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Insertion reactions of dimethylgermylene, Me2Ge, and their mechanisms as studied by CIDNP

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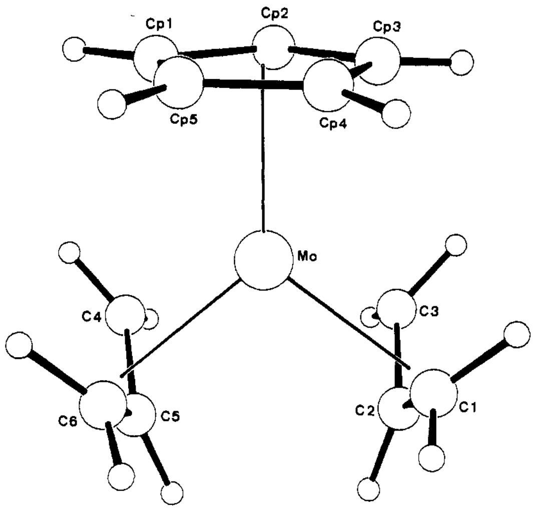

Figure 1. Molecular structure of $[Mo(\eta^3\text{-}C_3H_5)_2(\eta^5\text{-}C_5H_5)]$ (4) showing the atom numbering scheme.

Table I. Selected Bond Lengths (Å) and Bond Angles (deg) for $[Mo(\eta^3\text{-}C_3H_5)_2(\eta^5\text{-}C_5H_5)]$ (4)[a]

Bond Lengths			
Mo-C1	2.250 (3)	C1-C2	1.407 (4)
Mo-C2	2.248 (2)	C2-C3	1.407 (4)
Mo-C3	2.250 (3)	C4-C5	1.396 (4)
Mo-C4	2.262 (3)	C5-C6	1.414 (4)
Mo-C5	2.237 (2)	Mo-D1[b]	1.991
Mo-C6	2.252 (3)	Mo-D2[b]	1.993
Mo-C_5H_5(av)	2.345 (7)	Mo-D(Cp)[c]	2.025
Bond Angles			
C1-C2-C3	119.6 (2)	C2-Mo-C1	36.5 (1)
C6-C5-C4	119.5 (2)	C5-Mo-C2	79.8 (1)
C4-Mo-C6	65.0 (1)	C6-Mo-C1	91.6 (1)
C4-Mo-C5	36.1 (1)	C4-Mo-C3	88.6 (1)
C3-Mo-C1	65.4 (1)	D1-Mo-D2[b]	101.5
C3-Mo-C2	36.5 (1)	D1-Mo-D(Cp)[b,c]	128.4
C5-Mo-C6	36.7 (1)	D2-Mo-D(Cp)[b,c]	130.1

[a] Esd in parentheses. [b] D1 and D2 are the midpoints from the allyl groups C1-C2-C3 and C4-C5-C6, respectively. [c] D(Cp) is the midpoint from the cyclopentadienyl ring.

(cryoscopic); calcd for $C_{11}H_{15}Mo$ 243.2) and in the crystal form by the X-ray structural determination described below.

4 was recrystallized from diethyl ether as orange prisms.[5] The structure is shown in Figure 1 while important bond lengths and bond angles have been brought together in Table I. The organic ligands adopt an essentially trigonal-planar arrangement around the central metal atom.

A noncrystallographic mirror plane passes through the metal atom and bisects the five-membered ring. The two η^3-allyl groups adopt an endo, cis conformation with an angle of 25.6° between the two planes that brings the meso-hydrogen atoms H2 and H5 within 2.171 Å of each other. The plane (±0.011 Å) defined by the four terminal C atoms (C1, C3, C4, and C6) lies parallel to the plane of the cyclopentadienyl ring (±0.005 Å; 1.09°), the Mo atom being situated 2.024 (8) Å away from the latter plane and 1.029 (8) Å from the former. The geometry of the two allyl groups is very similar, the metal–carbon bonds being only slightly asymmetric: the metal atom is symmetrically bonded to the allyl group C1–C2–C3 but is closer (0.01 Å, >3 sd) to atom C6 than to atom C4 of the other group. Preliminary results of a detailed investigation of the electron deformation density by X–X methods indicate an octahedral distribution of electron density about the molybdenum atom similar to that observed in the related 17-electron compound $[Fe(\eta^2,\eta^2\text{-cod})(\eta^5\text{-}C_5H_5)]$.[6]

