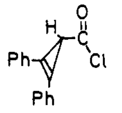
6b provides compounds for ^{1}H NMR spectroscopic comparison.[11]



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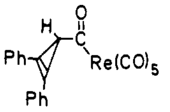

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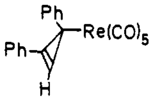

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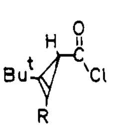
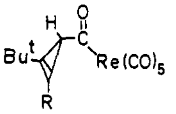
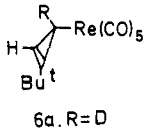


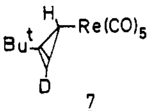
4a. R = D
4b. R = H



5a. R = D
5b. R = H



6a. R = D
6b. R = H



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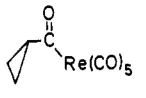

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The regioselective formation of **6a** from **5a** clearly illustrates that the cyclopropenyl migration from CO to Re occurs with allylic rearrangement of the migrating group and provides the first example of such a migration by other than a simple 1,2 shift. The absence of **7** precludes any dissociative migration pathway or a sequence of steps involving a 1,2 shift of the cyclopropenyl group from CO to Re followed by a shift of Re(CO)$_5$ around the ring. The facility with which **2** and **5** undergo thermal decarbonylation is noteworthy. The saturated acyl compound **8** has been reported to be thermally and photochemically inert with respect to cyclopropyl migration;[14] clearly, participation of the cyclopropene olefin in an allylic rearrangement provides a lower energy migration route.

Compound **6a** does not rearrange to produce detectable amounts of its isomer **7** over a period of 24 h (CDCl$_3$, 20 °C),[15] demonstrating quite unambiguously that migration of the Re(CO)$_5$ moiety around the cyclopropenyl periphery is not a chemically significant event at this temperature.[16] We note that the qualitative order of increasing activation energy for 1,2 migration of a ReL$_n$ moiety around cyclopolyenyl ligands is η^1-C$_5$H$_5$[17] < η^1-C$_7$H$_7$[8] < η^1-C$_3$H$_2$-*t*-Bu; this ordering is consistent with the expected ordering of activation energies for a sigmatropic rearrangement ([1,5] < [1,7] < [1,3]),[4,18] but it is not clear why a least motion mechanism should produce such widely differing rates. Even more unclear is the reason for the different migration pathways adopted by SnPh$_3$(η^1-C$_7$H$_7$)[7] and Re(CO)$_5$(η^1-C$_7$H$_7$).[8] Clearly the mechanisms of all such metal shifts require further experimental and theoretical elucidation.

Studies of the generality of allylic rearrangements in the migrations of cyclopropenyl and allyl moieties to and from coordinated CO, and of the chemistry of η^1-cyclopropenyl compounds, are currently in progress.

Acknowledgment. We gratefully acknowledge generous support of our research by the National Science Foundation (Grants CHE7717877 and CHE8022854), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Alfred P. Sloan Foundation.

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(14) Bruce, M. I.; Iqbal, M. Z.; Stone, F. G. A. *J. Organomet. Chem.* **1969**, *20*, 161-168.

(15) Barring an unprecedented isotope effect, this would constitute a degenerate arrangement.

(16) This corresponds to a *minimum* free energy of activation of ca. 30 kcal·mol^{-1} for this migration.

(17) The compound Re(CO)(NO)(PMe$_3$)$_2$(CH$_3$)(η^1-C$_5$H$_5$) is reported to be fluxional at -100 °C: Casey, C. P.; Jones, W. D. *J. Am. Chem. Soc.* **1980**, *102*, 6156-6157.

(18) This ordering assumes that the metal orbital involved in the transition state for a sigmatropic rearrangement is isolobal with, for example, a methyl group. Molecular orbital calculations on a square-pyramidal Re(CO)$_5$ fragment indicate that this may be the case: Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058-1076.

