematic absences, $0k0$ with k = odd and $h0l$ with h = odd. Data reduction and calculations were carried out by using the SHELXTL[11] program. The direct method routines produced an acceptable solution for the structure with positions

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[11] Sheldrick, G. M. SHELXTL; University of Göttingen: Göttingen, Federal Republic of Germany, 1978.

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Table I. Experimental Parameters for the X-ray Diffraction Study of Trimesitylaluminum–Tetrahydrofuran

compd: trimesitylaluminum–tetrahydrofuran
formula: $C_{31}H_{41}OAl$
mol. wt: 456.64
cryst color: colorless
cryst system: monoclinic
space group: $P2_1/c$ (No. 14) unequivocally determined from systematic absences
Z: 4
cell constants constrained from 25 high-angle reflections: a = 8.457 (1) Å, b = 14.318 (2) Å, c = 22.235 (3) Å, β = 98.271 (9)°, V = 2664.5 (5) $Å^3$, and d(calcd) = 1.13 g cm^{-3}
radiatn type: Cu $K\bar{\alpha}$, λ = 1.541 78 Å, Ni filtered, corrected for Lorentz and polarizatn effects
temp: room temp
type of data collection: $\theta/2\theta$ scan
2θ scan range: 8–110°
octants used: $+h,+k,\pm l$
scan rate: variable 2–5 deg/min
std reflctns: 3 measd per every 100 reflctns, no significant deviatn from the standard was observed; max deviatn was 5%
no. of data collected: 3894
no. of unique reflctns: 3339
obsd reflctns: 2062 with $F(0) \geq 2.5\sigma(F)$
linear abs coefft (μ): 7.31 cm^{-1}
$F(000)$ = 992 electrons
abs correctn: none applied
no. of parameters refined: 304
obsd/parameter ratio: 7:1
$R = \sum(|F_o| - |F_c|)/\sum|F_o|$ = 7.5%
$R_w = [\sum|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ = 4.5%, $w = 1/\sigma^2(F)$
overall shift/esd: 0.000
max shift/esd: 0.001
residual electron density: 0.31 e/$Å^3$, 1.02 Å away from C27

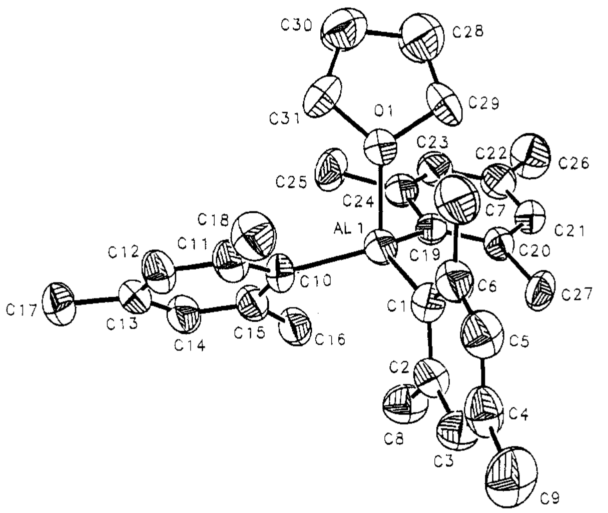

Figure 1. An ORTEP diagram of trimesitylaluminum–tetrahydrofuran with the labeling scheme. The atoms are represented by 50% probability thermal ellipsoids. Hydrogen atoms have been omitted for the sake of clarity.

Table II. Atomic Coordinates and Isotropic Thermal Parameters for the Trimesitylaluminum–Tetrahydrofuran