The analogy between the chemistry of $[Mo(\eta^3\text{-}C_3H_5)_4]$ and $[MoCl(\eta^3\text{-}C_3H_5)_3]_2$ on the one hand and that described by Green and co-workers[7] for $[Mo(\eta^6\text{-}C_6H_5R)_2]$ and $[MoCl(\eta^3\text{-}C_3H_5)(\eta^6\text{-}C_6H_5R)]$ on the other has not escaped us and is being explored further. In addition work is in progress which indicates that related reactions are to be expected with the chromium and tungsten allyls, and it has, for example, proved possible to synthesize the chromium analogue for 4.[8]

Acknowledgment. C.C.R. thanks the Alexander von Humboldt Stiftung for the award of a stipendium.

Registry No. **1**, 12336-10-6; **2**, 89922-74-7; **3**, 89922-75-8; **4** (Mo), 89922-76-9; **4** (Cr), 89922-80-5; $MoCl_4$, 13320-71-3; $[MoI(\eta^3\text{-}C_3H_5)_3]_2$, 89922-77-0; $[MoCl(\eta^3\text{-}C_3H_5)_3(Py)]$, 89922-78-1; $[MoCl(\eta^3\text{-}C_3H_5)_3(MeCN)]$, 89922-79-2; $[MoCl(\eta^3\text{-}C_3H_5)_3(PMe_3]$, 89936-25-4; allylmagnesium chloride, 2622-05-1; butadiene, 106-99-0; poly(1,2-butadiene), 9003-17-2.

Supplementary Material Available: Listings of observed and calculated structure factors, anisotropic thermal parameters, hydrogen isotropic thermal parameters, atomic coordinates, interatomic distances, and bond angles (14 pages). Ordering information is given on any current masthead page.

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(5) X-ray diffraction data for $C_{11}H_{15}Mo$, 4: crystal size (mm), 0.5 × 0.16 × 0.1; monoclinic of space group $P2_1/a$; $a = 11.241$ (3), $b = 7.4232$ (9), $c = 12.5643$ (8) Å; $\beta = 102.715$ (8)°; $Z = 4$; $V = 1022.7$ Å^3; $d_{calcd} = 1.579$ g/cm^3; μ(Mo K_α) = 11.98 cm^{-1} (no absorption correction); $f(000) = 492$; data were collected on an Enraf-Nonius CAD-4 diffractometer; radiation Mo Kα (graphite monochromated), $\lambda = 0.71069$ Å; measured reflections ([$\pm h$, $\pm k$, l], $2° \leq \theta \leq 30°$), 5923; redundant data set averaged to 3169 reflections ($R_{av} = 0.026$); unique observed reflections, 2493 ($I \geq 2\sigma(I)$); number of variables, 109; structure solved by heavy-atom method; all hydrogen atom positions were located and kept fixed in the final refinement stages; $R = 0.0220$, $R_w = 0.0280$; error in an observation of unit weight, 1.53; residual electron density, 0.39 e Å^{-3}.

(6) Goddard, R.; Krüger, C., to be submitted for publication.

(7) Green, M. L. H.; Silverthorn, W. E. *J. Chem. Soc., Dalton Trans.* 1973, 301. Green, M. L. H.; Mitchard, L. C.; Silverthorn, W. E. *Ibid.* 1973, 1403, 2177.

(8) Romão, C. C., unpublished work.

Insertion Reactions of Dimethylgermylene, Me_2Ge, and Their Mechanisms As Studied by CIDNP

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Summary: The insertion of germylenes into carbon-halogen bonds is shown to occur, in the case of thermally generated Me_2Ge and benzyl bromide, via a cage abstraction–recombination reaction, giving typical ^1H CIDNP effects proving the singlet state of Me_2Ge. Besides, an abstraction reaction of escaped $\cdot GeMe_2Br$ yields Me_2GeBr_2 also showing ^1H CIDNP effects, followed by an one-step insertion of Me_2Ge into Ge–Br bonds of Me_2GeBr_2, giving oligogermanes without ^1H CIDNP effects.