Spherands, the First Ligand Systems Fully Organized during Synthesis Rather than during Complexation[1]

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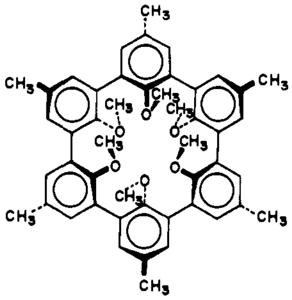
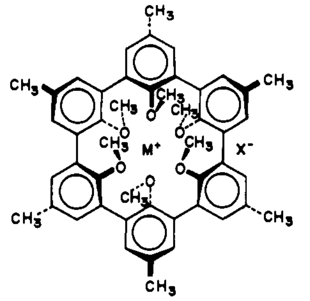
Received March 26, 1981

We report here four new syntheses of spherand **1**,[2] its crystal structure, and the crystal structures of its lithiospherium chloride complex **2**[2] and sodiospherium methylsulfate complex **3**.[3] The results establish that, unlike any organic ligand system previously prepared, **1** possesses the same conformational organization as that of its complexes, **2** and **3**. Thus the full burden of binding-site collection and organization in this spherand is transferred from the complexation process to the synthesis of the ligand system, whose conformation is enforced by its rigid support structure.

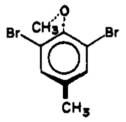


1



2, M$^+$ = Li$^+$; X$^-$ = Cl$^-$
3, M$^+$ = Na$^+$; X$^-$ = CH$_2$SO$_4$$^-$

The cyclohexametaarylene oligomeric system **2** was synthesized in a single experiment by coupling the *six* individual *monomeric units* of **4**[4] by its metalation with 3 mol of *sec*-butyllithium at -80 °C in THF. The mixture was cannulated into a refluxing solution of 4 mol of Fe(AcAc)$_3$ in benzene. After refluxing for 1 h, the mixture was cooled and stirred (3 h) with 3 N HCl aqueous solution containing FeCl$_3$·6H$_2$O. The organic solvent of the mixture was evaporated at 50 °C under vacuum. The remaining material after 8 h at 25 °C was collected, dried at 25 °C, and triturated with dry Et$_2$O to give crude **1**·LiFeCl$_4$. This material was converted directly to **2** as before[2] (2% overall). Similar lithiation and oxidative coupling of *three dimeric units* of **5**,[3,5] and *two trimeric units* of **6**[2] gave **2** in 7 and 25% yields, respectively. In a fourth new synthesis of **2**, **7**[6] was directly lithiated



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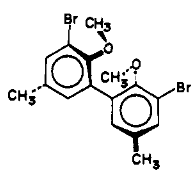

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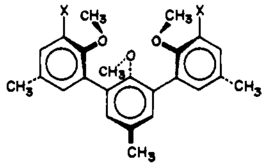

6, X = Br
7, X = H

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(1) Support for the X-ray crystal structure determinations by the National Science Foundation Grants GP-28248 and 77-18748 is gratefully acknowledged by K. N. Trueblood, C. B. Knobler, and E. Maverick. Support for the syntheses by the Division of Basic Sciences of the Department of Energy (Contract AT(04-3)34, P.A. 218) is gratefully acknowledged by R. C. Helgeson, S. B. Brown, and D. J. Cram.

(2) Cram, D. J.; Kaneda, T.; Helgeson, R. C.; Lein, G. M. *J. Am. Chem. Soc.* **1979**, *101*, 6752-6754.

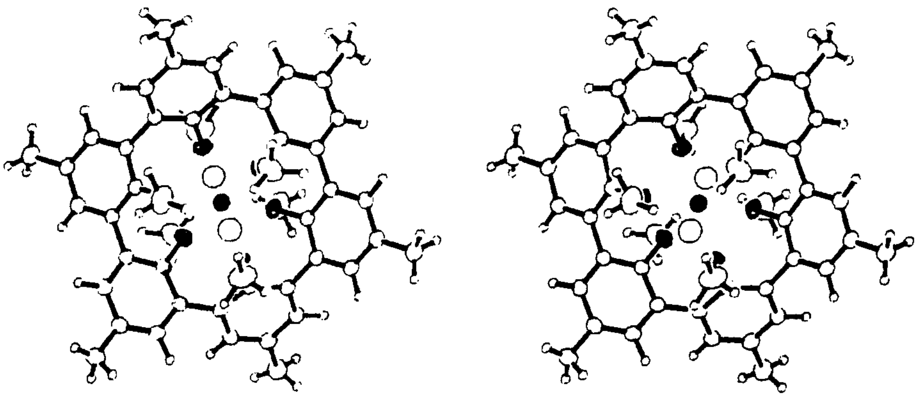
(3) Carbon and hydrogen analyses were within 0.30% of theory. Mass spectra and ^{1}H NMR spectra (200 MHz, Bruker) were as expected.