atom	x	y	z	U_{iso},[a] $Å^2$
Al	0.6749 (2)	0.7538 (2)	0.05538 (8)	0.0512 (8)
C1	0.7141 (9)	0.8723 (4)	0.1037 (3)	0.049 (3)
C2	0.8716 (9)	0.8820 (5)	0.1362 (3)	0.050 (3)
C3	0.9149 (9)	0.9560 (5)	0.1762 (3)	0.059 (3)
C4	0.806 (1)	1.0227 (5)	0.1879 (3)	0.062 (4)
C5	0.652 (1)	1.0159 (5)	0.1578 (3)	0.062 (4)
C6	0.6069 (9)	0.9438 (5)	0.1166 (3)	0.056 (3)
C7	0.4363 (9)	0.9471 (4)	0.0862 (3)	0.073 (3)
C8	0.9972 (8)	0.8104 (4)	0.1290 (3)	0.066 (3)
C9	0.854 (1)	1.0983 (5)	0.2356 (3)	0.094 (4)
C10	0.6882 (9)	0.6448 (4)	0.1136 (3)	0.045 (3)
C11	0.5808 (9)	0.6364 (5)	0.1564 (3)	0.058 (3)
C12	0.5762 (9)	0.5574 (5)	0.1925 (3)	0.061 (3)
C13	0.6804 (9)	0.4831 (5)	0.1905 (3)	0.057 (3)
C14	0.7984 (9)	0.4932 (5)	0.1529 (3)	0.062 (3)
C15	0.8025 (9)	0.5715 (5)	0.1154 (3)	0.054 (3)
C16	0.9430 (8)	0.5740 (4)	0.0789 (3)	0.062 (3)
C17	0.6659 (8)	0.3959 (5)	0.2278 (3)	0.081 (4)
C18	0.4676 (8)	0.7154 (5)	0.1678 (3)	0.071 (4)
C19	0.7573 (7)	0.7399 (5)	−0.0250 (2)	0.046 (3)
C20	0.8311 (8)	0.8130 (4)	−0.0547 (3)	0.051 (3)
C21	0.8504 (8)	0.8060 (5)	−0.1160 (3)	0.057 (3)
C22	0.8095 (9)	0.7268 (5)	−0.1495 (3)	0.062 (4)
C23	0.7439 (8)	0.6528 (5)	−0.1208 (3)	0.058 (3)
C24	0.7161 (8)	0.6594 (5)	−0.0607 (3)	0.055 (3)
C25	0.6384 (9)	0.5735 (4)	−0.0371 (3)	0.073 (3)
C26	0.8325 (9)	0.7189 (5)	−0.2157 (3)	0.086 (4)
C27	0.8899 (8)	0.9022 (4)	−0.0213 (3)	0.062 (3)
C28	0.279 (1)	0.7589 (8)	−0.0741 (4)	0.161 (6)
C29	0.405 (1)	0.8082 (5)	−0.0406 (4)	0.088 (4)
O1	0.4519 (5)	0.7531 (3)	0.0149 (2)	0.063 (2)
C31	0.314 (1)	0.6946 (5)	0.0238 (3)	0.083 (4)
C30	0.216 (1)	0.6852 (6)	−0.0347 (4)	0.102 (4)

[a] $U_{iso} = {}^1/_3 \sum_i\sum_j U_{ij}a_i^*a_j^*\bar{\mathbf{a}}_i\cdot\bar{\mathbf{a}}_j$.

Table III. A Listing of Selected Bond Distances and Bond Angles in the $Mes_3Al\bullet THF$ Molecule

	Bond Distances (Å)		
Al–O	1.969 (5)	Al–C1	2.011 (7)
Al–C10	2.021 (6)	Al–C19	2.020 (6)
	Bond Angles (deg)		
C1–Al–O	108.6 (3)	C10–Al–O	104.5 (3)
C19–Al–O	91.4 (2)	C1–Al–C10	108.6 (3)
C1–Al–C19	120.3 (3)	C10–Al–C19	119.8 (3)
Al–C1–C2	115.0 (5)	Al–C1–C6	130.8 (6)
C2–C1–C6	113.8 (6)	Al–C10–C11	121.0 (5)
Al–C10–C15	124.2 (5)	C11–C10–C15	114.8 (6)
Al–C19–C20	124.5 (5)	Al–C19–C24	119.2 (5)
C20–C19–C24	115.3 (5)		

for all of the non-hydrogen atoms. The aluminum atom was found to be in the general position of this space group since there are four molecules in the unit cell. Refinement was carried out by using SHELX-76.[12] Isotropic least-squares refinement of the coordinates obtained in the initial solution indicated some disorder or large thermal motions associated with two carbon atoms, C28 and C30 of the THF ring. An attempt to resolve this problem by use of a disorder model was made but was unsuccessful; therefore, average positions were used for atoms C28 and C30. The usual systematic correction for secondary extinction was applied; the value of the parameter x in the equation $F_c = F(1 - 0.001xF^2)/\sin\theta$ refined to 0.007 38. Full-matrix least-squares refinement of positional and thermal parameters for non-hydrogen atoms produced a better Fourier difference map. The scattering factors for neutral carbon and aluminum were used.[13] Each hydrogen atom was placed in a calculated position with a C–H bond distance of 1.08 Å and assigned an isotropic thermal parameter approximately 1.2 times the thermal parameter of the carbon atom to which it was bound. All hydrogen atom positional parameters were excluded from subsequent refinement. A few additional cycles of refinement of the data led to convergence with R = 7.5% and R_w = 4.5%. The final difference Fourier map showed a maximum residual electron density of 0.31 e/$Å^3$, 1.02 Å away from C27 atom with an overall shift/error of 0.000.

