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Registry No. SiH_3-SiH_3, 1590-87-0.

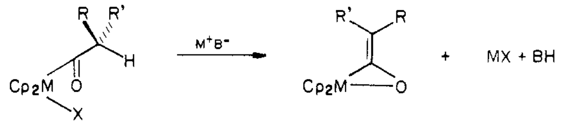
Trinuclear Zr_2,Al μ-Ketene Complexes Containing Bridging Ligands. Implications for Transmetallation Reactions and CO Reduction Chemistry[†]

Robert M. Waymouth, Bernard D. Santarsiero, Robert J. Coots, Michael J. Bronikowski, and Robert H. Grubbs*

Contribution No. 7192 from the Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91125. *Received June 18, 1985*

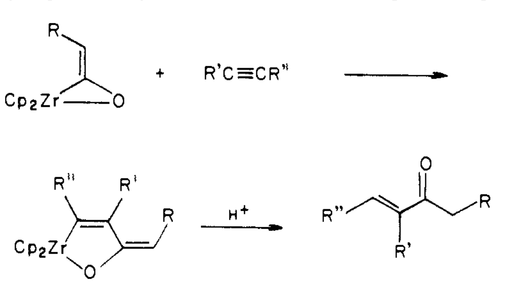
Abstract: A family of ketene–alkylaluminum complexes of formula $[(\eta^5\text{-}C_5H_5)_2Zr(C,O\text{-}\eta^2\text{-}OCCHR)]_2(\mu\text{-}AlR'_2)(\mu\text{-}X)$ has been prepared by treating the zirconocene ketene complexes $[(\eta^5\text{-}C_5H_5)_2Zr(C,O\text{-}\eta^2\text{-}OCCHR)]_2$ with alkylaluminum reagents R'_2AlX (II, III, R = CH_2CMe_3, R′ = Me, X = Me; VIa, VIIa, R = CH_2CMe_3, R′ = CH_3, X = Cl; VIIb, R = H, R′ = CH_3, X = Cl; IX, X, R = CH_2CMe_3, R′ = Et, X = H). The crystal and molecular structure of four compounds of this series (III, VIIa, IX, and X) have been determined. Complex VIIa crystallizes in space group $P2_1/c$ ($Z = 4$) with cell constants a = 10.2193 (14) Å, b = 20.237 (3) Å, c = 18.458 (3) Å, β = 94.303 (14)°, and V = 3802.8 (10) Å^3 (3567 reflections, R = 0.053). Complex IX crystallizes in space group $C2/c$ ($Z = 8$) with cell constants a = 11.777 (5) Å, b = 19.998 (4) Å, c = 32.636 (11) Å, β = 96.83 (5)°, V = 7631.8 (2) Å^3 (4989 reflections, R = 0.067). Complex X crystallizes in space group $C2/c$ ($Z = 4$) with cell constants a = 18.219 (2) Å, b = 10.364 (1) Å, c = 20.273 (2) Å, β = 94.565 (8)°, and V = 3816 (1) Å^3 (2845 reflections, R = 0.049). Structural comparisons of these molecules reveal several common features. Two zirconocene ketene monomers are spanned by symmetric dialkylaluminum and hydride, chloride, or methyl bridges to form slightly puckered six-membered rings. A notable feature of these structures is the coordination of the bridging ligand X (H, Cl, or Me), which is characterized by a large M–X–M angle and an unusual hybridization for the bridging methyl ligand. The coordination of the bridging methyl group in III represents a new bonding geometry for carbon. This geometry models the structure of intermediates in alkyl transmetallations that proceed with inversion. The reaction of III with acetylene produces a zirconocene cyclic enolate IV. Complex III also reacts with carbon monoxide to produce a zirconocene acyl-enol complex V—an unprecedented reaction for Group 4 ketene complexes that is relevant to the behavior of such species over early transition-metal Fischer–Tropsch catalysts. The greater reactivity of III is discussed in terms of the greater lability of the methyl bridge compared to the chloride or hydride bridge.

Transition-metal ketene complexes have been implicated as intermediates in heterogeneous CO reduction[1] and have been demonstrated to be involved in stoichiometric CO reduction processes.[2,4d] Ketene complexes also show considerable promise as intermediates in organic synthesis.[3] We have recently developed an efficient and general route to early transition-metal ketene complexes.[4] Deprotonation of Group 4 acyl halide metallocenes[5] cleanly affords ketene complexes in high yield (eq 1).[6]



(1)

The monomeric bis(η^5-pentamethylcyclopentadienyl)zirconocene ketene complexes and oligomeric bis(η^5-cyclopentadienyl)titanocene ketene complexes prepared by this route are reactive toward olefins and other substrates under mild conditions.[4a,d] We envisioned that an olefin or acetylene insertion reaction might be synthetically useful if applied to the readily prepared bis(η^5-cyclopentadienyl)zirconocene ketene complexes (eq 2).[7] However,



(2)

[†] In this paper, the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d transition elements comprise groups 3 through 12, and the p block elements comprise groups 13 through 18. (Note that the former Roman numeral designation is preserved in the last digit of the new numbering, e.g., III → 3 and 13.)

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(2) (a) Barger, P. T.; Santarsiero, B. D.; Armantrout, J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5178 and references therein. See also: (b) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. (c) Morrison, E. D.; Steinmetz, G. R.; Geoffroy, G. L.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 4783 and references therein. (d) Miyashita, A.; Grubbs, R. H. *Tetrahedron Lett.* **1981**, 1255. Miyashita, A. Abstracts of papers submitted to 3rd China–Japan–US Symposium on Organometallic Chemistry and Catalysis, Santa Cruz, CA, August 5, 1984.

(3) (a) Dotz, K. H. *Pure Appl. Chem.* **1983**, *55*, 1689. (b) Semmelhack, M. F.; Tamura, R.; Schnatter, W.; Springer, J. *J. Am. Chem. Soc.* **1984**, *106*, 5363.

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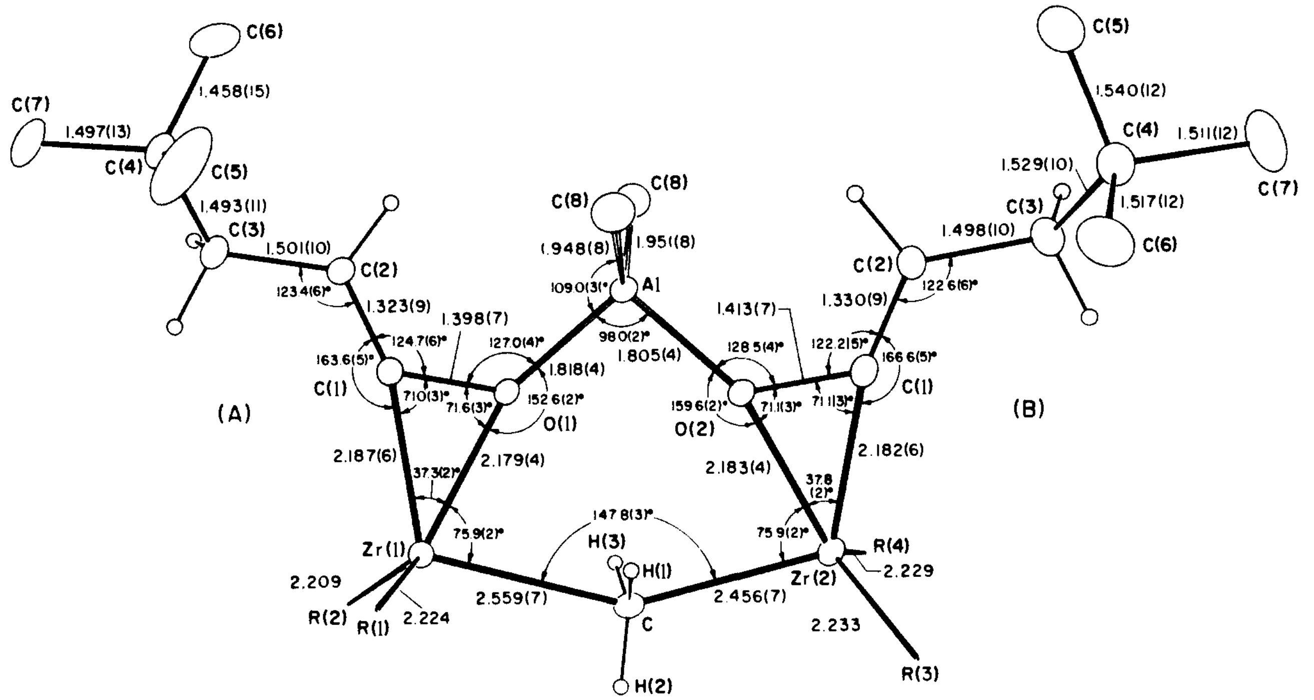

Figure 1. ORTEP diagram with selected bond lengths and angles for III. Cyclopentadienyl rings are represented by their centroids R(1–4).

these zirconocene ketene complexes are exceptionally inert, apparently due to the formation of strongly bound dimers. These complexes are inert even when generated in the presence of potential substates.[4b]

To develop the chemistry of these complexes, we have investigated their reactivity toward aluminum reagents[10] with two objectives in mind: (1) activation[9] of Zr ketene complexes toward insertion reactions of potential synthetic utility, and (2) study of the role of ketene complexes[1,4d] and Lewis acids[11] in Fischer–Tropsch model systems. In a preliminary communication,[12] we reported the crystal structure of the bridging methyl compound III prepared by treating the ketene dimer Ia with Me_3Al. A unique structural feature of this compound is a trigonal-bipyramidal bridging methyl ligand. Herein we report details of the synthesis, structure, and reactivity of this novel compound. In addition, we report our studies on the analogous bridging chloride (VIIa) and bridging hydride (X) compounds prepared by treating Ia with Me_2AlCl and Et_2AlH, respectively. The greater stability of VIIa and X has enabled us to characterize an intermediate in the reaction sequence (Scheme I) and rationalize the reactivity of these compounds in terms of the lability of the bridging ligands.

Results

Preparation of Ia,b.[4a,b] Treatment of the acyl complex (Cp = η^5-cyclopentadienyl) $Cp_2Zr(Cl)C(O)CH_2CH_2C(CH_3)_3$[8b] with a strong, bulky base such as $NaN[Si(CH_3)_3]_2$ affords the ketene dimer Ia (eq 1, M = Zr, R′ = CH_2CMe_3, R = H) in high yield (quantitative by ^{1}H NMR).[4] The deprotonation is highly stereoselective. Monitoring the reaction by ^{1}H NMR at room temperature reveals the following isomeric ratios for the dimer: 76% (*Z,Z*)-Ia, 22% (*Z,E*)-Ia, and 2% (*E,E*)-Ia.[13] These stereochemical assignments were based on NMR data and on crystallographic studies on complexes derived from stereochemically pure samples of (*Z,Z*)-Ia (vide infra).[14] Compound (*Z,Z*)-Ia can be isolated in 75% yield by this route.

The parent ketene complex Ib (eq 1, M = Zr, R = H, R′ = H) was prepared by treating the acyl complex $Cp_2Zr(Cl)COCH_3$[15] with $NaN[Si(CH_3)_3]_2$. Complex Ib has not been completely characterized due to its low solubility but is assumed to be oligomeric. Spectral comparison (^{1}H, ^{13}C NMR, IR) with its titanium[4a] and bis(η^5-pentamethylcyclopentadienyl)zirconium[4d]

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(4) (a) Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 5499. (b) Straus, D. A. Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 1982. (c) Ho, S. C. H.; Straus, D. A.; Armantrout, J.; Schaefer, W. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 2210. (d) Moore, E. J.; Straus, D. A.; Armantrout, J.; Santarsiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *Ibid.* **1983**, *105*, 2068.

(5) Deprotonation of alkyl–acyl metallocenes yields stable metallaenolate anions. The metallaenolate (ketene) anions have been shown to be versatile reagents for the synthesis of binuclear ketene complexes.[4c]

(6) Deprotonation of later transition metal acyl complexes generally yields stable enolate complexes: (a) Theopold, K. H.; Becker, P. N.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 5250. (b) Liebeskind, L. S.; Welker, M. E.; Goedken, V.; *Ibid.* **1984**, *106*, 441. (c) Baird, G. J.; Davies, S. G.; Jones, R. H. Prout, K.; Warner, P. *J. Chem. Soc., Chem. Commun.* **1984**, 745. (d) Doney, J. J.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1985**, *107*, 3724. (e) See also: Wulff, W. D.; Gilbertson, S. R. *J. Am. Chem. Soc.* **1985**, *107*, 503.

(7) A sequence involving hydrozirconation, carbonylation,[8] and depronation[4] affords zirconocene ketene complexes in yields of 60–70% with defined stereochemistry.

(8) (a) Wailes, P. C.; Weigold, H. *J. Organomet. Chem.* **1970**, *24*, 405. (b) Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1979**, *101*, 3521. (c) Bertelo, C. A.; Schwartz, J. *Ibid.* **1975**, *97*, 228.

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(10) For the reaction of η^2(C,C) bound tungsten ketene complexes with Lewis acids see: (a) Kreissl, F. R.; Sieber, W.; Wolfgraber, M. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 493. (b) Churchill, M. R.; Wasserman, H. J.; Holmes, S. J.; Schrock, R. R. *Organometallics* **1982**, *1*, 766–768.

(11) Wang, H. K.; Chai, H. W.; Muetterties, E. L. *Inorg. Chem.* **1981**, *20*, 2661. Demitras, G. C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1979**, *99*, 2796.

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(13) Priorities were assigned according to atomic weight: Zr > O > C > H. See: Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3002. IUPAC Commission on Nomenclature in Organic Chemistry *Pure Appl. Chem.* **1976**, *45*, 11.

(14) (a) (*Z,Z*)-VIIa is obtained stereospecifically from the major isomer of Ia. The chemical shifts for the vinyl protons [H(2)] (recorded by ^{1}H NMR during the reaction Ia → IIa → (*Z,Z*)-VIIa) fall in the range 5.6–6.2 ppm. However, (*E,Z*)-Ia shows a characteristically upfield chemical shift of 4.63 ppm for one of the vinyl protons that we assign to the *E* isomer (Table VI). Moreover, (*E,Z*)-VIIa prepared from this sample also shows an upfield vinyl proton chemical shift of 4.74 ppm. From these results we conclude that the major isomer of Ia, from which (*Z,Z*)-VIIa is obtained, is the *Z,Z* isomer. (b) (*Z,Z*)-Ia was used in all further experiments and for the remainder of this discussion will be referred to simply as Ia.