(4) Kohn, M.; Segel, A. *Monatsh. Chem.* **1925**, *46*, 661-669.

(5) We thank Dr. P. Stückler for preparing this new compound (mp 84-85 °C) by conventional reactions[2] from 2,2'-dihydroxy-5,5'-dimethylbiphenyl.

(6) Koenig, K. E.; Lein, G. M.; Stückler, P.; Kaneda, T.; Cram, D. J., *J. Am. Chem. Soc.* **1979**, *101*, 3553-3566.

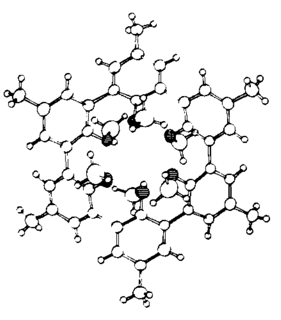
0002-7863/81/1503-5594$01.25/0



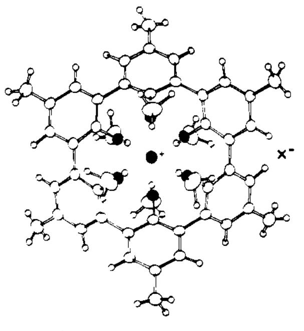
9

and coupled. The yield of **2** was 6% when carried out in the absence of any added LiBr but increased to 17% in the presence of 2 mol of LiBr generated in situ.[7] These results suggest that the ring-closure step is templated by Li^+. Decomplexations of **2** to give **1** were driven by phase transfer (crystallization)[2] at 120 °C for 1 week in 1:4 (v/v) $MeOH-H_2O$ in ~90% yield. Complex **3**[3] was prepared by treating monodemethylated **1**[2] with NaOH and $(CH_3)_2SO_4$.

The single crystal structures of **1**–**3** were determined from diffractometer measurements.[8] The resulting structures, **1a**–**3a**, were refined to give R values of 0.053, 0.047, and 0.15, respectively. Table I records values of selected distances and angles of interest. Structures **1a** and **2a** possess $\bar{3}$ symmetry. Although the sodiospherium cation of **3a** has only $\bar{1}$ symmetry within the crystal, it has, in fact, approximately $\bar{3}$ symmetry. The structures of **1a** and **2a** are very similar, with a slight lengthening along the $\bar{3}$ axis in **2a** compared to **1a**. The Li^+ in **2a** fills the octahedral cavity defined by the six oxygens, and the Cl^- occupies a cavity lined by 12 methyl groups—three methoxymethyls above, three more below, and six arylmethyls surrounding it in the median plane. Each Li^+ has two Cl^- neighbors at 5.2 Å along the $\bar{3}$ axis and six more at 10.7 Å in adjacent parallel stacks of complexes. Drawing **8** represents superimposed cross sections of seven parallel stacks of spherand complexes viewed along the $\bar{3}$ molecular axes.



1a

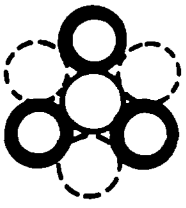


$2a = 1a \cdot LiCl$
$3a = 1a \cdot NaCH_3SO_4$

Table I. Distances (Å) and Angles (deg) in Crystal Structures of Spherand 1a, Lithiospherium Chloride (2a), and Sodiospherium Methyl Sulfate (3a)

structure		1a	2a	3a[a]
hole diam		1.62	1.48	1.75
distances between O's:	pseudoortho	2.92	2.78	3.00
	pseudometa	3.32	3.24	3.43
	pseudopara	4.42	4.28	4.55
distances O's are bent out of the best planes of their attached aryls		0.20	0.07	0.12
angles of aryl folds around $O-Ar-CH_3$ axes		6.3	2.6	4.8
distances C's of attached aryls are bent out of best planes of their reference aryls		0.16[a]	0.16[a]	0.16
Ar–Ar best plane dihedral angles		52	56	61
angles between C–O–C and best aryl planes		62	85	84
$Ar-O-CH_3$ bond angle (normal is 118°)		115	112	113

[a] Average values for all aryl rings.