Germylenes Me_2Ge can behave as heavy carbene analogues. Thus, they undergo concerted addition to a number of 1,3-dienes via a thermal [2 + 4] cheletropic mechanism.[1] Besides, several insertion reactions into σ bonds

Table I. ^1H CIDNP during Reaction of 1 with $PhCH_2Br$[a] (See Figure 1a)

δ	assignmt	CIDNP
0.20	GeMe (1)	N
0.55	$PhCH_2\mathit{Me}_2GeBr$	E
0.93	GeMe (1)	N
1.06	Me_2GeBr_2	A
2.57	$Ph\mathit{CH}_2Me_2GeBr$	E

[a] E = emission; A = enhanced absorption; N = normal.

Table II. ^1H NMR Spectrum after 2-h Reaction (See Figure 1b)

δ	assignmt
0.55–0.62	oligogermanes ($GeMe_2GeGe$) + $PhCH_2\mathit{Me}_2GeBr$
0.90–0.93	oligogermanes (Me_2GeBr)
1.06	Me_2GeBr_2
2.22	$Ph\mathit{CH}_3$ (trace)
2.58	$Ph\mathit{CH}_2Me_2GeBr$
2.84	$(PhCH_2)_2$

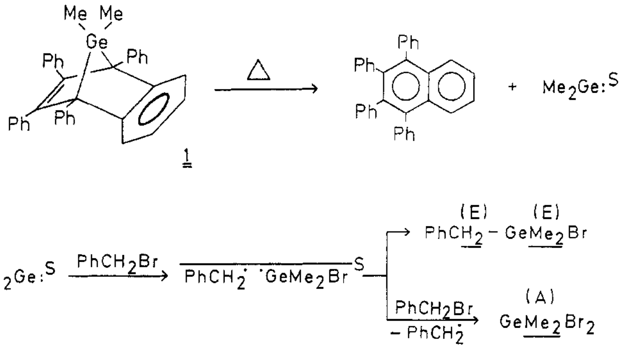
have been described.[1] But, no detailed mechanistic studies of insertions have been preformed sofar, e.g., for the insertion into a carbon–halogen bond.

Accordingly, we generated the free germylenes Me_2Ge in the presence of $PhCH_2Br$, and observed $PhCH_2Me_2GeBr$, the product to be expected in an insertion reaction. But, Me_2GeBr_2, $PhCH_2CH_2Ph$, and bromine-containing oligogermanes were identified as well.

A closer insight into the reaction pathway and the mechanisms was offered by ^1H CIDNP signals[2] that appear in the reaction mixture. Figure 1a shows a ^1H NMR spectrum of the germylene precursor 7-germanorbornadiene 1 as it reacts with excess $PhCH_2Br$ in the probe of a Bruker HFX 90 FT-NMR spectrometer. The assignment of the signals (δ) is given in Table I. Figure 1b and Table II give the ^1H NMR signals of the products after completion of the reaction.

The signals at δ 0.20 and 0.93 can be observed before, during, and immediately after the reaction was interrupted by cooling. In contrast, the emission signals (E) at δ 0.55 and 2.57 and the strong absorption signal (A) at δ 1.06 assigned to $PhCH_2Me_2GeBr$[3] and Me_2GeBr_2[3] were only observed during the reaction, indicating that they are CIDNP signals.

The CIDNP effects are consistent with the reaction scheme shown in eq 1.



(1)