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Table I. Selected Bond Lengths (Å) and Angles (deg)

	III(μ-CH_3)		VIIa(μ-Cl)		IX(μ-H)		
	fragment A	fragment B	fragment A	fragment B	fragment A	fragment B	X(μ-H)
			Bond Lengths				
Zr–Zr	4.817 (1)		4.864 (1)		4.263 (1)		3.976 (1)
Zr–X	2.559 (7)	2.456 (7)	2.636 (2)	2.632 (2)		2.014 (34)	2.01 (4)
Al–X	3.739 (8)		3.986 (2)			1.703 (34)	3.94 (4)
Zr–C(1)	2.187 (6)	2.183 (6)	2.170 (6)	2.173 (6)	2.198 (6)	2.175 (5)	2.188 (4)
Zr(1)–O	2.179 (4)		2.172 (4)		2.160 (4)	2.193 (4)	2.195 (2)
Zr(2)–O		2.183 (4)		2.147 (4)		2.194 (4)	2.195 (2)
C(1)–O	1.398 (7)	1.413 (7)	1.390 (7)	1.393 (7)	1.406 (7)	1.372 (6)	1.392 (4)
Al–O	1.818 (4)	1.805 (4)	1.809 (4)	1.818 (4)	1.778 (4)		1.812 (3)
Al–C(8)	1.948 (8)	1.951 (8)	1.941 (8)	1.950 (8)	1.933 (9)	1.965 (9)	1.956 (5)
C(1)–C(2)	1.323 (9)	1.330 (9)	1.319 (9)	1.339 (9)	1.308 (8)	1.318 (8)	1.315 (5)
C(2)–C(3)	1.501 (10)	1.498 (10)	1.493 (9)	1.492 (10)	1.496 (8)	1.496 (8)	1.501 (6)
C(3)–C(4)	1.493 (11)	1.529 (10)	1.498 (11)	1.519 (10)	1.527 (9)	1.549 (10)	1.519 (6)
C–H(1)	0.94 (5)						
C–H(2)	0.98 (5)						
C–H(3)	0.86 (5)						
			Bond Angles				
Zr–X–Zr	147.8 (3)		134.87 (7)			152.6 (1)[a]	163 (2)
O–Al–O	98.0 (2)		98.6 (2)				94.4 (1)
Zr–O–Al	152.6 (2)	159.6 (2)	151.0 (2)	159.4 (2)	153.5 (2)		139.9 (1)
Cp–M–Cp	129.7	130.1	129.6	130.2	130.8	131.4	130.1
X–Zr–C(1)	113.2 (2)	113.5 (2)	117.7 (2)	118.4 (2)		122.8 (9)	113.9 (11)
Zr–C(1)–C(2)	163.6 (5)	166.6 (5)	162.8 (5)	164.9 (5)	166.4 (5)	160.2 (5)	162.5 (3)
H(1)–C–H(2)	119 (4)						
H(2)–C–H(3)	122 (4)						
H(3)–C–H(1)	117 (4)						
Zr–C–H(1)	74 (3)	80 (3)					
Zr–C–H(2)	99 (3)	111 (3)					
Zr–C–H(3)	81 (3)	93 (3)					

[a] X = O(B).

analogues along with characterization of its Me_2AlCl derivative (vida infra) supports its assignment as the unsubstituted ketene complex of zirconocene.

Preparation of II and III. The ketene dimer Ia reacts instantly at 25 °C with 1 equiv of Me_3Al in toluene to afford the adduct II (Scheme I). Complex II could not be isolated but was observed spectroscopically. The NMR spectra of II (Table VI) exhibit inequivalent cyclopentadienyl, ketene, and methyl resonances. The methyl resonances appear in the ^1H NMR as slightly broad singlets in a ratio of 2:1, indicating that these groups do not exchange at 25 °C on the NMR time scale. The inequivalent methyl groups also have different $^1J_{CH}$ coupling constants, 110.5 and 125.7 Hz (Table VI).

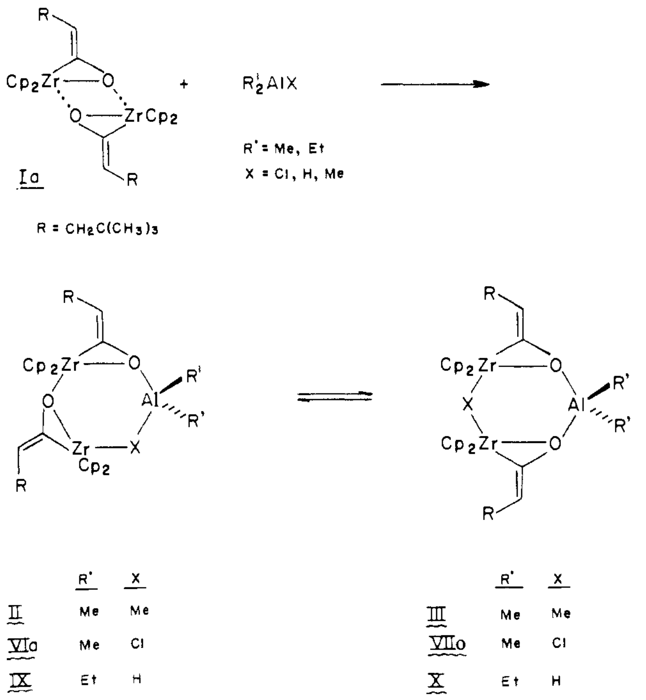
Complex II is unstable under vacuum; evacuating solutions of II regenerates the ketene dimer Ia and Me_3Al. Treatment of II with Lewis bases (Et_2O, THF, pyridine) generates Ia and the Me_3Al–Lewis base adduct. In toluene at room temperature, II slowly isomerizes to III in approximately 9 h at 25 °C (Scheme I). If II is formed in the presence of excess Me_3Al, the isomerization is faster, requiring approximately 1 h at 25 °C. Complex III does not react cleanly with excess Me_3Al, but does decompose faster in the presence of that reagent.

Complex III is a colorless crystalline compound that is stable at 25 °C in aromatic solvents but decomposes slowly ($t_{1/2}$ = 2.5 h) at 60 °C to unidentified products.

The NMR spectra of III exhibit equivalent cyclopentadienyl and ketene resonances along with inequivalent methyl resonances in a ratio of 2:1. The appearance of a sharp singlet at −9.24 ppm in the ^{13}C NMR spectrum implies that one of the methyl groups is no longer bonded to aluminum.[16] In addition, this methyl group exhibits an anomalously high $^1J_{CH}$ coupling constant of 136.2 Hz. Typical $^1J_{CH}$ coupling constants for terminally bound alkyl groups of zirconium fall in the range 116–120 Hz.

The details of the structure determination have been previously reported.[12] An ORTEP diagram of III with relevant bond angles and lengths is given in Figure 1. Additional bond angles and lengths are given in Table I. The structure reveals two zirconocene ketene monomers connected via nearly symmetric dialkylaluminum and methyl bridges. The zirconium atoms in III adopt pseudotetrahedral configurations if the Cp and ketene ligands are considered to occupy single coordination sites. The angles between the equatorial ligands, calculated from the midpoint of the C–O bond to the methyl C atom, average to 99.4°, similar to the angle of 95.6° reported for dimethylzirconocene.[17]

Scheme I



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[16] Aluminum has a large quadrupole moment, which often broadens the signal of bound nuclei in the NMR.

[17] Hunter, W. E.; Hrncir, D. C.; Bynum, R. V.; Pentilla, R. A.; Atwood, J. L. *Organometallics* **1983**, *2*, 750.

The bond angles and lengths of the ketene ligand are typical of those for structurally characterized zirconium ketene complexes.[4,18] As with other early transition-metal ketene complexes,[4,18,19] large M–C–C angles [163.6 (5)°, 166.6 (5)°], short M–C distances [2.187 (6), 2.182 (6) Å], and long C–O distances [1.398 (7), 1.413 (7) Å] point toward significant metallaoxirane character in the η^2-CO portion of the ketene ligand.[20] Due to the limited number of structurally characterized zirconium ketene complexes, it is difficult to assess the effect of the Lewis acid on the bonding properties of the ketene ligand. However, the C–O bond lengths of III are slightly longer than those of ketene complexes without coordinated Lewis acids.[21]

Coordination at aluminum is a distorted tetrahedron. The C(8)–Al–O angles are closest to typical tetrahedral values at 109.6 (3)° and 109.0 (2)°, but the C(8)–Al–C(8) angle is larger at 120.5 (3)° and the O(1)–Al–O(2) angle smaller at 98.0 (2)°. This type of coordination for aluminum has recently been observed by Atwood for $[AlMe_2(OPh)_2]$.[22] The Al–C distances of 1.948 (8) and 1.951 (8) Å are normal, but the Al–O distances of 1.818 (4) and 1.805 (4) Å fall on the short side of the range normally observed for O-bonded alkylaluminum complexes.[22]

A remarkable feature of the structure is the $Zr–CH_3–Zr$ bridge. The carbon atom adopts a distorted trigonal-bipyramidal configuration between the two zirconium centers. The positions of the hydrogen atoms (determined from a difference Fourier map and refined),[12] in conjunction with the high ${}^1J_{CH}$ coupling constant observed in the ${}^{13}C\{{}^1H\}$ NMR spectrum, suggest an sp^2-hybridized configuration for this methyl group. The H–C–H angles of 119 (4)°, 117 (4)°, and 122 (4)° are consistent with this formulation. Another unusual feature of the alkyl bridge is the large $Zr–C-H_3–Zr$ angle of 147.8 (3)°. Typical values for bridging alkyl groups are less than 90°.[23] The Zr–C bond lengths to the methyl group are not unusually long[25] but differ from one another by approximately 0.1 Å. This difference is reflected in the slight displacement (0.08 Å) of the carbon atom out of the hydrogen atom plane. The origin of this dissymmetry is unclear but might be attributed to crystal packing forces.

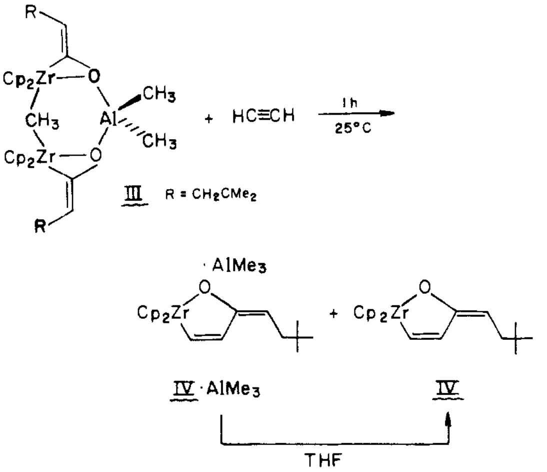
Reactivity of III. Treatment of III with pyridine (eq 3) regenerates the dimer Ia and the pyr·AlMe₃ adduct after 12 h at 25 °C.

$$\text{III} + \text{pyr} \rightarrow \text{Ia} + \text{pyr}\cdot AlMe_3 \qquad (3)$$

The stronger Lewis base 4-dimethylaminopyridine (DMAP) reacts rapidly (eq 4) with III to give two products by ${}^1H$ NMR. One product was spectroscopically characterized as the ketene·$AlMe_3$·DMAP adduct XI by comparison with the analogous Me_2AlCl adduct VIII (vide infra). The other product formed was assigned as the ketene·DMAP adduct XII.

$$\text{III} + 2\text{DMAP} \xrightarrow[25\ ^\circ C]{C_6D_6} \underset{\text{XI}}{[Cp_2Zr(OCCHCH_2CMe_3)\cdot AlMe_3\cdot \text{DMAP}]} + \underset{\text{XII}}{[Cp_2Zr(OCCHCH_2CMe_3)\cdot \text{DMAP}]} \qquad (4)$$

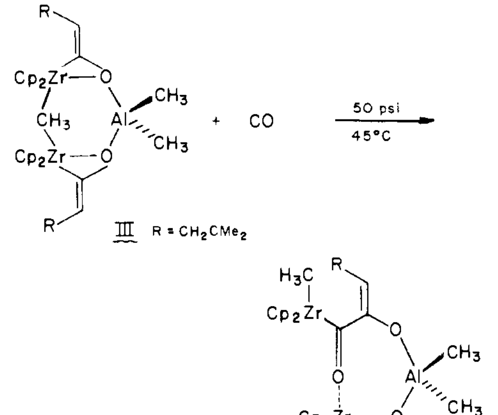
Treatment of III with excess acetylene in toluene yields IV and its adduct IV·$AlMe_3$ in nearly quantitative yield by ${}^1H$ NMR (eq 5). Performing the reaction in the presence of an equivalent of THF affords IV exclusively (under these conditions IV·$AlMe_3$ is converted to IV). This reaction is best run in the presence of a Lewis base to inhibit the polymerization of acetylene by $AlMe_3$.[26] The structure given for IV is supported by its spectral and analytical data. In particular, in the ${}^1H$ NMR spectrum, the exocyclic vinyl proton appears as a broad triplet of doublets with allylic coupling to the β-vinyl proton of 1.4 Hz.



(5)

Although III reacts cleanly with acetylene, it does not react with ethylene or substituted acetylenes under similar conditions.

Toluene solutions of III react after 3 h at 45 °C under 50 psi of carbon monoxide to afford the acyl complex V (eq 6). The structure of V was assigned on the basis of its ${}^1H$ and ${}^{13}C$ NMR, and IR spectra. The solution IR spectrum (C_6D_6) of V displays an absorption at 1440 cm⁻¹ that we assign as the acyl carbonyl stretching frequency. Such low carbonyl stretching frequencies have been observed previously for transition-metal acyl complexes coordinated to Lewis acids,[9b] thus suggesting that the acyl oxygen of V is coordinated to the other Lewis acidic zirconium center. The ${}^1J_{CH}$ coupling constant of 120 Hz for the zirconium methyl group implies that it occupies a terminal position.