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The three heavy circles represent cross sections above the plane; the ordinary circle is in the plane; and the three dashed circles are below the plane of the page. In the center of each circle is a Li^+, and above and below each circle is a Cl^-. Some of these relationships are visible in stereodrawing **9** of **2a** viewed 10° from the $\bar{3}$ axis of the molecule.

Results to be published elsewhere demonstrate that in $CDCl_3$ saturated with water at 25 °C, spherand **1** is a much more powerful binder of Li^+ than of Na^+ and that both ions are better bound than by the crowns or cryptands.[9] Most of this superior binding power is attributed to the fact that the host is fully organized for complexation prior to complexation, as is shown by comparisons of **1a**–**3a**. Structure **1a** possesses a snowflake-like shape with a near spherical hole in the middle lined with 24 unshared electrons. In **2a** this cavity is filled with a Li^+ and in **3a** with Na^+. Although nonbonded distances and bond angles of **1** change slightly upon

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(7) Under argon and very dry conditions (throughout), 7.4 mL (19 mmol) of *n*-butyllithium in *n*-hexane was added dropwise by syringe with stirring to a solution of 1.37 g (10 mmol) of $(CH_3)_3CBr$ in 100 mL of Et_2O. The turbid mixture was stirred for 20 min at 25 °C, and 1.81 g (5 mmol) of **7** was added, followed by 7.8 mL (20 mmol) of *n*-butyllithium. The mixture was stirred at reflux for 3.5 h and cannulated through a double-ended needle into a vigorously stirred and refluxing solution of 13.6 g (38.5 mmol) of $Fe(AcAc)_3$ in 1 L of benzene. The ether and some benzene were allowed to evaporate during the additon (5 min). The distillation was continued for an additional 1.5 h to reduce the volume to ~500 mL, the mixture was cooled to 25 °C, and treated as in the other runs to give 0.473 g (20.5%) of crude $1 \cdot LiFeCl_4$. This material gave 0.32 g (17%) of **2**.

(8) Data were collected at 22 °C on a Syntex P$\bar{1}$ diffractometer for each structure. Crystals of **1** and **2** have space group $R\bar{3}$ with one formula unit in the unit cell and, respectively, $a = 11.697$ (3) Å, $\alpha = 114.25$ (2)° and $a = 11.152$ (1) Å, $\alpha = 110.60$ (1)°. Crystals of **3** have space group $P2/c$ with $Z = 2$ and $a = 11.572(5)$, $b = 10.467(5)$, $c = 22.072(7)$ Å; $\beta = 108.97$ (3)°. Each structure was solved by direct methods and refined by full-matrix least squares. The structure of **3** is not yet fully refined; there is some disorder of the $CH_3OSO_3^-$ ion and of a molecule of solvation. Full details on all three structures will be presented elsewhere. Position and thermal parameters are availabe as supplementary material.

(9) Cram, D. J.; Lein, G. M.; Kaneda, T.; Helgeson, R. C.; Knobler, C. B.; Maverick, E.; Trueblood, K. N., *J. Amer. Chem. Soc.*, in press.

complexation, the conformations of **1a**–**3a** are essentially the same, as was predicted from molecular model examination.[2]