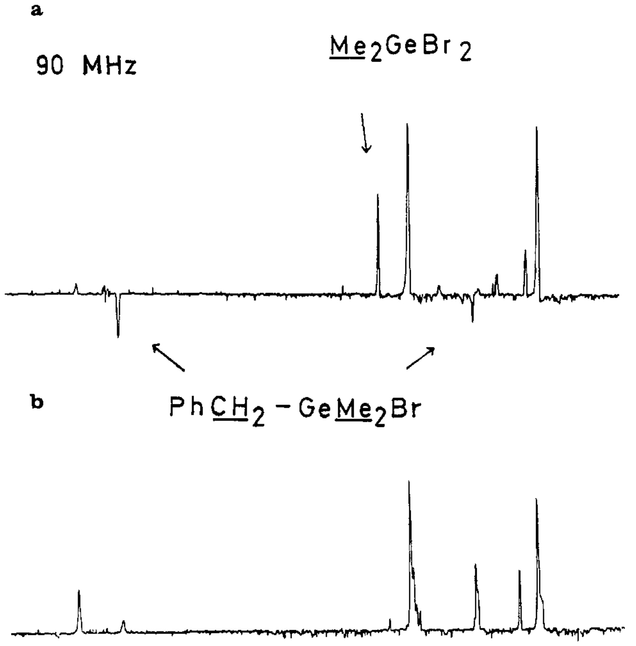
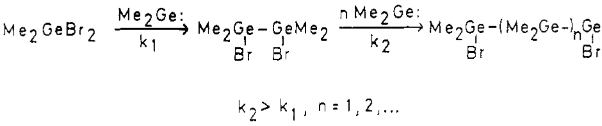


Figure 1. ^1H NMR spectra of 1 with 2.8-fold excess of $PhCH_2Br$ in chlorobenzene at 85 °C: (a) during reaction; (b) after 2-h reaction.

Germylenes Me_2Ge formed thermally from 1 abstract bromine from $PhCH_2Br$ leading to singlet geminate radical pairs in which the nuclear polarizations are built up. $PhCH_2Me_2GeBr$ is formed by recombination of the pair (cage product) and Me_2GeBr_2 by the reaction of freely diffusing radicals $\cdot GeMe_2Br$ (escape product); see eq 1. The first-order decay of 1 is not affected by the addition of $PhCH_2Br$.

Applying Kaptein's first rule,[4-7] a singlet character of the germylene has to be deduced from the emission vs. enhanced absorption pattern of the CIDNP signals.

After the reaction is completed, $PhCH_2Me_2GeBr$ and Me_2GeBr_2 are found; see Figure 1b. But, the latter turns out to be a more effective scavenger for Me_2Ge, yielding oligogermanes containing bromine[8] with an average *n* of ~2 (eq 2).



$$Me_2GeBr_2 \xrightarrow[k_1]{Me_2Ge:} Me_2\underset{Br}{Ge}-\underset{Br}{Ge}Me_2 \xrightarrow[k_2]{n\,Me_2Ge:} Me_2\underset{Br}{Ge}-(Me_2Ge-)_n\underset{Br}{Ge}Me_2$$

$$k_2 > k_1,\ n = 1, 2, \ldots \qquad (2)$$

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(1) Schriewer, M.; Neumann, W. P. *J. Am. Chem. Soc.* **1983**, *105*, 897. Further literature is given there.

(2) First observed by: Bargon, J.; Fischer, H.; Johnsen, U. *Z. Naturforsch.* **1967**, *22A*, 1551. Ward, H. R.; Lawler, R. G. *J. Am. Chem. Soc.* **1967**, *89*, 5518. For Ge-centered radicals, first observed by: Lehnig, M.; Werner, F.; Neumann, W. P. *J. Organomet. Chem.* **1975**, *97*, 275.

(3) After the reaction was completed in a worked-up reaction mixture the structure of the two reaction products was identified by GC–MS analysis and Me_2GeBr_2 by NMR also. After methylation of the reaction mixture, the expected $PhCH_2GeMe_3$ could be detected by H NMR, GC, and GC–MS analysis and compared with an authentic sample.

(4) Kaptein, R. *Chem. Commun.* **1971**, 732. In the present case, the following signs of the ESR parameters involved have to be taken: $g(PhCH_2\cdot) - g(\cdot GeMe_2Br) < 0$,[5-7] $a_H{}^{CH_3}(\cdot GeMe_2Br) > 0$,[5-7] and $a_H{}^{CH_2}(PhCH_2\cdot) < 0$.[6]

(5) $g(\cdot GeMe_2Br)$ and the sign of $a_H{}^{CH_3}(\cdot GeMe_2Br)$ are not known. But, the *g* values of all the germanium-centered radicals known are bigger than $g(PhCH_2\cdot)$; a positive sign for $a_H{}^{CH_3}(\cdot GeMe_2Br)$ is to be assumed in accordance with the signs of $a_H{}^{CH_3}(\cdot CMe_3)$ and $a_H{}^{CH_3}(\cdot SnMe_3)$.[6,7] The CH_3 emission in $PhCH_2Me_2GeBr$ is weak compared with the A signal of Me_2GeBr_2 and the CH_2 E signal of $PhCH_2Me_2GeBr$ due to unpolarized Me_2GeBr_2 enhancing the A signal and the overlap with unpolarized oligogermanes and the difference of the H splittings in the radicals[6,7] which both diminish the CH_2 E signal.