(6)

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(21) CO bond lengths for representative complexes: $Cp_2{}^*Zr(py)(C,O\text{-}\eta^2\text{-}OCCH_2)$, 1.338 (2) Å;[4d] $[Cp_2Zr(CH_3)(C,O\text{-}\eta^2\text{-}OCCH_2)]^-Na^+\cdot 2THF$, 1.339 (9) Å;[4c] $(Cp_2ZrCl)_2(\eta\text{-}Ph_2PCH{=}CO)$, 1.330 (16) Å;[18d] 1.319 (10) Å;[18b] $(Cp_2ZrCl)_2(\mu\text{-}Me_2PCH{=}CO)$, 1.35 (2) Å;[18c] $Cp_2{}^*Zr(H)(C,O\text{-}\eta^2\text{-}OCCHPMe_3)$, 1.303 (3) Å; Moore, E. J. Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 1984.

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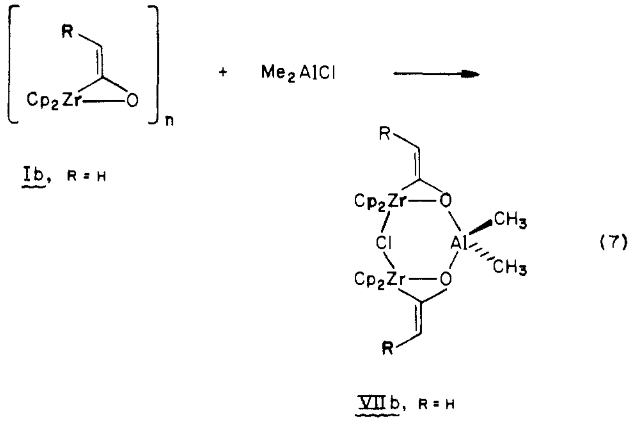
Preparation and Reactivity of VIa and VIIa,b. The stable zirconocene ketene dimer Ia reacts instantly with 1 equiv of Me_2AlCl in toluene to yield the isolable adduct VIa (Scheme I). Inequivalent cyclopentadienyl and ketene-ligand resonances in the ^1H and ^{13}C NMR spectra (Table VI) support its formulation as the Me_2AlCl-bridged adduct. This colorless crystalline compound undergoes slow thermal rearrangement (18–20 h, 25 °C) to the more symmetric complex VIIa. The rearrangement is catalyzed by Lewis bases such as THF or pyridine (instantaneous, 1 equiv, 25 °C). Treatment of the dimer Ia with $Me_2AlCl·THF$ etherate affords only VIIa (3 days, 25 °C); VIa is not observed by ^1H NMR. The dimer Ia reacts only with 1 equiv of Me_2AlCl as neither VIa nor VIIa react further with that reagent.

The unsubstituted complex VIIb can also be prepared from the oligomeric Ib (eq 7). Complex VIIb forms upon addition of Me_2AlCl to Ib (1 h, 25 °C). In this case, an intermediate adduct analogous to VIa was not observed.

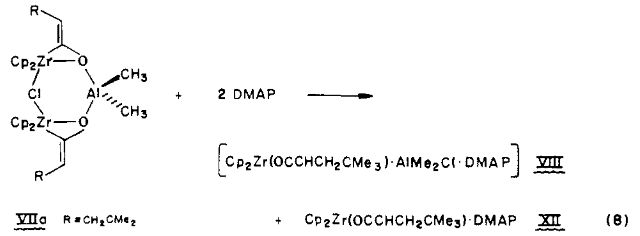


(7)

Complexes VIIa,b are colorless crystalline compounds that are stable indefinitely in aromatic solvents at 25 °C under an inert atmosphere. Complex VIIa slowly decomposes at 110 °C ($t_{1/2}$ = 4.5 h) to unidentified products.

X-ray quality crystals of VIIa were obtained by slowly cooling a toluene–pentane solution of VIIa. A summary of crystal and intensity data collection information is given in Table II, and fractional coordinates of non-hydrogen atoms are given in Table III. An ORTEP diagram of VIIa is given in Figure 2; selected bond angles and lengths are presented in Table I. The structure of VIIa is remarkably similar to that of III. The bond angles and lengths of the ketene ligands are very similar to those of III, as are the bond lengths and angles about the six-membered ring. The coordination about the chlorine atom is slightly different from that of the methyl group in III. The chlorine atom is bonded symmetrically between the two zirconium centers. The Zr–Cl bond distances are analogous to those of other bridging zirconium chloride complexes,[27] but the Zr–Cl–Zr angle is large at 134.87 (7)° (see Discussion). The Zr–Zr distance of 4.864 (1) Å is just slightly longer than that of III and implies little direct M–M interaction.

Complex VIa is stable in the presence of pyridine but reacts with 2 equiv of the stronger Lewis base 4-dimethylaminopyridine (DMAP) to afford the complex VIII (ca. 50% yield ^1H NMR) and another product which is apparently the ketene·DMAP adduct XII (eq 8). The structures of VIII and its $AlMe_3$ analogue XI (vide supra) were difficult to assign on the basis of spectral data. Analytical data on VIII indicates one DMAP and one Me_2AlCl molecule per zirconium. A solution molecular weight determination indicated a monomeric species. The appearance of two inequivalent methyl signals in a ratio of 6:3 in the ^1H NMR and



(8)

Table II. Summary of Crystal and Intensity Data Collection Information for VIIa, IX, and X

compd	VIIa	IX	X
formula	$C_{36}H_{50}Zr_2O_2AlCl$	$C_{38}H_{55}Zr_2O_2Al$	$C_{38}H_{55}Zr_2O_2Al$
mol wt	759.57	753.27	753.27
space group	$P2/c$	$C2/c$	$C2/c$
a, Å	10.2193 (14)	11.777 (5)	18.219 (2)
b, Å	20.237 (3)	19.998 (4)	10.3644 (9)
c, Å	18.458 (3)	32.636 (11)	20.273 (2)
β, deg	94.303 (14)	96.83 (5)	94.565 (8)
V, Å^3	3802.8 (10)	7632 (4)	3815.8 (7)
Z	4	8	4
λ, Å	0.7107	0.7107	0.7107
D_{calcd}, g cm^{-3}	1.33	1.31	1.21
cryst size, mm^3	0.06 × 0.18 × 0.34	0.01 × 0.28 × 0.76	0.35 × 0.30 × 0.25
μ, mm^{-1}	0.660	0.587	0.544
scan mode	θ–2θ	ω	ω
scan range, deg	2.0 (in 2θ) plus dispersion	1.0 (in ω)	1.0 (in ω)
reflectns	$+h, \pm k, \pm l$	$\pm h, \pm k, \pm l$	$\pm h, \pm k, \pm l$
collect.	8116	22163	9443
av	3567 ($3332 I > 0$) ($2596 I > 3\sigma I$)	4989 ($4369 I > 0$) ($3651 I > 3\sigma_I$)	2845 ($2845 I > 0$) ($1848 I > 3\epsilon_I$)

Table III. Atom Coordinates (×10^5) and U_{eq}'s (Å^2, × 10^4) in VIIa

	x	y	z	U_{eq}
Zr(1)	13 579 (6)	34 989 (3)	13 117 (3)	406 (1)
Zr(2)	−17 356 (6)	16 685 (3)	12 796 (3)	444 (1)
Cl	−2 579 (18)	26 353 (8)	18 368 (8)	566 (4)
Al	7 846 (21)	21 271 (9)	−1 288 (10)	498 (5)
O(A)	15 219 (40)	27 050 (18)	5 299 (19)	456 (10)
O(B)	−5 878 (42)	18 595 (20)	3 726 (20)	544 (11)
C(1A)	24 012 (65)	32 031 (28)	3 807 (32)	479 (16)
C(2A)	32 578 (71)	31 750 (30)	−1 196 (35)	597 (18)
C(3A)	42 169 (73)	37 100 (33)	−2 555 (35)	664 (20)
C(4A)	42 731 (97)	39 406 (42)	−10 246 (44)	836 (25)
C(5A)	45 807 (184)	34 014 (71)	−14 940 (67)	2 426 (65)
C(6A)	29 886 (163)	42 316 (83)	−12 693 (69)	2 245 (67)
C(7A)	52 776 (114)	44 885 (54)	−10 651 (53)	1 506 (41)
C(8A)	603 (86)	26 044 (38)	−9 801 (34)	845 (25)
C(1B)	−14 964 (60)	13 686 (30)	1 651 (34)	510 (18)
C(2B)	−15 864 (67)	10 656 (33)	−4 825 (34)	584 (19)
C(3B)	−25 662 (70)	5 364 (33)	−6 813 (37)	653 (20)
C(4B)	−34 583 (79)	6 665 (36)	−13 627 (40)	724 (22)
C(5B)	−26 884 (95)	7 217 (45)	−20 237 (43)	1 043 (30)
C(6B)	−42 687 (97)	12 868 (47)	−12 831 (49)	1 123 (31)
C(7B)	−43 853 (98)	858 (49)	−14 779 (48)	1 235 (33)
C(8B)	19 824 (80)	13 877 (35)	−2 322 (40)	818 (22)
C(11A)	9 792 (89)	46 347 (39)	8 241 (69)	951 (33)
C(12A)	2 161 (105)	45 934 (39)	14 224 (51)	906 (31)
C(13A)	−7 433 (81)	41 431 (38)	12 538 (47)	718 (24)
C(14A)	−6 330 (83)	39 047 (37)	5 632 (49)	734 (23)
C(15A)	4 285 (111)	42 074 (50)	2 881 (44)	917 (29)
C(21A)	22 338 (91)	37 969 (55)	25 642 (44)	847 (28)
C(22A)	24 375 (89)	31 309 (51)	25 226 (44)	797 (27)
C(23A)	33 241 (95)	30 181 (43)	20 045 (52)	820 (27)
C(24A)	36 965 (77)	36 324 (60)	17 521 (39)	789 (28)
C(25A)	30 131 (112)	40 841 (41)	21 029 (55)	904 (29)
C(11B)	−40 870 (85)	17 007 (54)	15 510 (69)	987 (33)
C(12B)	−41 192 (86)	16 927 (60)	8 269 (72)	1 027 (37)
C(13B)	−36 293 (105)	22 573 (72)	6 027 (57)	1 020 (35)
C(14B)	−32 524 (78)	26 507 (37)	12 046 (94)	1 070 (47)
C(15B)	−35 498 (91)	22 700 (63)	18 162 (50)	927 (30)
C(21B)	−17 533 (206)	8 962 (91)	23 309 (98)	1 478 (53)
C(22B)	−5 031 (213)	11 519 (49)	23 477 (74)	1 266 (51)
C(23B)	558 (98	9 183 (64)	17 920 (95)	1 059 (38)
C(24B)	−7 338 (175)	5 367 (48)	13 920 (52)	992 (34)
C(25B)	−18 709 (141)	5 126 (52)	16 990 (96)	1 120 (42)

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(27) Erker, G.; Kropp, K.; Atwood, J. L.; Hunter, W. E. *Organometallics* **1983**, *2*, 1555–1561 and references therein.

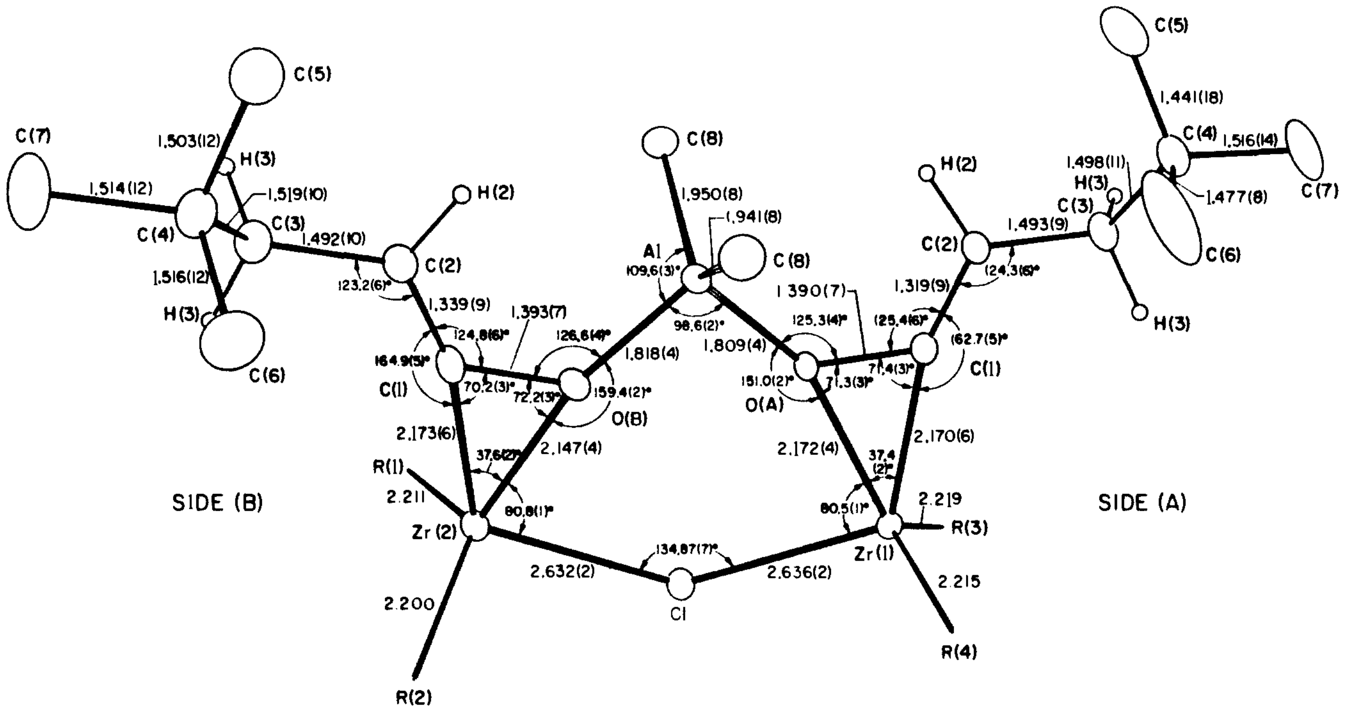
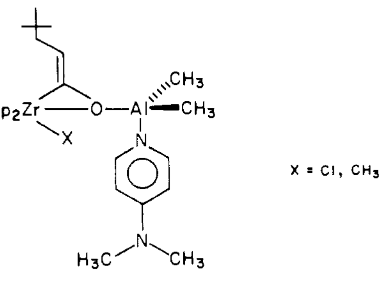


Figure 2. ORTEP diagram with selected bond lengths and angles for VIIa. Cyclopentadienyl rings are represented by their centroids R(1–4).

a methyl signal at 15.1 ppm in the ^{13}C NMR spectrum for the $AlMe_3$ adduct XI is consistent with the structure given below. Attempts to obtain crystals of VIII or XI suitable for an X-ray analysis are in progress.