Comparisons of the distances and bond angles of Table I provide interesting conclusions. (1) Oxygen–oxygen repulsions in the free ligand (**1a**) deform the aryl groups and their attached atoms from their normally coplanar arrangements. Although the usual van der Waals oxygen-to-oxygen distance is 2.80 Å, the pseudoortho distances in **1a** are 2.92 Å. This is attributed to the enforced orientations of the electron pairs and the accumulation of six contiguous pseudoortho oxygen relationships. (2) Introduction of Li^+ into the hole shrinks the diameter from 1.62 Å to a filled-hole diameter of 1.48 Å,[10] which provides a pseudoortho oxygen–oxygen distance at 2.78 Å, slightly below the usual van der Waals distance. The hole shrinkage must increase the oxygen–oxygen repulsions, an effect compensated for by introduction of the positive charge and relaxation of the angle strains in the aryl support structures. For example, the distance the oxygens are bent out of the best planes of their attached aryls decreases from 0.20 in **1a** to 0.07 Å in **2a**. Likewise, the angles of aryl folds around their O–Ar–CH_3 axes decrease from 6.3 in **1a** to 2.6° in **2a**. Thus some of the strong binding that **1** shows for Li^+ is associated with compensation for oxygen–oxygen repulsion and relaxation of deformation strain in the support structure. (3) Introduction of Na^+ into the hole expands its diameter from 1.62 Å in **1a** to a filled-hole diameter of 1.75 Å in **3a**.[11] The resulting pseudoortho oxygen–oxygen distance is 3.00 Å, well above the usual van der Waals distance. The hole expansion must relieve oxygen–oxygen repulsion, and the positive charge therefore becomes less important in compensating for these repulsions in **3a** than in **2a**. Some relief of angle strain in the support structure of **1a** is seen in passing to **3a**. Thus the distances the oxygens are bent out of the best planes of their attached aryls decrease from 0.20 in **1a** to 0.12 Å in **3a**. Likewise the angles of the aryl folds around the O–Ar–CH_3 axes decrease from 6.3 in **1a** to 4.8° in **3a**. (4) Interestingly, the average distances that the carbons of the attached aryls are bent out of the best planes of their parent aryls are identical (0.16 Å) in the three structures. In contrast, the Ar–Ar best plane dihedral angles go from 52 to 56 to 61° for the empty, Li^+, and Na^+ filled spherands, respectively, in spite of the fact that the hole diameters increase in a different order (**2a** < **1a** < **3a**). The dihedral angles within the $CH_3OC_6H_2$ units between the C–O–C planes and the best aryl planes are 62 in **1a**, 85 in **2a**, and 84° in **3a**. These differences probably reflect adjustments to the differing demands of molecular packing. Although Ar–O–CH_3 bond angles are normally about 118°, they are 115, 112, and 113° in **1a**, **2a**, and **3a**, respectively. This trend is compatible with the intuitive generalization that the larger the number of ligands attached to an element, the smaller the bond angles must be to spatially accommodate those ligands.

These results demonstrate that a moderately strained and highly organized hexameric host can be assembled by oxidation with $Fe(AcAc)_3$ of monomeric, dimeric, or trimeric aryldilithium. High-energy aryl radicals are probably intermediates that couple to produce aryl–aryl bonds in these syntheses. It seems likely that only highly exothermic reactions will produce spherands as strained as **1**. The immediate open-chain precursor of the lithiospherium salt (**2**) was probably the open-chain hexaaryl diradical, which possesses 1024 different possible conformations.[12] Only two of these (enantiomerically related) could lead directly to the enforced conformation of cycle **1** or its complexes. The Li^+ present in the medium probably provided much of the organization this diradical needed to ring close. Its very short life insured its high dilution.

Supplementary Material Available: Position and vibration parameter for the spherand, lithiospherium chloride, and sodiospherium methyl sulfate (3 pages). Ordering information is given on any current masthead page.

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(10) The diameter of the hole organized and occupied by Li^+ in the [2.1.1]cryptand complex of LiI (six heteroatoms) is about 1.50 Å [Moras, P. D.; Weiss, R. *Acta Crystallogr. Sect. B* **1973**, *b29*, 400–403].

(11) The diameter of the hole organized and occupied by Na^+ in benzo-15-crown-5-H_2O·NaI (six heteroatoms) is 1.97 Å [Bush, M. A.; Truter, M. R., *J. Chem. Soc. Perkin, Trans. 2* **1972**, 341–344]. This and other diameters are calculated by averaging the O–M^+ distances and subtracting the radius of an O atom (1.40 Å) [Pauling, L. C. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 260].