(6) Fischer, H.; Paul, H.; Berndt, H. In Landolt-Börnstein, New Series, "Magnetic Properties of Free Radicals", Part b, Hellwege, K.-H., Ed.; Springer-Verlag: Berlin, Heidelberg, New York, 1977; Group II, Vol. 9.

(7) Lehnig, M., ref 6, 1979; Part c2.

(8) The linear oligogermanes Me_8Ge_3 and $Me_{10}Ge_4$ are found by GC–MS analysis after methylation of the reaction mixture and $Et_2Me_6Ge_3$ and $Et_2Me_8Ge_4$ by GC–MS analysis after ethylation of the reaction mixture. Me_8Ge_3 and $Me_{10}Ge_4$ have also been obtained from the reaction of Me_2Ge with pure Me_2GeBr_2 after methylation. In a competition experiment, Me_2Ge was shown to prefer the reaction with Me_2GeBr_2 (0.5 mol) rather than with $PhCH_2Br$ (2.8 mol): less $PhCH_2Me_2GeBr$ and $(PhCH_2)_2$ could be detected but more bromo oligogermanes.

No CIDNP effects can be observed which indicates that these insertions most likely proceed concertedly. It follows that singlet germylenes, like singlet carbenes,[9,10] are capable to use different mechanism pathways during an insertion reaction.

Acknowledgment. We thank Prof. Dr. W. P. Neumann for his continuous interest and for helpful discussions.

Registry No. 1, 76054-64-3; Me_2Ge:, 74963-95-4; $PhCH_2Br$, 100-39-0; $PhCH_2Me_2GeBr$, 90030-12-9; $BeMe_2Br_2$, 1730-66-1.

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(9) Closs G. L. In "Carbenes"; Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, London, Sidney, Toronto, 1975; p 159.

(10) Roth, H. D. *Acc. Chem. Res.* **1977,** *10,* 85.

Homoleptic Organolanthanoid Hydrocarbyls. The Synthesis and X-ray Crystal Structure of Tris[*o*-((dimethylamino)methyl)phenyl]lutetium

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Summary: The synthesis, characterization, and X-ray crystal structure (Ln = Lu) of stable homoleptic organolanthanoid aryl complexes $Ln[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$ (Ln = Er, Yb, Lu) incorporating the sterically demanding, internally chelating *o*-((dimethylamino)methyl)phenyl ligand are reported. $Lu[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$ crystallizes in the *C*2/*c* space group with unit cell dimensions of a = 24.237 (6) Å, b = 9.388 (3) Å, c = 26.423 (6) Å, β = 123.95 (6)°, and D_{calcd} = 1.54 g cm^{-3} for Z = 8. Least-squares refinement resulted in a final R value of 0.023 based on 2607 independent observed reflections. The Lu–C distances range from 2.425 (7) to 2.455 (7) Å and average 2.435 (14) Å. The Lu–N distances fall into a two-short, one-long pattern: 2.468 (6), 2.478 (5), and 2.588 (5) Å. In the five-membered metallocyclic rings, the three carbon atoms and the lutetium atom are planar to 0.02 Å and the nitrogen atom resides 0.7 Å out of the plane. The torsion angles that involve the nitrogen and three carbon atoms of the rings are −25, 31, and −38°. Unfortunately, the synthesis is not general for all lanthanoids since analogous complexes cannot be isolated when Ln = Pr, Nd, Sm, or Tb.