Results and Discussion

A view of the trimesitylaluminum–tetrahydrofuran molecule is given in Figure 1 with the atoms labeled. The positional coordinates for all the non-hydrogen atoms are

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(12) Sheldrick, G. M. SHELX-76; University of Chemical Laboratory: Cambridge, England, 1976.

(13) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV (present distributor D. Reidel, Dordrecht).

Table IV. A Comparison of Average Bond Distances and Angles in Selected Organoaluminum Compounds and Organoaluminum–Ether Adducts

compound	Al–C, Å	C–Al–C, deg	O–Al, Å	C–Al–O, deg
$Mes_3Al{\cdot}THF$	2.017	116.2	1.969	101.3
Mes_3Al[a]	1.995			
Me_3Al[b]	1.957			
$Me_3Al{\cdot}OMe_2$ (gas)[c]	1.976	117.8	2.014	98.7
$(Me_3Al)_2{\cdot}$(dibenzo-18-crown-6)[d]	1.960	115.5	1.967	102.4
$(Me_3Al)_4{\cdot}$(15-crown-5)[d]				
Al(1)	1.93	115.9	2.005	101.8
Al (2)	1.95	116.2	2.005	101.4
$(Me_3Al)_2{\cdot}$*p*-dioxane[e]	1.96	116.8	2.02	100.4
(*o*-Tol)$_3$Al·OEt$_2$[f]	1.990	114.4	1.928	103.8
$(PhCH_2)_3Al{\cdot}OEt_2$[g]	1.986	113.0	1.901	105.6
$MeAl(BHT)_2$[h]	1.927		1.686	123.7
$Et_2AlBHT{\cdot}MeC_6H_4CO_2Me$[h]	1.964	116.4	1.749 (alcox) 1.887 (ester)	115.7 101.8
(cyclopropyl)$_6$Al$_2$[i]	1.944 (terminal) 2.074 (bridge)			
(*o*-Tol)$_6$Al$_2$[f]	1.997 (terminal) 2.128 (bridge)			
Ph_6Al_2[j]	1.958 (terminal) 2.182 (bridge)			
$Ph_2Al[Si(SiMe_3)_3]{\cdot}THF$[k]	1.985	114.8	1.927	103.2
1,4-diethyl-2,3,5,6-tetraphenyl-1,4-dialumina-2,5-cyclohexadiene–tetrahydrofuran[l]	1.907			
(pentaphenyl)aluminacyclopentadiene–tetrahydrofuran[m]	1.907			

[a] Reference 1. [b] Reference 5. [c] Haaland, A.; Samdal, S.; Stokkeland, O. *J. Organomet. Chem.* **1977**, *134*, 165. [d] Atwood, J. L.; Hrncir, D. C.; Shakir, R.; Dalton, M. S.; Priester, R. D.; Rogers, R. D. *Organometallics* **1982**, *1*, 1021. [e] Atwood, J. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1967**, *89*, 5362. [f] Barber, M.; Liptak, D.; Oliver, J. P. *Organometallics* **1982**, *1*, 1307. [g] Rahman, A. F. M.; Siddiqui, K. F.; Oliver, J. P. *J. Organomet. Chem.* **1987**, *319*, 161. [h] Reference 7; BHT = 2,6-di-*tert*-butylphenoxide. [i] Ilsley, W. H.; Glick, M. D.; Oliver, J. P.; Moore, J. W. *Inorg. Chem.* **1980**, *19*, 3572. [j] Malone, J. F.; McDonald, W. S. *J. Chem. Soc., Dalton Trans.* **1972**, 2646. [k] Sierra, M.; De Mel, S.; Oliver, J. P. unpublished results. [l] Hoberg, H.; Gotor, V.; Milchereit, A.; Kruger, C.; Sekutowski, J. C. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 539. [m] Kruger, C.; Sekutowski, J. C.; Hoberg, H.; Krause-Going, R. *J. Organomet. Chem.* **1977**, *141*, 141.

given in Table II. Selected bond distances and angles are given in Table III. Other parameters are available in the supplementary material.