(12) The open-chain hexameric diradical is constitutionally like ended. It contains five potentially chiral elements associated with Ar–Ar rotations and six associated with CH_3O–Ar rotations, eleven in all. The number of stereoisomers (conformers) for a constitutionally like-ended system containing an odd number of potential chiral elements is 2^{n-1} [Mislow, K. "Introduction to Stereochemistry", W. A. Benjamin: New York, 1965; p 88].

Transition-Metal-Mediated Hydrogenation of CO to Olefins: Intermediacy of Coordinated Carbenes

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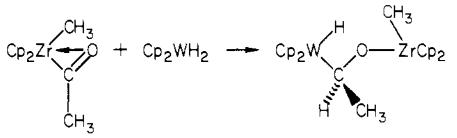
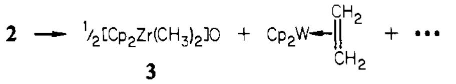
Received May 18, 1981

We recently reported that the reaction of $Cp_2Zr(CH_3)[\eta^2\text{-}C(O)CH_3]$ (**1**) with several transition-metal hydrides yields products arising from hydrogen transfer to the unsaturated carbon of the η^2-acetyl unit.[1a] For example, Cp_2MoD_2 gave $Cp_2Zr(CH_3)(OCD_2CH_3)$ immediately on mixing. At that time, we noted that the reaction of **1** and Cp_2WH_2 permits detection of a bimetallic complex (**2**), the consequence of a single hydrogen transfer by a dihydrido complex. We report here the identity of the unexpected products of further reaction of **2**. We also report the first detailed observation of a stoichiometric synthesis of ethylene incorporating carbon from CO and the intermediacy (and structure) of a W(II) carbene complex in the reaction which ultimately forms ethylene.



1 2 (1)

Treatment of a solution of $Cp_2Zr(CH_3)_2$ and Cp_2WH_2 in C_6D_6 (unreactive at 25 °C) with CO (1 atm) leads to the formation of **2**; this reaction is characterized by a color change from yellow to orange.[1b] The lifetime of **2** in solution is limited and resonances due to $[Cp_2Zr(CH_3)]_2O$ (**3**)[2] and $Cp_2W(\eta^2\text{-}C_2H_4)$ (**4**)[3] soon appear (eq 2). The use of ^{13}CO leads to carbon-13 incorporation in the



$$\mathbf{2} \longrightarrow \tfrac{1}{2}[Cp_2Zr(CH_3)]_2O + Cp_2W\leftarrow\underset{CH_2}{\overset{CH_2}{\|}} + \cdots \qquad (2)$$

3 4

ethylene ligand of **4** (i.e., $H_2{}^{13}C^{12}CH_2$). Additional resonances are observed in the zirconium cyclopentadienyl region as eq 2 proceeds and the ^1H NMR resonances of $CH_4 + C_5H_6$ also appear. The cyclopentadienylzirconium compounds responsible for these additional resonances have not been identified; however, similar resonances are observed when either $Cp_2Zr(CH_3)_2$ or **3** is hydrolyzed with water. We have established, by comparison to an

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(1) (a) Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 1747. Marsella, J. A.; Huffman, J. C.; Caulton, K. G. *ACS Symp. Ser.* **1981**, *No. 152*. (b) Cp_2ZrMe_2 reacts rapidly with CO to form $Cp_2Zr[C(O)Me]Me$. Formation of **2** has also been demonstrated by using isolated samples of $Cp_2Zr[C(O)Me]Me$.

(2) (a) This new complex may also be synthesized from $[Cp_2ZrCl]_2O$ and CH_3Li. ^1H NMR (C_6D_6): δ 5.73 (s, 10 H, Cp_2Zr), 0.23 (s, 3 H, CH_3). MS; heaviest ion observed *m/e* 471, corresponding to M-15; $[Cp_4{}^{90}Zr_2(CH_3)O]^+$. (b) This complex has also been referenced in a recent publication: Hunter, W. E.; Atwood, J. L.; Fachinetti, G.; Floriani, C. *J. Organomet. Chem.* **1981**, *204*, 67.

(3) (a) Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1324. (b) Thomas, J. L. *J. Am. Chem. Soc.* **1973**, *95*, 1838.

0002-7863/81/1503-5596$01.25/0