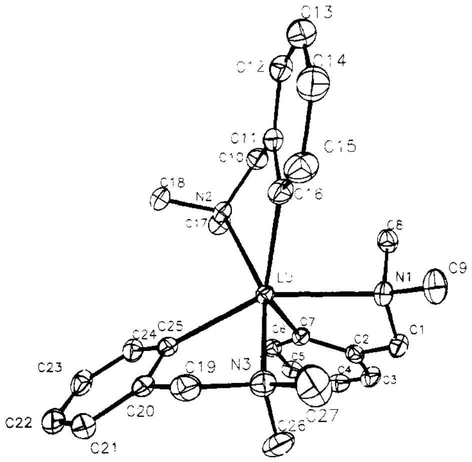

Figure 1. A perspective ORTEP diagram of $Lu[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$. Important parameters are listed in Table I and the text.

The sterically demanding, chelating *o*-((dimethylamino)methyl)phenyl ligand has been used successfully in the synthesis and stabilization of early transition-metal aryl complexes such as $(\eta^5\text{-}C_5H_5)_2Ti[o\text{-}C_6H_4CH_2N(CH_3)_2]$ and $Cr[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$. The synthesis and characterization of the related group 3A metal scandium complexes have also been reported.[1] However, apart from a brief note in the patent literature reporting the synthesis of $Er[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$,[2] the utility of this ligand in stabilizing homoleptic organolanthanoid complexes has not been explored.[3] As part of our general synthetic program aimed at the synthesis of inclusive homologous series of organolanthanoid hydrocarbyls,[4] we have examined the ability of this ligand to yield stable neutral organolanthanoid aryl complexes as a function of lanthanoid element. We report at this time the synthesis, characterization, and X-ray crystal structure (Ln = Lu) of the late lanthanoid compounds $Ln[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$ (Ln = Er, Yb, Lu). Unfortunately, corresponding stable complexes cannot be isolated for the early and middle lanthanoid elements (e.g., Ln = Pr, Nd, Sm, Tb).

The title complexes are synthesized by the slow, ambient-temperature addition of a THF solution of 3 equiv of $Li[o\text{-}C_6H_4CH_2N(CH_3)_2]$[5] to a magnetically stirred suspension of the respective anhydrous metal chlorides in THF.[6] After a reaction time of 24 h, solvent is removed from the characteristically colored, slightly cloudy solutions (pink-orange for erbium, bright orange for ytterbium, and light yellow for lutetium) to yield sticky, semisolid residues. Trituration of the crude products with pentane produces free-flowing powders that are extracted with toluene to remove insoluble byproduct lithium chloride. Concentration of the toluene extracts followed by cooling at −40 °C allows the separation of microcrystalline products in 75% yield. The complexes are then recrystallized in order to separate all traces of chloride-containing byproducts.[7]

The bright pink, yellow, and white complexes (Ln = Er, Yb, and Lu, respectively) are extremely air and moisture sensitive. They are marginally soluble in alkane solvents and soluble in aromatic and ethereal solvents. They are characterized by infrared,[8] ^1H NMR, and ^{13}C NMR

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(1) Manzer, L. E. *J. Am. Chem. Soc.* **1978,** *100,* 8068 and references therein.

(2) Manzer, L. E. U.S. Patent 4 057 565, 1977; *Chem. Abstr.* **1978,** *88,* 62468.

(3) Homoleptic organolanthanoid hydrocarbyls are not an unknown compound class. Several types of neutral and anionic hydrocarbyl complexes have been synthesized and crystallographically characterized (see references cited in: Marks, T. J.; Ernst, R. D. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W. Eds.; Pergamon Press. New York, 1982; Vol. 3, Chapter 21 pp 197–201.). However, these complexes owe their stability to the steric bulk of the ligand utilized. The present study (taken with the work described in ref 4) represents the first systematic attempt to synthesize stable organolanthanoid hydrocarbyls by exploiting the stability conferred by internally chelating ligands.

(4) Wayda, A. L. *Organometallics* **1983,** *2,* 565.

(5) Cope, A. C.; Gourley, R. N. *J. Organomet. Chem.* **1967,** *8,* 527.

(6) All manipulations are conducted with rigorous exclusion of air and moisture. Anhydrous metal chlorides are prepared by the method of Taylor and Carter (Taylor, M. D.; Carter, C. P. *J. Inorg. Nucl. Chem.* **1962,** *24,* 387).

(7) Complexes are assayed for absence of chloride-containing contaminants by X-ray fluorescence.

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