In order to assess the steric interactions of the mesityl groups on the coordination about the aluminum atom, there are several parameters that should be examined. These are the Al–C and Al–O bond distances and the overall arrangement that is reflected by orientation of the various groups and by the distortion of the angles around the aluminum atom.

Triarylaluminum compounds are stated to be better Lewis acids than the trialkylaluminum derivatives,[14] and, further, the enthalpy of formation of THF adducts is reported to be greater than that of the diethyl ether complexes.[15] For these reasons one might expect that the Al–C and Al–O distances in 2 would be less than those observed in trialkylaluminum adducts and comparable to those found in triarylaluminum–tetrahydrofuran derivatives.

Examination of the data shows that the carbon to aluminum distances range from 2.011 (7) to 2.021 (6) Å, and all are substantially greater than those observed in other organoaluminum adducts which lie in the range of 1.93–1.99 Å and also are greater than the terminal Al–C distances observed in a series of bis(triorgano)aluminum dimers. The observed distances are somewhat less than those in symmetrical Al–C bridge bonds which range from 2.074 Å in the tricyclopropylaluminum dimer to 2.184 Å in Al_2Ph_6. These features can readily be seen in Table IV. Further, it should be noted that the average Al–C distance in the complex has increased by about 0.02 Å from that observed in the uncoordinated $AlMes_3$ where the Al–C distance is 1.995 (8) Å. The only other system for which comparable data are available is the $AlMe_3$ monomer and the corresponding $Me_3Al{\cdot}OMe_2$ adduct. In this instance there is also an increase of 0.019 Å. Thus, the increased Al–C distance may be a reflection of the increase in coordination number from 3 to 4 and the bonding to oxygen. Alternatively, the observed longer bond distances may result from steric interactions, a point also made for the parent $AlMes_3$.

The Al–O distance (1.969 Å) in this complex is somewhat greater than that found in the two other THF adducts of organoaluminum compounds (see Table IV) for which the X-ray structures have been reported and is longer than the Al–O distances in the ether adducts of tri-*o*-tolylaluminum, tribenzylaluminum, and pentaphenylaluminacyclopentadiene. However, the Al–O distance in 2 is shorter than those found for the diethyl ether, *p*-dioxane, and 15-crown-5 adducts of trimethylaluminum and about equal to that of the dibenzo-18-crown-6 adduct. These results are insufficient to yield any support for either steric interference or for enhanced stability of the $Mes_3Al{\cdot}THF$ adduct.

Further examination of Figure 1 shows that the three mesityl rings are nonequivalent with the angles formed between the plane described by the three ipso-carbon atoms and the planes of the mesityl rings of 96.6 (2)° with ring A (carbons 1–9), of 45.4 (2)° with ring B (carbons 10–18), and of 20.4 (3)° with ring C (carbons 19–27). This is in contrast to the arrangement found in 1 in which all three mesityl rings form an angle of 56° with the plane described by the ipso-carbon atoms. The strain is further relieved by the fact that the Al atom is 0.3940 Å above this plane. Another manifestation of this is shown by the C–Al–O angles. The observed angle for C19–Al–O (91.4°) is quite sharp while the other two ipso-carbon–aluminum–oxygen angles are approximately equivalent at 108.6° for C1–Al–O and 104.5° for C10–Al–O. These angles are in the same range as observed in other triorganoaluminum–ether complexes. Likewise, the C–Al–C angles formed

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[14] Manzer, L.; Parshall, G. W. *Inorg. Chem.* **1976**, *15*, 3114.

[15] Hendrickson, C. H.; Duffy, D.; Eyman, D.P. *Inorg. Chem.* **1968**, *7*, 1047.

between the ipso-carbons of the mesityl rings and the Al atom show two which are approximately 120° and one which is much smaller, 108.6°. Again, C19 is the ipso-carbon atom (ring C) that is unique.

These observations and inspection of Figure 1 provide a qualitative explanation for this structural arrangement. Ring A is at the furthest position form the THF molecule; ring B is oriented so that the ortho-methyl group closest to the THF molecule is pointed away from it. Ring C lies nearly under the THF molecule and is twisted such that it is almost coplanar with respect to the plane of the ipso-carbon atoms, thus minimizing the steric interactions with the THF molecule.