In contrast to the μ-CH_3 complex III, the μ-Cl complex VIIa does not react with either acetylene or carbon monoxide. Solutions of VIIa in toluene-d_8 in sealed NMR tubes remain unchanged under several atmospheres of these reagents after weeks at 25 °C.

Preparation of IX and X. Complex Ia reacts instantly with Et_2AlH to afford the adduct IX (Scheme I). A broad resonance at −1.59 ppm, inequivalent cyclopentadienyl and ketene ligand resonances in the ^1H NMR spectrum (Table VI), and a broad absorption at 1800 cm^{-1} in the IR spectrum support its formulation as an adduct containing an Al–H–Zr bridge.[28]

Complex IX is a colorless crystalline compound that shows no tendency to isomerize in toluene at 25 °C. Crystals of IX were obtained from the concentrated pentane washings of the crude product IX. A summary of crystal and intensity data collection information is given in Table II. Fractional coordinates of non-hydrogen atoms are presented in Table IV. The bridging hydrogen atom was located from a difference map and refined.

The structure of IX (Figure 3) reveals a roughly planar six-membered ring formed from one Et_2AlH and two Zr ketene molecules. The bond angles and lengths of the ketene ligands are similar to those of the other three complexes. The Al–H and Zr–H distances are not unusual, but the C(1A)–Zr–H angle is slightly

Table IV. Atom Coordinates ($\times 10^5$) and U_{eq}'s (Å^2, $\times 10^4$) in IX

	x	*y*	*z*	U_{eq}
Zr(1)	604 (5)	21 049 (3)	37 890 (2)	436 (2)
Zr(2)	35 508 (5)	22 597 (3)	35 733 (2)	461 (2)
Al	19 868 (17)	36 560 (10)	38 966 (6)	537 (5)
O(A)	8 129 (32)	30 907 (18)	38 404 (11)	517 (11)
O(B)	18 015 (30)	19 335 (17)	36 367 (11)	408 (10)
C(1A)	−2 936 (49)	31 414 (29)	39 584 (17)	434 (17)
C(2A)	−7 421 (50)	37 010 (29)	40 699 (18)	469 (17)
C(3A)	−19 206 (52)	37 382 (30)	41 962 (18)	527 (18)
C(4A)	−20 623 (56)	41 095 (33)	45 956 (19)	547 (19)
C(5A)	−16 400 (70)	48 172 (40)	45 707 (23)	913 (26)
C(6A)	−33 071 (64)	41 250 (38)	46 540 (23)	857 (24)
C(7A)	−13 910 (74)	37 716 (46)	49 537 (22)	1 078 (35)
C(8A)	18 615 (78)	43 149 (37)	34 600 (31)	1 218 (38)
C(9A)	14 796 (107)	50 129 (55)	35 579 (38)	1 826 (51)
C(1B)	24 070 (48)	14 027 (29)	35 080 (15)	376 (19)
C(2B)	20 456 (51)	7 834 (30)	34 463 (17)	463 (17)
C(3B)	28 243 (55)	2 552 (30)	33 137 (18)	570 (19)
C(4B)	23 730 (73)	−1 739 (35)	29 380 (21)	735 (25)
C(5B)	20 265 (82)	2 482 (39)	25 688 (23)	1 099 (35)
C(6B)	13 440 (94)	−5 721 (42)	30 341 (26)	1 252 (37)
C(7B)	33 158 (88)	−6 536 (41)	28 553 (25)	1 241 (35)
C(8B)	23 951 (63)	38 662 (44)	44 838 (24)	1027 (29)
C(9B)	34 551 (102)	43 208 (47)	45 467 (30)	1 470 (41)
C(11A)	−2 462 (63)	18 235 (55)	30 308 (21)	775 (29)
C(12A)	−6 204 (74)	24 705 (42)	30 598 (21)	701 (25)
C(13A)	−15 863 (71)	24 469 (45)	32 635 (25)	780 (26)
C(14A)	−17 587 (63)	17 955 (55)	33 583 (25)	833 (28)
C(15A)	−9 295 (82)	14 056 (38)	32 189 (27)	810 (27)
C(21A)	−3 829 (129)	20 345 (47)	45 221 (27)	977 (34)
C(22A)	7 468 (96)	19 000 (54)	45 291 (23)	883 (34)
C(23A)	8 848 (90)	13 102 (56)	43 442 (28)	864 (29)
C(24A)	−1 614 (132)	10 733 (43)	42 069 (27)	1 003 (35)
C(25A)	−9 474 (75)	15 247 (76)	43 172 (34)	1 051 (36)
C(11B)	40 703 (70)	19 367 (88)	43 108 (26)	979 (38)
C(12B)	46 568 (123)	25 132 (56)	42 670 (37)	1 074 (38)
C(13B)	54 280 (82)	23 798 (66)	40 034 (38)	1 020 (36)
C(14B)	53 157 (86)	17 258 (67)	38 983 (28)	916 (32)
C(15B)	45 029 (105)	14 552 (43)	40 852 (39)	954 (34)
C(21B)	31 528 (124)	21 130 (66)	28 120 (23)	1 031 (40)
C(22B)	28 990 (77)	27 577 (70)	28 833 (26)	945 (31)
C(23B)	38 741 (122)	30 847 (43)	30 228 (27)	933 (29)
C(24B)	47 481 (83)	26 368 (84)	30 312 (29)	1 109 (37)
C(25B)	42 915 (144)	20 215 (66)	29 130 (35)	1 176 (39)
H[a]	3 054 (29)	3 168 (17)	3 750 (11)	9 (10)

[a] Hydrogen atom coordinates × 10^4, isotropic U × 10^3.

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(28) (a) Toogood, G. E.; Wallbridge, M. G. H. *Adv. Inorg. Chem. Radiochem.* **1982**, *25*, 267–341. (b) Wailes, P. C.; Coutts, R. S. P.; Weigold, H. "Organometallic Chemistry of Titanium, Zirconium, and Hafnium"; Academic Press: New York, 1974.

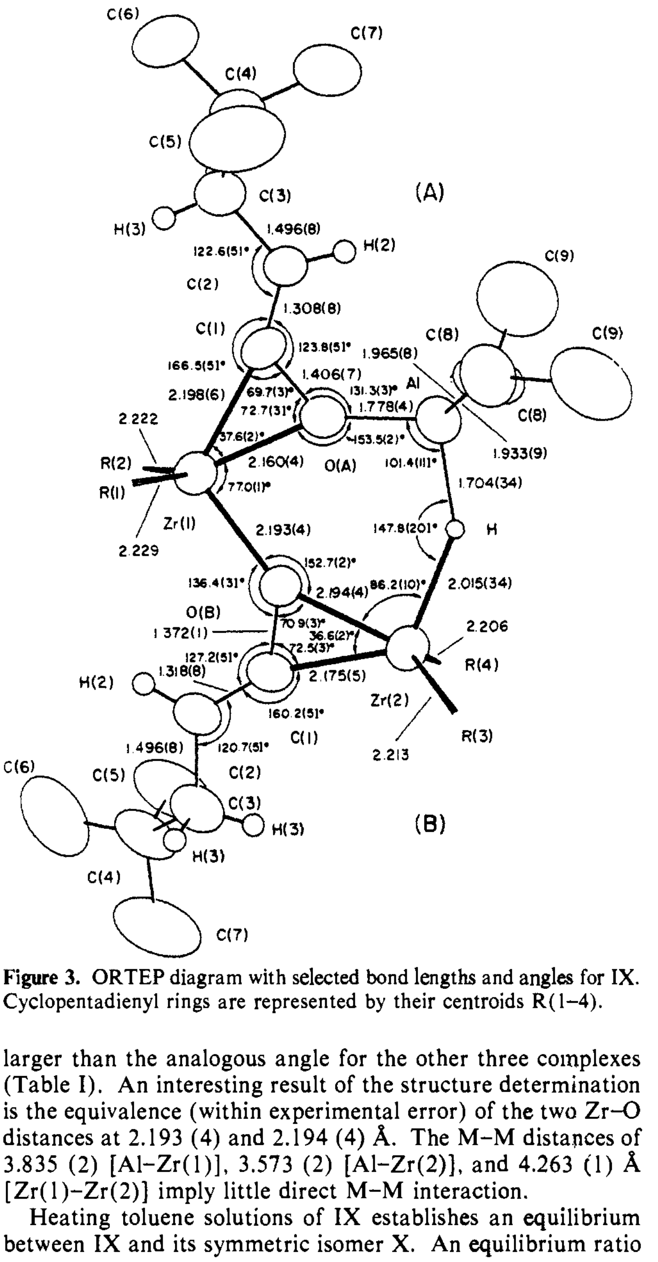

Figure 3. ORTEP diagram with selected bond lengths and angles for IX. Cyclopentadienyl rings are represented by their centroids R(1–4).

larger than the analogous angle for the other three complexes (Table I). An interesting result of the structure determination is the equivalence (within experimental error) of the two Zr–O distances at 2.193 (4) and 2.194 (4) Å. The M–M distances of 3.835 (2) [Al–Zr(1)], 3.573 (2) [Al–Zr(2)], and 4.263 (1) Å [Zr(1)–Zr(2)] imply little direct M–M interaction.

Table V. Atom Coordinates (×10^5) and U_{eq}'s (Å^2, × 10^4) in X

	x	y	z	U_{eq}
Zr	6 870 (2)	15 034 (4)	17 857 (2)	523 (1)
Al	0	45 893 (16)	25 000	447 (4)
O	1 700 (13)	34 024 (23)	18 745 (11)	462 (6)
C(1)	5 955 (19)	34 184 (41)	13 336 (18)	470 (11)
C(2)	6 470 (21)	43 920 (41)	9 236 (19)	530 (12)
C(3)	10 802 (24)	42 999 (45)	3 254 (20)	659 (13)
C(4)	16 717 (25)	53 033 (48)	2 415 (21)	661 (13)
C(5)	21 991 (35)	53 853 (76)	8 422 (34)	1 595 (28)
C(6)	20 374 (35)	50 513 (66)	−3 818 (30)	1 364 (23)
C(7)	13 284 (38)	65 893 (67)	1 762 (39)	1 541 (27)
C(8)	−8 840 (26)	55 803 (46)	22 158 (24)	803 (15)
C(9A)[a]	−10 786 (56)	67 442 (103)	25 787 (80)	814 (41)
C(9B)[a]	−8 543 (57)	67 659 (95)	18 967 (79)	1 086 (43)
C(11A)	15 682 (25)	20 262 (60)	27 649 (24)	725 (15)
C(12A)	16 267 (28)	7 038 (64)	26 597 (30)	889 (19)
C(13A)	19 394 (33)	5 337 (64)	20 634 (38)	1 017 (21)
C(14A)	20 586 (26)	17 158 (77)	17 999 (26)	930 (20)
C(15A)	18 393 (25)	26 410 (48)	22 311 (29)	721 (15)
C(11B)	2 134 (36)	10 778 (49)	6 086 (23)	790 (16)
C(12B)	7 815 (32)	2 161 (72)	7 624 (31)	941 (19)
C(13B)	5 548 (47)	−6 481 (56)	12 216 (35)	1 082 (24)
C(14B)	−1 508 (41)	−3 181 (62)	13 688 (28)	969 (20)
C(15B)	−3 569 (30)	7 548 (55)	9 905 (28)	778 (16)
H[b]	0	1 203 (39)	25 000	545 (141)

[a] Methyl group C(9) disordered, population 0.45 for following atoms: C(9A), H(81A), H(91A), H(92A), H(93A). [b] Atom coordinates (× 10^4).

Heating toluene solutions of IX establishes an equilibrium between IX and its symmetric isomer X. An equilibrium ratio of 1:1.35 (IX:X) is obtained upon heating isolated samples of IX or X at 100 °C overnight.

Compound X was isolated by washing IX away from a solid mixture of IX and X. Compound X is a colorless crystalline compound that exhibits equivalent cyclopentadienyl and ketene resonances and a sharp hydride resonance at −3.03 ppm in the ^{1}H NMR (Table VI). This compound is stable indefinitely in aromatic solvents at 25 °C; heating toluene solutions of X to 120 °C reestablishes the IX–X equilibrium but does not result in significant decomposition after several weeks.

Recrystallization of X from Et_2O–hexane affords X-ray-suitable crystals. A summary of crystal and intensity data collection is given in Table II and fractional coordinates of non-hydrogen atoms in Table V. An ORTEP diagram of X is given in Figure 5; selected bond lengths and angles are presented in Figure 4 and Table I.

Complex X crystallizes in space group $C2/c$ on a crystallographic $C2$ axis passing through the hydrogen and aluminum atoms. The bridging hydrogen atom was located from a difference

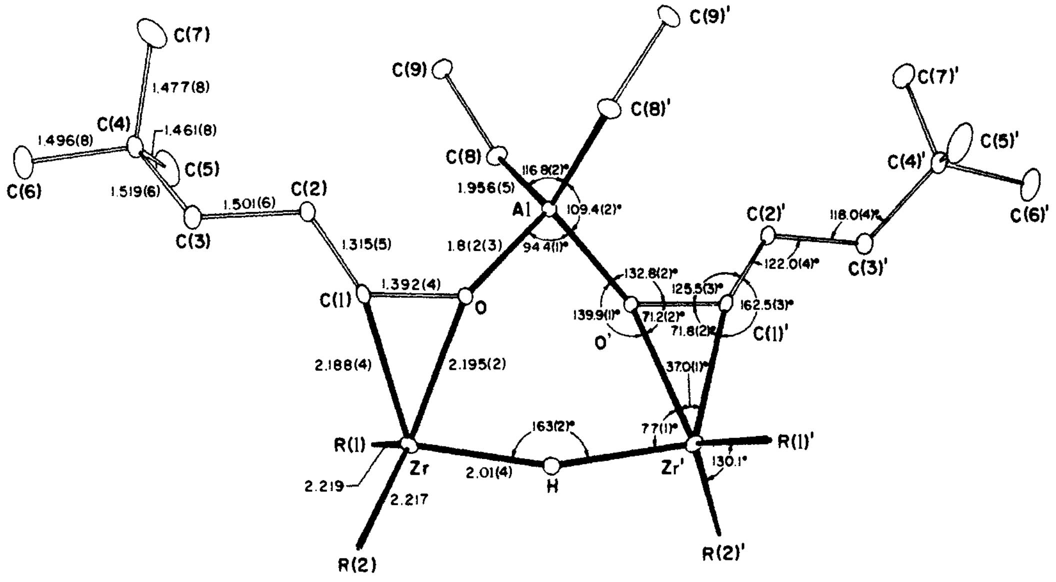

Figure 4. ORTEP diagram with selected bond lengths and angles for X. Cyclopentadienyl rings are represented by their centroids R(1,2). Like-numbered atoms are related by a C_2 axis.