The geometry is further modified by the steric repulsion of the ortho methyl groups of the mestyl rings. These groups on ring C then force the angle between itself and rings A and B to be larger than expected for an ether adduct of a triorganoaluminum while the angle between these latter two rings is smaller than expected. Likewise, the rings are oriented such that the steric repulsions between the ortho methyl groups is minimized. This overall arrangement also provides a reasonable orientation for molecular packing.

It appears from this structure that considerable steric crowding exists in this molecule but that the energy gained by formation of the THF adduct, although probably less than optimal, is sufficient to yield a reasonably stable addition product. We are in the process of investigating the structure of other adducts of 1 to further explore this fine balance between steric and electronic effects in other sterically crowded organoaluminum complexes.

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Registry No. Trimesitylaluminum–tetrahydrofuran, 99654-31-6.

Supplementary Material Available: Complete listings of bond lengths (Table S-I), bond angles (Table S-II), anisotropic thermal parameters (Table S-III), and hydrogen atom positional coordinates and isotropic thermal parameters (Table S-IV) and a packing diagram (Figure S-1) (7 pages); a listing of observed and calculated structure factors (Table S-V) (23 pages). Ordering information is given on any current masthead page.

C,C Couplings in the Reactions of Unsaturated Group 4 Metal *s-cis*-Butadiene Complexes with 2,6-Xylyl Isocyanide

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A group of electronically unsaturated (14-electron) diene complexes of Hf and Ti has been reacted with 2,6-xylyl isocyanide. $Cp^*Hf(diene)Cl$ (diene = 2,3-dimethyl-1,3-butadiene, 2-methyl-1,3-butadiene; $Cp^* = \eta\text{-}C_5Me_5$) reacts with 2 mol of isocyanide to form the unusual heterospiro complexes $Cp^*Hf(Cl)N(xy)CCH_2C(Me){=}C(R)CH{=}CHN(xy)$ (R = H, Me; xy = 2,6-xylyl) involving a 1,2-hydrogen shift and a ring closure after insertion of isocyanide into the Hf–diene bond. In Cp^*Hf(2,3-dimethyl-1,3-butadiene)R (R = Me, Ph, neopentyl) the size of R determines whether insertion into the Hf–R bond (R = Me) or the Hf–diene bond (R = Ph, neopentyl) takes place. Cp^*Ti(2,3-dimethyl-1,3-butadiene)Cl reacts through elimination of the diene ligand and C,C coupling of two isocyanides to form $(Cp^*TiCl)_2[\mu\text{-}N_2C_2(xy)_2]$. This compound crystallizes in space group $P2_1/c$ with $a = 11.111$ (8) Å, $b = 19.435$ (17) Å, $c = 8.592$ (4) Å, $\beta = 109.68$ (5)° at 170 K, $Z = 2$, and $d_{calcd} = 1.33$ g cm^{-3}. The molecule is centered around an approximately planar raftlike $Ti_2N_2C_2$ structure with a bridging nonlinear (xy)NCCN(xy) ligand. As side products two enediamide complexes deriving from double and triple insertion of isocyanide into the Ti–diene bond could be identified. The difference in reactivity between the Ti and Hf complexes demonstrates the decrease in σ^2,π-metallacyclopentene character in Cp^*M(diene)Cl going from M = Hf to M = Ti.

Introduction

Group 4 transition-metal compounds containing an *s-cis*-butadiene ligand have been shown to exhibit pronounced σ^2,π-metallacyclopentene character, both in the 18-electron Cp_2M(diene) (M = Zr, Hf)[1] and in the 14-electron Cp^*M(diene)Cl (M = Ti, Zr, Hf; $Cp^* = \eta^5\text{-}C_5Me_5$)[2] system. This causes Cp^*M(diene)Cl to react with polar organic substrates like ketones,[3a] nitriles,[3b] and CO,[4] as a

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[1] Extensive information on the Cp_2M(butadiene) (M = Zr, Hf) system can be found in: Yasuda, H; Tatsumi, K.; Nakamura, A. *Acc. Chem. Res.* **1985**, *18*, 120. Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1 and references cited therein.

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[3] (a) Ausema, J.; Hessen, B.; Teuben, J. H. *Recl. Trav. Chim. Pays-Bas* **1987**, *106*, 465. (b) Hessen, B.; Ausema, J.; Teuben, J. H., in preparation.

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