Table VI. NMR Data[a]

	chemical shift, multiplicity, coupling constant	
assignment	^{1}H	^{13}C
	$(Z,Z)\text{-}\mathrm{(Cp_2Zr(OCCHCH_2C(CH_3)_3))_2}$ (Ia)	
$\mathrm{C_5H_5}$	5.88 s	109.0
$\mathit{OC}\mathrm{CHCH_2C(CH_3)_3}$		187.8 dt $^2J_{\mathrm{CH}} = 8.1$ $^3J_{\mathrm{CH}} = 8.1$
$\mathrm{OC}\mathit{CH}\mathrm{CH_2C(CH_3)_3}$	5.68 t $J = 7.3$	99.9 d $^1J_{\mathrm{CH}} = 146$
$\mathrm{OCCH}\mathit{CH_2}\mathrm{C(CH_3)_3}$	2.13 d $J = 7.3$	44.6 t $^1J_{\mathrm{CH}} = 127$
$\mathrm{OCCHCH_2}\mathit{C}\mathrm{(CH_3)_3}$		31.4 s
$\mathrm{OCCHCH_2C(}\mathit{CH_3}\mathrm{)_3}$	1.17 s	30.0 q $^1J_{\mathrm{CH}} = 124$
	$(Z,E)\text{-}\mathrm{(Cp_2Zr(OCCHCH_2C(CH_3)_3))_2}$ (Ia)	
$\mathit{C_5H_5}$	5.89 s	108.8
	5.82 s	109.3
$\mathit{OC}\mathrm{CHCH_2C(CH_3)_3}$		187.0 dt $^2J_{\mathrm{CH}} = 8.1$ $^3J_{\mathrm{CH}} = 8.1$
		185.2 dt $^2J_{\mathrm{CH}} = 11.0$ $^3J_{\mathrm{CH}} = 5.4$
$\mathrm{OC}\mathit{CH_2}\mathrm{C(CH_3)_3}$	5.59 t $J = 7.3$	101.0
	4.55 t $J = 7.3$	99.1
$\mathrm{OCCH}\mathit{CH}\mathrm{C(CH_3)_3}$	2.16 d $J = 7.3$	44.3
	2.14 d $J = 7.3$	44.3
$\mathrm{OCCHCH_2}\mathit{C}\mathrm{(CH_3)_3}$		31.8
		31.5
$\mathrm{OCCHCH_2C(}\mathit{CH_3}\mathrm{)_3}$	1.18 s	29.9
	1.16 s	29.8
	$\mathrm{(Cp_2Zr(OCCH_2))}_n$ (Ib)	
$\mathit{C_5H_5}$	5.84 s	109.4
$\mathit{OC}\mathrm{CH_2}$		*e*
$\mathrm{OC}\mathit{CH_2}$	5.25 s	87.1
	4.40 s	
	$\mathrm{(Cp_2Zr(OCCHCH_2C(CH_3)_3))_2(\mu\text{-}Al(CH_3)_3)}$ (II)[b]	
$\mathit{C_5H_5}$	5.84 s	108.8
	5.48 s	107.9
$\mathit{OC}\mathrm{CHCH_2C(CH_3)_3}$		187.3
		180.6
$\mathrm{OC}\mathit{CH}\mathrm{CH_2C(CH_3)_3}$	6.22 t $J = 7.3$	101.8 d $^1J_{\mathrm{CH}} = 146$
	5.67 t $J = 7.3$	99.5 d $^1J_{\mathrm{CH}} = 144$
$\mathrm{OCCH}\mathit{CH_2}\mathrm{C(CH_3)_3}$	2.20 d $J = 7.3$	45.5 t $^4J_{\mathrm{CH}} = 120$
	2.07 d $J = 7.3$	45.1 t $^1J_{\mathrm{CH}} = 122$
$\mathrm{OCCHCH_2}\mathit{C}\mathrm{(CH_3)_3}$		32.2
		32.1
$\mathrm{OCCHCH_2C(}\mathit{CH_3}\mathrm{)_3}$	1.21 s	30.7 q $^1J_{\mathrm{CH}} = 123$
	1.19 s	30.6
$\mathrm{Al(}\mathit{CH_3}\mathrm{)_2}$	−0.11 s	−6.9 q $^1J_{\mathrm{CH}} = 110.5$
$\mathrm{Zr}\mathit{CH_3}\mathrm{Al}$	−0.46 s	−16.2 q $^1J_{\mathrm{CH}} = 125.7$
	$\mathrm{(Cp_2Zr(OCCHCH_2C(CH_3)_3))_2(\mu\text{-}CH_3)(\mu\text{-}Al(CH_3)_2)}$ (III)	
$\mathit{C_5H_5}$	5.64 s	107.1 m $^1J_{\mathrm{CH}} = 171.3$
$\mathit{OC}\mathrm{CHCH_2C(CH_3)_3}$		178.3 d $^2J_{\mathrm{CH}} = 7.3$
$\mathrm{OC}\mathit{CH}\mathrm{CH_2C(CH_3)_3}$	6.05 t $J = 7.3$	102.1 d $^1J_{\mathrm{CH}} = 147.9$
$\mathrm{OCCH}\mathit{CH_2}\mathrm{C(CH_3)_3}$	2.14 d $J = 7.3$	44.9 t $^1J_{\mathrm{CH}} = 123.7$
$\mathrm{OCCHCH_2}\mathit{C}\mathrm{(CH_3)_3}$		31.6
$\mathrm{OCCHCH_2C(}\mathit{CH_3}\mathrm{)_3}$	1.14 s	30.0 q $^1J_{\mathrm{CH}} = 124.5$
$\mathrm{Zr}\mathit{CH_3}\mathrm{Zr}$	−0.19 s	−9.2 q $^1J_{\mathrm{CH}} = 136.2$
$\mathrm{Al(}\mathit{CH_3}\mathrm{)_2}$	−0.46 s	*c*
	$\mathrm{Cp_2\overline{ZrOC(CHCH_2C(CH_3)_3)CHC}H}$ (IV)	
$\mathit{C_5H_5}$	5.88 s	110 m $^1J_{\mathrm{CH}} = 170$
$\mathit{OC}\mathrm{(CHCH_2C(CH_3)_3)CHCH}$		167
$\mathrm{OC(}\mathit{CH}\mathrm{CH_2C(CH_3)_3)CHCH}$	4.89 td $^3J = 8.3$	103 d $^1J_{\mathrm{CH}} = 147$
$\mathrm{OC(CH}\mathit{CH_2}\mathrm{C(CH_3)_3)CHCH}$	2.21 d $^3J = 8.3$	42.9 t $^1J_{\mathrm{CH}} = 125$
$\mathrm{OC(CHCH_2}\mathit{C}\mathrm{(CH_3)_3)CHCH}$		32.3 s
$\mathrm{OC(CHCH_2C(}\mathit{CH_3}\mathrm{)_3)CHCH}$	1.10 s	29.7 q $^1J_{\mathrm{CH}} = 123$
$\mathrm{OC(CHCH_2C(CH_3)_3)}\mathit{CH}\mathrm{CH}$	7.05 d $^3J = 11.2$	*f*
$\mathrm{OC(CHCH_2C(CH_3)_3)CH}\mathit{CH}$	7.37 dd $^3J = 11.2$	187.9 d $^1J_{\mathrm{CH}} = 133$
	$\mathrm{Cp_2Zr(C^aH_3)C^bOC^c(C^dHC^eH_2C^f(C^gH_3)_3)OAl(C^hH_3)_2(Cp_2Zr(OC^iC^jHC^kH_2C^l(C^mH_3)_3))}$ (V)	
$\mathit{C_5H_5}$	5.85 s	108.4
	5.46 s	108.6
a	0.56 s	18.4 q $^1J_{\mathrm{CH}} = 120.1$
b		297.5 s
c		157 s
d	6.13 t	109
e	2.71 d	40.7 t $^1J_{\mathrm{CH}} = 123$
		31.5 s

Table VI (Continued)

		chemical shift, multiplicity, coupling constant	
assignment		^{1}H	^{13}C
g		1.05 s	29.9 q $^1J_{CH} = 124$
h		−0.53 s	−7.6 q $^1J_{CH} = 112$
i			183.9
j		6.11 t	99.8
k		2.29 d	44.8
l			31.2 s
m		1.15 s	29.7
$(\mathit{Z,Z})\mathrm{\text{-}(Cp_2Zr(OCCHCH_2C(CH_3)_3))_2(}\mu\mathrm{\text{-}ClAl(CH_3)_2)}$ (VIa)			
$\mathrm{C_5}\mathit{H}_5$		5.85 s	109.0
		5.67 s	*c*
$\mathit{OC}\mathrm{CHCH_2C(CH_3)_3}$			188.8 dt $^2J_{CH} = 7.3$ $^3J_{CH} = 7.3$
			183.3 dt $^2J_{CH} = 8.8$ $^3J_{CH} = 7.3$
$\mathrm{OC}\mathit{CH}\mathrm{CH_2C(CH_3)_3}$		6.16 t $J = 7.3$	103.4
		d	99.6
$\mathrm{OCCH}\mathit{CH}_2\mathrm{C(CH_3)_3}$		2.14 d $J = 7.3$	45.0
		2.07 d $J = 7.3$	44.7
$\mathrm{OCCHCH_2}\mathit{C}\mathrm{(CH_3)_3}$			31.9
			c
$\mathrm{OCCHCH_2C(}\mathit{CH}_3\mathrm{)_3}$		1.18 s	30.3
		1.16 s	30.0
$\mathrm{Al(}\mathit{CH}_3\mathrm{)_2Cl}$		−0.08 s	−6.49
$(\mathit{Z,Z})\mathrm{\text{-}(Cp_2Zr(OCCHCH_2(CH_3)_3))_2(}\mu\mathrm{\text{-}Cl)(}\mu\mathrm{\text{-}Al(CH_3)_2)}$ (VIIa)			
$\mathit{C_5H_5}$		5.77 s	109.1
$\mathit{OC}\mathrm{CHCH_2C(CH_3)_3}$			179.5 dt $^2J_{CH} = 8.8$ $^3J_{CH} = 7.3$
$\mathrm{OC}\mathit{CH}\mathrm{CH_2C(CH_3)_3}$		6.15 t $J = 7.3$	102.6
$\mathrm{OCCH}\mathit{CH}_2\mathrm{C(CH_3)_3}$		2.09 d $J = 7.3$	44.8
$\mathrm{OCCHCH_2}\mathit{C}\mathrm{(CH_3)_3}$			31.6
$\mathrm{OCCHCH_2C(}\mathit{CH}_3\mathrm{)_3}$		1.14 s	29.9
$\mathrm{Al(}\mathit{CH}_3\mathrm{)_2}$		−0.25 s	*c*
$(\mathit{Z,E})$-VIIa			
$\mathit{C_5H_5}$		5.79 s	109.5
		5.75 s	109.3
$\mathit{OC}\mathrm{CHCH_2C(CH_3)_3}$			178.8 dt $^2J_{CH} = 8.8$ $^3J_{CH} = 7.3$
			178.8 dt $^2J_{CH} = 8.8$ $^3J_{CH} = 5.9$
$\mathrm{OC}\mathit{CH}\mathrm{CH_2C(CH_3)_3}$		6.17 t $J = 7.3$	103.4
		4.74 t $J = 7.8$	103.3
$\mathrm{OCCH}\mathit{CH}_2\mathrm{C(CH_3)_3}$		2.47 d $J = 7.8$	45.4
		2.09 d $J = 7.3$	45.2
$\mathrm{OCCHCH_2}\mathit{C}\mathrm{(CH_3)_3}$			32.6
			32.1
$\mathrm{OCCHCH_2C(}\mathit{CH}_3\mathrm{)_3}$		1.14 s	30.5
		1.14 s	30.1
$\mathrm{(Cp_2Zr(OCCH_2))_2(}\mu\mathrm{\text{-}Cl)(}\mu\mathrm{\text{-}Al(CH_3)_2)}$ (VIIb)			
$\mathit{C_5H_5}$		5.70 s	109.5
$\mathit{OC}\mathrm{H_2}$			187.5
$\mathrm{OC}\mathit{H}_2$		5.78 d $J = 1.5$	90.0
		4.57 d $J = 1.5$	
$\mathrm{Al(}\mathit{CH}_3\mathrm{)_2}$		−0.21 s	*c*
$\mathrm{(Cp_2Zr(OCCHCH_2C(CH_3)_3))(C_7H_{10}N_2)(Al(CH_3)_2Cl)}$ (VIII)			
$\mathit{C_5H_5}$		5.95 s	109.3
$\mathit{OC}\mathrm{CHCH_2C(CH_3)_3}$			186.3
$\mathrm{OC}\mathit{CH}\mathrm{CH_2C(CH_3)_3}$		6.15 t	101.5
$\mathrm{OCCH}\mathit{CH}_2\mathrm{(CH_3)_3}$		2.26 d	44.9
$\mathrm{OCCHCH_2}\mathit{C}\mathrm{(CH_3)_3}$			31.7
$\mathrm{OCCHCH_2C(}\mathit{CH}_3\mathrm{)_3}$		1.20 s	30.1
$\mathrm{Al(}\mathit{CH}_3\mathrm{)_2}$		0.01	−7.7
$C_7H_{10}N$	CH	8.13 d	147.1
	CH	5.71 d	106.4
	C		155.3
	CH_3	1.92 s	38.1
$\mathrm{(Cp_2Zr(OCCHCH_2C(CH_3)_3))_2(}\mu\mathrm{\text{-}HAl(CH_2CH_3)_2)}$ (IX)			
$\mathit{C}_5\mathrm{H_5}$		5.76 s	108.5
		5.60 s	105.5
$\mathit{OC}\mathrm{CHCH_2C(CH_3)_3}$			188.1
			183.0

Table VI (Continued)

		chemical shift, multiplicity, coupling constant	
assignment		^{1}H	^{13}C
$OCC\mathit{H}CH_2C(CH_3)_3$		6.11 t $J = 7.3$	103.2
		d	100.7
$OCCH\mathit{CH}_2C(CH_3)_3$		2.21 d $J = 7.3$	45.6
		2.20 d $J = 7.3$	44.9
$OCCHCH_2\mathit{C}(CH_3)_3$			32.2
			32.0
$OCCHCH_2C(\mathit{CH}_3)_3$		1.23 s	30.7
		1.20 s	30.6
$\mathit{H}Al(CH_2CH_3)_2$		−1.59 s, br	−2.7
$HAl(CH_2\mathit{CH}_3)_2$		1.56 t $J = 7.8$	10.8
$(Cp_2Zr(OCCHCH_2C(CH_3)_3))_2(\mu\text{-}H)(\mu\text{-}Al(CH_2CH_3)_2)$ (X)			
$C_5\mathit{H}_5$		5.68 s	106.4
$\mathit{O}CCHCH_2C(CH_3)_3$			175.7
$OC\mathit{CH}CH_2C(CH_3)_3$		6.14 t $J = 7.3$	103.4
$OCCH\mathit{CH}_2C(CH_3)_3$		2.20 d $J = 7.3$	44.9
$OCCHCH_2\mathit{C}(CH_3)_3$			31.7
$OCCHCH_2C(\mathit{CH}_3)_3$		1.17 s	30.0
ZrHZr		−3.03 s	
$Al(\mathit{CH}_2CH_3)_2$		0.29 q $J = 7.8$	*c*
$Al(CH_2\mathit{CH}_3)_2$		1.55 t $J = 7.8$	10.1
$(Cp_2Zr(OCCHCH_2C(CH_3)_3))(C_7H_{10}N_2)(Al(CH_3)_3)$ (XI)			
$C_5\mathit{H}_5$		5.79 s	106.9
$\mathit{O}CCHCH_2C(CH_3)_3$			190.1
$OC\mathit{CH}CH_2C(CH_3)_3$		*d*	102.1
$OCCH\mathit{CH}_2C(CH_3)_3$		2.34 d $J = 7.3$	45.5
$OCCHCH_2\mathit{C}(CH_3)_3$			30.4
$OCCHCH_2C(\mathit{CH}_3)_3$		1.18 s	30.2
$Zr\mathit{CH}_3$		0.0 s, br	15.1
$Al(CH_3)_2$		−0.13 s, br	−8.5 br
$C_7H_{10}N_2$	CH	8.24 d $J = 5.7$	149.0
	CH	5.95 d $J = 5.7$	106.7
	CH_3	2.13	38.3
$(Cp_2Zr(OCCHCH_2C(CH_3)_3))\cdot(C_7H_{10}N_2)$ (XII)			
$C_5\mathit{H}_5$		5.75 s	106.5
$\mathit{O}CCHCH_2C(CH_3)_3$			186.2
$OC\mathit{CH}CH_2C(CH_3)_3$		4.88 d $J = 7.3$	99.9
$OCCH\mathit{CH}_2C(CH_3)_3$		2.88 t $J = 7.3$	44.6
$OCCHCH_2\mathit{C}(CH_3)_3$			31.7
$OCCHCH_2C(\mathit{CH}_3)_3$		1.35 s	30.1
$C_7H_{10}N_2$	CH	8.24 d $J = 5.7$	150.9
	CH	5.95 d $J = 5.7$	106.6
	CH_3	2.13 s	38.3

[a] ^{1}H (90 MHz) and ^{13}C (22.5 or 100.5 MHz) NMR spectra taken in benzene-d_6 at ambient temperature unless otherwise noted. Chemical shifts are reported in δ relative to Me_4Si or to residual protons/carbon in solvent. Coupling constants are reported in Hz. [b] ^{13}C NMR recorded in toluene-d_8 at −10 °C. [c] Not resolved at 22.5 MHz. [d] Not observed at 90 MHz. [e] Not resolved at 100.5 MHz. [f] Obscured by benzene solvent resonance.

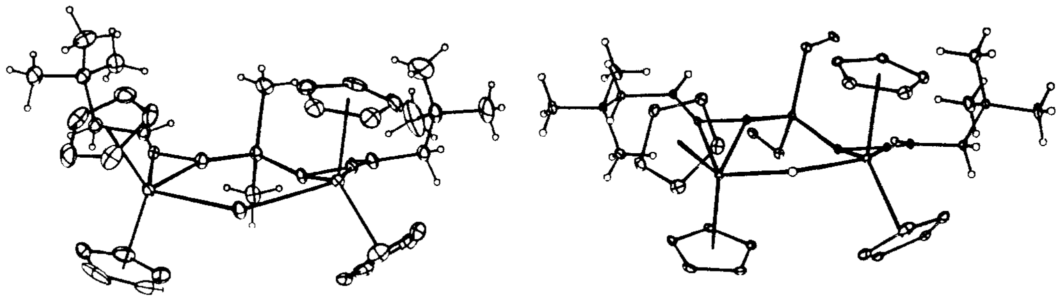

Figure 5. ORTEP diagram of VIIa and X.

map and refined (see Experimental Section).

The molecule adopts a puckered six-membered ring conformation similar to that in III and VIIa; however, the angles about the ring differ substantially from those of III and VIIa. In particular, the O–Al–O angle is approximately 4° smaller at 94.4 (1)° and the Zr–O–Al angle smaller by approximately 20° at 139.9 (1)°. The significance of these differences in ring conformation for X is considered in the Discussion.

The bond angles and lengths of the ketene ligands for X are symmetry related and analogous to those of III, IX, and VIIa. The Zr–H bond lengths of 2.01 (4) Å are normal for bridging hydrides of zirconium,[29,30] but the Zr–H–Zr angle is unusually large. Although typical M–H–M angles[31] are less than 140°, larger angles have recently been observed between Lewis acidic

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metal centers, particularly titanium,[32] zirconium,[33a] and aluminum.[33b]

The Zr–Zr distance of 3.975 (1) Å is long for any significant metal–metal interaction[27] but is substantially shorter than those observed for III or VIIa (see Discussion).

Complexes IX and X are thermally robust and chemically inert. They do not react under several atmospheres of CO or CO–H_2 mixtures, even at elevated temperatures. They are both stable in the presence of excess acetylene and do not react with excess Et_2AlH or with Lewis bases such as THF, pyridine, or dimethylaminopyridine.

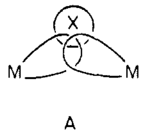
Discussion

Synthesis. The addition of alkylaluminum reagents to the ketene dimer Ia (Scheme I) has led to a family of alkylaluminum–ketene complexes with novel structural characteristics. This reaction sequence is surprisingly general and involves the formation of an adduct resulting from the addition of an Al–X bond into a Zr–O dative bond of the dimer. The μ-$AlMe_3$ adduct II is unstable under vacuum and could not be isolated. The complexes VIa and IX could be isolated and in the case of IX crystallographically characterized. The crystal structure of IX provides some indication why these intermediates do not react further with the aluminum reagent. From Figure 3, it can be seen that the cyclopentadienyl rings of Zr(1) and the hydrogen atom H(3) sterically inhibit attack at the Zr(1)–O(B) bond.

Thermal rearrangement of complexes II, VIa, and IX proceeds via transmetallation and migration of the X group (X = CH_3, Cl, H) to a symmetric, or nearly symmetric, position between the two zirconium centers. The mechanism of this transformation and the role of Lewis bases in the isomerization VIa → VIIa are still not well understood.

Structure. The structures of III, VIIa, and IX share several common features. The dialkylaluminum center is chelated by the oxygen atoms of two ketene ligands. The structural constraints of this chelation have a dramatic effect on the coordination environment of the bridging ligand X (X = CH_3, Cl, H). Two highly Lewis acidic zirconium centers are structurally disposed such that they are able to stabilize unusual coordination geometries for the bridging ligands. Two features of this coordination are noteworthy: the large M–X–M angles for these complexes and the hybridization of the methyl group in III.

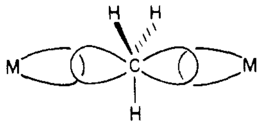
For the majority of transition-metal bridging chloride[27] and alkyl complexes,[23] M–X–M angles are less than 90°. For transition-metal bridging hydrides these angles can be larger[31] (angles up to 180° have been reported where one or both of the metals is aluminum)[33] but the vast majority prefer angles less than 140°. This preference for sharp M–X–M angles appears to be due to a tendency on the part of metal complexes to adopt a "closed" bonding configuration (A), where there is significant M–M overlap.[31] For the complexes reported here, large M–X–M angles (from 136° to 162°) and large Zr–Zr distances (from 3.6 to 4.8 Å) suggest that the bonding description for these bridging ligands is better described via an "open" bonding configuration (B).



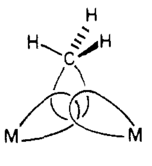
A

B

As a consequence of the large M–X–M angle, the methyl group of III is forced to adopt a trigonal-bipyramidal configuration between the two zirconium centers. We previously offered[12] a qualitative orbital bonding description for the methyl group as one involving a three-center two-electron bond utilizing a carbon p orbital as in C, which contrasts with the more typical bonding description D offered for the majority of bridging hydrocarbyl groups.



C



D

A trigonal-bipyramidal geometry for carbon[34-36] has recently been discussed theoretically for $CH_3Li_2^+$.[37] In addition, several examples have recently appeared in the literature,[38] particularly involving electrophilic metal centers, where large M–C–M angles imply a similar type of coordination for the bridging carbon atoms. A noteworthy example is the complex $[Zr_2Cp_4(\mu\text{-}CH_2CH_2)(ClAlEt_2)_2]$ prepared by Kaminsky et al.,[38a] where an ethylene group is coordinated between two zirconium centers.

The present work and the examples listed above suggest that this type of coordination for carbon may be general for metal centers where steric constraints disfavor a bonding mode as in D. The effects of this coordination on the reactivity of the alkyl ligand are unknown and warrant further investigation. The structure of III should be helpful in the development of bimetallic systems specifically designed to favor this type of coordination.

Model for Alkyl Transfer. Bridging ligands serve as structural models for intermediates in ligand-transfer processes. The methyl group of III represents an intermediate in an alkyl-transfer process that proceeds with inversion. Many bimolecular electrophilic substitution (S_E2) reactions proceed with retention of configuration at carbon,[39] but selected examples proceed with inversion.[40] The transfer of an alkyl group from an alkylcobalamine to a mercury(II) center has been shown to proceed with inversion.[41] This alkyl transfer undoubtedly proceeds through an intermediate or transition state of configuration similar to the methyl group of III.

In a more closely related system, III serves as a direct model for the proposed transition state that equilibrates the isomers of the aldehyde complexes prepared by Schwartz,[42] Erker,[43] and Floriani.[44] In this case, NMR studies on the chiral aldehyde complex indicated that the isomerization proceeds with inversion at the carbon center.[42a]

These results point out that alkyl transmetallations are likely to proceed with inversion[45] between metal centers where steric

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[34] In general, carbanions are believed to be tetrahedral[35] unless stabilized by delocalization.[36]

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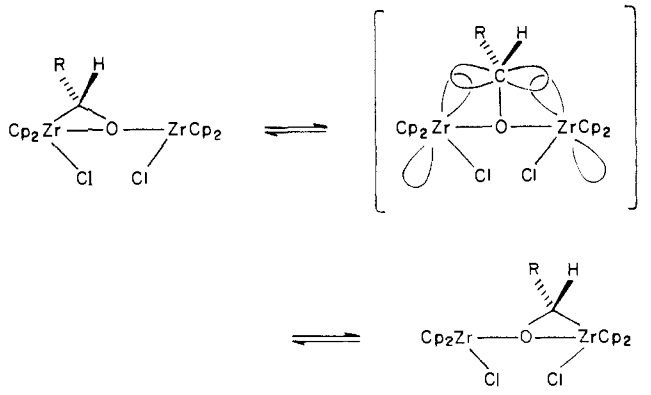
[44] (a) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1983**, *105*, 1690. (b) Fachinetti, G.; Floriani, C.; Roselli, A.; Pucci, S. *J. Chem. Soc., Chem. Commun.* **1978**, 269.

and electronic constraints disfavor a transition state analogous to D.



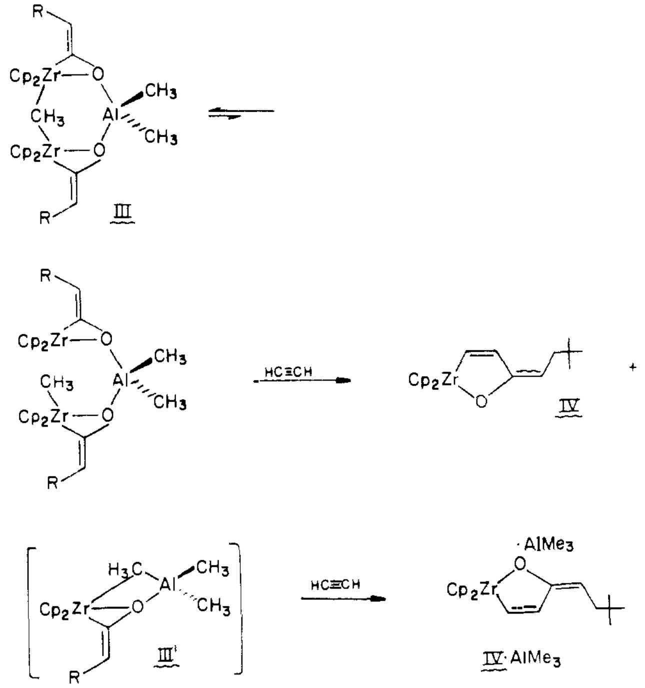
Structural Comparisons. The Zr–Zr distances of III, VIIa, and X appear to be influenced by the size of the bridging ligand. The chloride and methyl ligands are of similar size and the Zr–Zr distances of the complexes containing these ligands are correspondingly similar [4.864 (1) and 4.817 (1) Å, respectively]. For the hydride complex, where the bridging ligand is smaller, the Zr–Zr distance is approximately 0.9 Å shorter at 3.975 (1) Å. Larger M–X–M angles and smaller O–Al–O angles also appear to correspond with smaller bridging ligands and shorter Zr–Zr distances.

One feature of the hydride complex that may be a consequence of the shorter Zr–Zr distance is the amount of puckering in the six-membered ring (Figure 5). The degree of puckering is measured by considering the angles between the planes defined by the atoms of the ketene ligands [Zr, O, C(1), C(2), C(3)]. For III and VIIa, these angles are 21 (6)° and 22 (6)°, respectively. For X, this angle is much larger at 36 (5)°. We attribute the increased puckering of the ring in the hydride complex X to an increase in the nonbonded contacts between the Cp ligands on adjacent zirconium centers as the Zr–Zr distance decreases. To minimize nonbonded contacts between adjacent Cp ligands, the zirconium centers must twist with respect to each other, causing an increased distortion in the six-membered ring. As can be seen from Figure 5, the Cp ligands of VIIa are almost eclipsed, while those of X are staggered.

Reactivity. The complexes formed from the addition of alkylaluminum reagents to the ketene dimer Ia exhibit different reactivities depending on the bridging ligand X (X = CH_3, Cl, H). This difference in reactivity was first probed with Lewis bases. Of the initial adducts II, VIa, and IX, the μ-$AlMe_3$ complex II reacts with the mild Lewis base Et_2O to give Ia and $Me_3Al{\cdot}Et_2O$. Neither VIa nor IX react with Et_2O, but the μ-Cl VIa reacts instantly with the stronger Lewis bases THF or pyridine to give VIIa. The μ-H IX does not react with THF or pyridine. The symmetric complexes III, VIIa, and X are stable to Et_2O, but the μ-CH_3 compound III reacts slowly with pyridine (12 h, 25 °C) to yield the dimer Ia and pyridine·$AlMe_3$. In contrast, the μ-Cl VIIa and μ-H X are stable to pyridine. The μ-CH_3 III and μ-Cl VIIa complexes both react with 4-dimethylaminopyridine; the μ-H complex X does not. In contrast to the other reactions with Lewis bases, the product from the reactions of III and VIIa with DMAP is not the dimer Ia but the Lewis base adducts XI and VIII, respectively. Another product is apparently formed and, although not isolated, is assigned as the ketene DMAP adduct $Cp_2Zr(OCCHCH_2CMe_3){\cdot}DMAP$ XII.

The reactivity of complexes III, VIIa, and X toward unsaturated substrates is also sensitive to the nature of the bridging ligand. The μ-CH_3 compound III is the only one observed to react with unsaturated substrates. Group 4 ketene complexes react with a variety of unsaturated substrates including olefins, acetylenes,[4] aldehydes,[46] and organic ketenes.[19] An open coordination site is presumed to be a prerequisite for these insertion reactions. For the complexes described, it is likely that dissociation of the ligand bridge provides the necessary open coordination site. Dissociation of the chloride or hydride bridge is expected to be less facile than the methyl bridge,[47] and thus the reactivity of these compounds appears to reflect the lability of the bridging ligands with respect to dissociation. The results from the reactions with Lewis bases and unsaturated substrates allow the following order of reactivity to be established: μ-CH_3 (III) > μ-Cl (VIIa) > μ-H (X).

Scheme II



Treatment of the μ-CH_3 III with acetylene generates two products, the cyclic enolate IV and its Me_3Al adduct IV·$AlMe_3$. The reaction probably proceeds by cleavage of the methyl bridge followed by coordination and insertion of acetylene into one of the ketene ligands (Scheme II). Migration of the methyl group back to aluminum via an intermediate such as III′ results in a second acetylene insertion to generate IV·$AlMe_3$.

The formation of IV via III provides one route to the desired activation of the ketene dimer Ia (eq 2). Although low yield of IV (20% from Ia) limits the usefulness of this strategy, our results further demonstrate the effectiveness of using alkylaluminum reagents to coordinate and stabilize reactive organometallic species.[48]

Metal-bound ketene complexes have been proposed as intermediates in CO reduction processes.[1,2] Several homogeneous systems have been developed that model the production of metal-bound ketenes via the coupling of metal–methylenes and CO.[2,50] However, the reactivity of metal ketene complexes under Fischer–Tropsch conditions is less well investigated, particularly with regard to further carbon–carbon bond formation.[49-51]

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(45) We previously proposed a series of rapid transmetallations with inversion to account for stereochemical scrambling of the α-carbon of a titanacyclobutane upon treatment with Me_2AlCl: Ott, K. C.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 2942.

(46) Waymouth, R. M.; Pierre, L.; Grubbs, R. H. unpublished results.

(47) Although comparisons are difficult, alkyl bridges are more labile than chloride or hydride bridges in organoaluminum compounds. (a) Reference 26, p 32. (b) Eisch, J. J. in "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 1.

(48) For example, coordinated Me_2AlCl stabilizes the reactive $Cp_2Ti{=}CH_2$ species in the "Tebbe" reagent $Cp_2Ti{=}CH_2{\cdot}AlMe_2Cl$: (a) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. (b) Howard, T. R.; Lee, J. B.; Grubbs, R. H. *Ibid.* **1980**, *102*, 6876.

(49) Hydrogenolysis of ketene complexes yields aldehydes,[2c,50] alcohols[50] or metal enolates,[2a,b] and hydrolysis/alcoholysis yields the acetates,[2c] but in only one case has further C–C coupling been observed for a ketene intermediate.[51]

(50) Hermann, W. A.; Plank, J. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 525.

The carbonylation of III to IV models a key carbon–carbon bond forming step of a CO reduction sequence involving metal ketene intermediates. The insertion of CO into one of the ketene ligands is an unprecedented transformation for a metal-bound ketene complex[52] and may be due to the effect of the aluminum species in this system. Aluminum species have been used as cocatalysts in homogeneous CO reduction systems,[11] and aluminum oxides are widely used as catalyst supports in heterogeneous systems. However, the role of these supports in CO reduction is not well established.[53] Our results support the suggestion[53b] that these supports play an active role in promoting CO reduction.

A related observation concerns the relevance of reaction 6 to CO reduction over heterogeneous metal oxide catalysts.[54] Maruya et al.[54a] have shown that metal oxides of Groups 3, 4, and 5 are active Fischer–Tropsch catalysts. The Zr–O–Al–O–Zr structural framework of complexes III, VIIa, and X provides a homogeneous model for such surfaces, and the carbonylation of III models the insertion of CO into a metal oxide bound alkylidene.

Summary

We have demonstrated that the zirconocene ketene complex Ia reacts with a variety of alkylaluminum reagents to afford trinuclear bridging ketene complexes. Single-crystal X-ray diffraction studies of all three members of this series have provided useful structural comparisons of these molecules. The chelating arrangement of the aluminum atom and the ketene ligands provides a unique coordination environment for the bridging chloride, hydride, and methyl ligands. In particular, the methyl group of III represents a new coordination mode for carbon between metal centers. The trigonal-bipyramidal configuration of this methyl group models the transition state of transmetallation reactions that proceed with inversion. Despite the large number of transmetallation reactions observed between early transition metals, a clear picture of the stereochemistry of such reactions has not yet emerged.[8b,45] Our results imply that the stereochemistry of transmetallation reactions is highly dependent on the steric and electronic properties of the metal centers, and transmetallations with inversion can be the dominant pathway, especially at highly oxidized metal centers.

The reactivity of these molecules appears to be dominated by the availability of open coordination sites at the metal centers. For III, where an open coordination site becomes available by dissociating the methyl bridge, facile insertion reactions are observed. The reaction of III with CO models a key chain-carrying step in CO reduction processes over Lewis acidic and metal oxide catalyst surfaces. We are continuing to explore the reactivity of these complexes to determine the role of aluminum and early transition-metal complexes in CO reduction.

Experimental Section

General Considerations. All manipulations were carried out under argon with standard Schlenk techniques or in a nitrogen-filled glovebox equipped with a −40 °C freezer. Argon was purified by passage through columns of Chemalog R3-11 catalyst and Linde 4-Å molecular sieves. Toluene, benzene, diethyl ether, pentane, THF, and hexane, including NMR solvents, were stirred over CaH_2 and transferred onto sodium benzophenone ketyl. Solvents dried in this manner were vacuum transferred and stored under argon in flasks equipped with Teflon screw valves. Me_2AlCl was purchased from Texas Alkyls and was used neat or as prepared solutions in C_6D_6. Et_2AlH was obtained from Texas Alkyls as a 6% solution in heptane. Heptane was removed in vacuo to afford neat Et_2AlH, which was used without further purification. 2,2-Dimethyl-1-butene was obtained from Aldrich, distilled from CaH_2, and stored over molecular sieves. $NaN[Si(CH_3)_3]_2$ was prepared by refluxing freshly distilled $HN[Si(CH_3)_3]_2$ (Analabs) with NaH in toluene under argon for 24 h. Carbon monoxide (Matheson) and ^{13}C-labeled CO (99%, MRC-Mound) were used as received.

^1H NMR spectra were recorded in C_6D_6, $CDCl_3$, or C_7D_8 by using residual protiosolvent resonances as an internal reference on Varian EM-390, JEOL FX-90Q, JEOL GX400, or Bruker WM-500 spectrometers. ^{13}C spectra were obtained on the JEOL instruments. IR spectra were recorded as Nujol mulls or in solution in C_6D_6 on a Beckman IR-4240 or Shimadzu IR-435 instrument. Elementary analyses were performed at the California Institute of Technology Analytical Facility or by Dornis and Kolbe Microanalytical Laboratory. All reactions were carried out at room temperatures unless otherwise indicated.

Procedures. $[Cp_2Zr(C,O\text{-}\eta^2\text{-}OCCHCH_2CMe_3)]_2$ (Ia). This complex was prepared by the method of Straus.[4a] A mixture of 3.727 g (10.0 mmol) of the acyl complex $Cp_2Zr(Cl)C(O)CH_2CH_2C(CH_3)_3$[8b] and 1.880 g (10.0 mmol) of $NaN[Si(CH_3)_3]_2$ was dissolved in 75 mL of benzene. A gelatinous yellow mixture formed and was stirred for 2.5 h. The mixture was filtered through a pad of Celite on a coarse frit and washed repeatedly with benzene. The clear yellow filtrate was stripped of solvent and washed with two 15-mL portions of pentane to afford (*Z*,*Z*)-Ia as a pale yellow powder (2.476 g, 7.42 mmol). The washings were stripped of solvent to yield 0.425 g (0.60 mmol) of a yellow powder that was identified as (*Z*,*E*)-Ia by ^1H and ^{13}C NMR (80% purity by ^1H NMR): (*Z*,*Z*)-Ia IR (solution C_6D_6) 2950 (s), 2900 (s), 2860 (s), 1690 (w), 1620 ($\nu_{C=C}$, m), 1475 (m), 1460 (m), 1385 (m), 1360 (s), 1290 (w), 1250 (m), 1195 (w), 1085 (s), 1040 (vs), 1015 (vs), 990 (vs), 900 (m), 875 (m), 790 (s) cm^{-1}.

$[Cp_2Zr(C,O\text{-}\eta^2\text{-}OCCH_2)]_n$ (Ib).[4b] A mixture of 2.793 g (9.34 mmol) of the acyl $Cp_2Zr(Cl)C(O)Me$[14] and 1.737 g (9.47 mmol) of $NaN[Si(CH_3)_3]_2$ was suspended in 50 mL of toluene at −50 °C. A yellow suspension formed, was allowed to warm to room temperature, and stirred for 2 h. After the reaction mixture was allowed to settle overnight at −20 °C, the orange supernantant was cannulated off and the resulting off-white powder was washed with two 5-mL portions of toluene and one 5-mL portion of ether to yield 2.593 g of Ib as a 1:1 mixture with NaCl. This material was used without further purification: IR (Nujol) 2900 (s), 2850 (s), 1595 (m), 1530 (m), 1460 (m), 1375 (w), 1350 (w), 1075 (m), 1050 (m), 940 (s), 810 (s), 790 (s), 765 (s) cm^{-1}.

$[Cp_2Zr(C,O\text{-}\eta^2\text{-}OCCHCH_2CMe_3)]_2(\mu\text{-}AlMe_3)$ (II). To an NMR tube charged with Ia (21 mg, 0.031 mmol) at −40 °C was added 0.450 mL of a 0.067 M solution of Me_3Al in toluene-d_8. At −10 °C, the proton NMR spectrum indicated the immediate formation of II. The ^{13}C and $^{13}C\{^1H\}$ NMR spectra could be recorded before II began to isomerize to III by maintaining the probe temperature at −10 °C.

$[Cp_2Zr(C,O\text{-}\eta^2\text{-}OCCHCH_2CMe_3)]_2(\mu\text{-}AlMe_2)(\mu\text{-}Me)$ (III). The ketene dimer Ia (0.818 g, 1.226 mmol) in 8 mL benzene was treated with 0.12 mL (1.25 mmol) of neat Me_3Al via syringe. After the yellow solution was stirred for 8 h at 25 °C, the solvent was removed in vacuo to afford a waxy solid. This solid was washed with two 5-mL portions of pentane to give III as a white powder (0.517 g, 0.699 mmol). Crystals suitable for X-ray analysis[12] were obtained by the addition of 6 mL of pentane to 4 mL of a 0.17 M toluene solution of III. The resulting cloudy solution was quickly filtered through a pad of Celite on a fine frit and placed in a 10 °C refrigerator overnight to afford beautiful colorless needles of III: IR (Nujol) 2910 (vs), 2850 (vs), 1625 ($\nu_{C=C}$, m), 1460 (ν_{nuj}, s), 1382 (m), 1375 (ν_{nuj}, m), 1360 (s), 1325 (w), 1290 (w), 1260 (w), 1240 (w), 1195 (w), 1180 (m), 1165 (m), 1030 (m), 1010 (s), 970 (s), 900 (m), 870 (m), 800 (vs).

Anal. Calcd for $C_{37}H_{53}O_2AlZr_2$: C, 60.12; H, 7.23. Found: C, 59.99; H, 7.19.

Reaction of III with Pyridine. A 27-mg (0.037 mmol) sample of III was placed in a 5-mm NMR tube, dissolved in benzene-d_6, and capped with a rubber septum. To this solution was added 9.0 μL (0.112 mmol) of pyridine. After 12 h the NMR spectrum indicated complete formation of Ia (Table VI) and $Me_3Al{\cdot}pyr$ (−0.31 ppm, C_6D_6).

Reaction of III with 4-Dimethylaminopyridine. A 20-mg (0.027 mmol) sample of III was combined with 7 mg (0.057 mmol) of 4-dimethylaminopyridine and dissolved in C_6D_6. After 15 min the ^1H NMR indicated the formation of $Cp_2Zr(OCCHCH_2CMe_3){\cdot}AlMe_3{\cdot}DMAP$ XI and another product assigned as $Cp_2Zr(OCCHCH_2CMe_3){\cdot}DMAP$ XII.

$Cp_2\overline{ZrOC(CHCH_2CMe_3)CHCH}$ (IV). A 0.385-g (0.521 mmol) sample of III was weighted into a medium Schlenk tube and dissolved in 10 mL of benzene. To this yellow solution was added 0.05 mL (0.616 mmol) of THF. Argon was evacuated from the Schlenk tube and replaced with an atmosphere of acetylene that had been passed through a −78 °C trap (CAUTION: Purified acetylene is highly shock sensitive and explo-

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(51) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, V. W.; Vollmer, S. H.; Day, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 5393.

(52) Carbonylation of early transition-metal ketene complexes often leads either to decomposition or displacement of the ketene ligand with concomitant generation of the metallocene dicarbonyl: Meinhart, J. D.; Grubbs, R. H. unpublished results.

(53) (a) Roper M. In "Catalysis in Cl Chemistry"; Keim, W., Ed.; D. Reidel Publishing: Dordrecht, 1983; p 58. (b) Shriver, D. F. In "Catalytic Activation of Carbon Monoxide"; Ford, P. C., Ed.; American Chemical Society: Washington, DC, 1981; ACS Symp. Ser. No. 152, pp 1–19.

(54) (a) Maruya, K.; Inaba, A.; Maehashi, T.; Domen, K.; Onishi, T. *J. Chem. Soc., Chem. Commun.* **1985**, 487. (b) Saussey, J.; Lavalley, J-C.; Lamotte, J.; Rais, T. *Ibid.* **1982**, 278. (c) Wang, G.; Hattori, H.; Itoh, H.; Tanabe, K. *Ibid.* **1982**, 1256.

sive).[55] The clear yellow solution turned metallic green and then dark grey, suggesting the formation of polyacetylene. The reaction mixture was stirred for 1.5 h at 25 °C and filtered through a fine frit to yield a clear yellow solution. Removal of solvent in vacuo gave a waxy yellow solid that was washed with 5 mL of Et_2O and 5 mL of pentane to afford IV as a white powder (0.150 g, 0.417 mmol): IR (Nujol) 2900 (s), 2850 (s), 1610 ($\nu_{C=C}$, m), 1360 (m), 1285 (w), 1200 (w), 1190 (w), 1140 (w), 1040 (m), 1010 (m), 825 (m), 800 (s), 780 (m) cm^{-1}.

Anal. Calcd for $C_{19}H_{24}OZr$: C, 63.46; H, 6.73. Found: C, 63.44; H, 6.70.

Cp$_2$Zr(CH$_3$)COC(CHCH$_2$CMe$_3$)OAlMe$_2$[Cp$_2$Zr(C,O-η^2-OCCHCH$_2$CMe$_3$)] (V). A 20-mL benzene solution of III (1.014 g, 1.37 mmol) was placed in a glass pressure bottle, warmed to 45 °C in an oil bath, flushed twice with carbon monoxide, and pressurized to 50 psi with carbon monoxide. After being stirred for 2 h at 45 °C, the dark orange solution was transferred to a Schlenk tube. Solvent was removed in vacuo to afford a waxy orange residue. This residue was washed with three 5-mL portions of hexane to yield V as a light yellow powder (0.657 g, 0.856 mmol): IR (solution C_6D_6) 2950 (s), 2930 (s), 2860 (s), 2820 (m), 1610 ($\nu_{C=C}$, m), 1470 (m), 1440 ($\nu_{C=O}$, s), 1385 (w), 1360 (m), 1325 (w), 1285 (m), 1255 (w), 1240 (w), 1225 (w), 185 (s), 1150 (m), 1100 (w), 1090 (m), 1040 (s), 1015 (vs), 990 (vs), 900 (m), 800 (vs) cm^{-1}.

Anal. Calcd for $C_{38}H_{53}O_3Zr_2Al$: C, 59.49; H, 6.96. Found: C, 59.51; H, 6.89.

[Cp$_2$Zr(C,O-η^2-OCCHCH$_2$CMe$_3$)]$_2$(μ-AlMe$_2$Cl) (VIa). Me_2AlCl (0.074 mL, 0.796 mmol) was added dropwise via syringe to an 8-mL precooled (−40 °C), stirred toluene solution of Ia (0.530 g, 0.794 mmol). The yellow solution was allowed to warm to room temperature and was stirred for 30 min. Toluene was removed in vacuo and the resultant yellow waxy solid washed twice with 5 mL of hexane to give VIa (0.422 g, 0.555 mmol) as an off-white powder. Running the reaction (0.809 mmol of Ia) in 3.5 mL of toluene and slowly cooling to −50 °C afforded colorless crystals of VIa suitable for analysis (0.448 mmol, 55%): IR (solution C_6D_6) 2950 (s), 2900 (s), 2860 (s), 1710 (bw), 1620 ($\nu_{C=C}$, m), 1475 (m), 1460 (m), 1390 (m), 1360 (s), 1290 (w), 1260 (m), 1190 (m), 1150 (w), 1085 (m), 1070 (m), 1035 (s), 1015 (s), 990 (s), 900 (m), 875 (m), 810 (s), 790 (s) cm^{-1}.

Anal. Calcd for $C_{36}H_{50}O_2ClZr_2Al$: C, 56.93; H, 6.63; Cl, 4.67. Found: C, 56.97; H, 6.60; Cl, 4.65.

[Cp$_2$Zr(C,O-η^2-OCCHCH$_2$CMe$_3$)]$_2$(μ-AlMe$_2$)(μ-Cl) (VIIa). A solution of Ia (0.818 g, 1.23 mmol) in 30 mL of toluene was treated with 0.11 mL (1.18 mmol) of neat Me_2AlCl followed by 0.095 mL (1.18 mmol) of pyridine via syringe. After the pale yellow solution was stirred for 1 h, solvent was removed in vacuo and the pale yellow residue washed with two 5-mL portions of pentane to yield VIIa as a white powder (0.678 g, 0.893 mmol). Crystals suitable for X-ray diffraction were obtained by layering pentane onto a concentrated (0.3 M) toluene solution of VIIa and cooling slowly to −20 °C: IR (solution C_6D_6) 3100 (w), 2950 (s), 2900 (s), 2860 (s), 2820 (m), 1710 (w), 1670 (w), 1620 ($\nu_{C=C}$, m), 1595 (w), 1475 (m), 1460 (m), 1435 (m), 1385 (m), 1360 (s), 1290 (w), 1260 (m), 1180 (s), 1110 (m-br), 1095 (m-br), 1080 (m-br), 1060, 1030 (s), 985 (m), 970 (s), 900 (m), 875 (m) cm^{-1}.

Anal. Calcd for $C_{36}H_{50}O_2ClZr_2Al$: C, 56.93; H, 6.63; Cl, 4.67. Found: C, 56.95; H, 6.67; Cl, 4.75.

X-ray Structure Determination of [Cp$_2$Zr(C,O-η^2-OCCHCH$_2$CMe$_3$)]$_2$(μ-AlMe$_2$)(μ-Cl) (VIIa). A thin crystalline plate (0.057 × 0.184 × 0.342 mm) of VIIa was mounted approximately along *c* in a glass capillary under N_2. A series of oscillation and Weissenberg photographs indicated monoclinic symmetry and the space group $P2_1/c$ ($0k0$ absent for k odd, $h0l$ absent for l odd); data were collected on a locally modified Syntex $P2_1$ diffractometer with a graphite monochromator and Mo Kα radiation (λ = 0.7107 Å). The unit cell parameters (Table II) were obtained by least-squares refinement of the average 2θ values from 4 sets of 30 reflections: "$\pm 2\theta$" hkl and "$\pm 2\theta$" $\overline{hkl}$, $16 < 2\theta < 38°$. The three check reflections indicated some decomposition; the best least-squares fit was to a quadratic curve with a maximum decay of 6.8%. The correction for absorption was negligible (μ = 0.660 mm^{-1}, $0.80 < \mu l < 0.92$). The data were averaged over the Laue symmetry and reduced to F_o^2; the form factors for H are from Stewart et al. (1965) and the "International Tables for X-ray Crystallography" (1974) for the other atoms, and those for Zr, Cl, and Al were corrected for anomalous dispersion. The details of data collection are summarized in Table II.

The position of the two independent Zr atoms were derived from the Patterson map, and the Fourier map phased on these two atoms revealed the remainder of the structure. All H atoms were introduced into the model with fixed coordinates at idealized positions and isotropic U = 0.0756 Å^2. Least-squares refinement of the non-hydrogen atoms with anisotropic U_{ij}'s, minimizing $\sum w[F_o^2 - (F_c/k)^2]^2$, using all the data (3567 reflections) led to S = 1.48, R_F = 0.053, and R'_F = 0.073;[56] final shift/errors <0.10. The maximum deviations found in the $\Delta\rho$ map are close to the *tert*-butyl group in fragment A and are less than 0.4 e Å^{-3}. All calculations were carried out on a Vax 11/780 computer with the CRYRM system of programs.

[Cp$_2$Zr(C,O-η^2-OCCH$_2$)]$_2$(μ-Cl)(μ-AlMe$_2$) (VIIb). A suspension of Ib (0.358 g, 1.11 mmol of monomer) in 2 mL of toluene was treated with neat Me_2AlCl (0.05 mL, 0.538 mmol) dropwise via syringe. The resultant deep yellow solution was stirred 1 h, filtered through Celite on a medium frit, and evacuated to dryness. The slightly orange residue was washed with two 5-mL portions of pentane to yield VIIb as an off-white powder (0.130 g, 0.365 mmol). An analytical sample was prepared by crystallization from toluene at −50 °C for 3 weeks: IR (Nujol) 2900 (vs), 2850 (vs), 1615 ($\nu_{C=C}$, m, br), 1560 (m, br), 1180 (s), 1080 (s), 1010 (s), 905 (s), 800 (vs), 725 (s) cm^{-1}.

Anal. Calcd for $C_{26}H_{30}O_2AlZr_2$: C, 50.43; H, 4.88; Cl, 5.72. Found: C, 50.29; H, 4.79; Cl, 5.83.

[Cp$_2$Zr(C,O-η^2-OCCHCH$_2$CMe$_3$)](C$_7$H$_{10}$N$_2$)(AlMe$_2$Cl) (VIII). A 0.769-g (1.153 mmol) sample of Ia in 5 mL of toluene was treated with 0.10 mL (1.153 mmol) of neat Me_2AlCl via syringe. A solution of 0.422 g (3.460 mmol) of 4-dimethylaminopyridine in toluene was then added via cannula. The solution was stirred for 30 min at 25 °C and then evacuated to dryness. The resulting residue was redissolved in 25 mL of toluene, layered with 10 mL of Et_2O, and placed in the −50 °C freezer to give colorless microcrystals of VIII after 8 h (0.246 g, 0.449 mmol): IR (Nujol) 2900 (vs), 2850 (vs), 1630 (s), 1620 (s), 1550 (m), 1530 (w), 1500 (w), 1290 (w), 1260 (w), 1225 (m), 1180 (w), 1115 (vw), 1065 (m), 1030 (m), 1020 (s), 990 (m), 820 (m), 815 (s), 800 (6), 680 (s) cm^{-1}.

Anal. Calcd for $C_{26}H_{38}ON_2ClZrAl$: C, 56.96; H, 6.99; N, 5.11. Found: C, 56.99; H, 6.90; N, 4.97. Molecular weight (solution, C_6H_6)[57]. Calcd for $C_{26}H_{38}ON_2ClZrAl$: 548.4. Found: 554.9.

[Cp$_2$Zr(C,O-η^2-OCCHCH$_2$CMe$_3$)]$_2$(μ-HAlEt$_2$) (IX). Complex Ia (0.704 g, 1.055 mmol) was dissolved in 10 mL of toluene and treated with neat Et_2AlH (0.23 mL, 2.20 mmol) dropwise via syringe. The light yellow solution was stirred for 2.5 h and evacuated to dryness. Washing the residue with two 5-mL portions of pentane yielded IX as an off-white powder (0.320 g, 0.425 mmol). Recrystallization from Et_2O–hexane afforded colorless crystals suitable for analysis: IR (Nujol) 2800 (vs), 2870 (vs), 1800 ($\nu_{Zr-H-Al}$, w-br), 1620 (m) ($\nu_{C=C}$), 1360 (m), 1290 (w), 1230 (w), 1220 (w), 1195 (w), 1250 (w), 1040 (m), 1015 (m), 990 (m), 900 (m), 875 (m) cm^{-1}.

Anal. Calcd for $C_{38}H_{55}O_2Zr_2Al$: C, 60.59; H, 7.36. Found: C, 60.55; H, 7.28.

X-ray Structure Determination of [Cp$_2$Zr(C,O-η^2-OCCHCH$_2$CMe$_3$)]$_2$(μ-HAlEt$_2$) (IX). A crystal 0.01 × 0.28 × 0.76 mm of IX was mounted in a glass capillary under N_2. Oscillation and Weissenberg photographs indicated monoclinic symmetry and the space group $C2/c$ (hkl absent for $h + k$ odd, $h0l$ absent for l odd). Data were collected on an Enraf–Nonius CAD4 diffractometer with a graphite monochromator and Mo Kα radiation (λ = 0.7107 Å). The unit cell parameters (Table II) were obtained by least-squares refinement of the θ values for 25 reflections in the range $6.3 < \theta < 15.0$. A complete sphere of data was collected with $\theta \leq 45$, yielding 22163 reflections. Three check reflections, recollected after every 10000 s of exposure time, showed no significant deviations in their intensities. The data were averaged over the Laue symmetry and reduced to F_o^2. No decay or absorption corrections were deemed necessary. Form factors for H were taken from Stewart et al. (1975) and the "International Tables for X-ray Crystallography" for the other atoms; those for Zr and Al were corrected for anomolous dispersion.

The position of one of the independent Zr atoms was derived from the Patterson map, and the Fourier map phased on this atom revealed the other Zr atom, the Al atom, and several of the lighter atoms in the coordination spheres of the two Zr atoms. Further structure factor calculations and Fourier maps revealed the remainder of the structure, including the bridging H atom. The remaining H atoms were introduced into idealized positions after verifying their positions on a difference map. The H atoms (except for the bridging hydride atom) were given fixed isotropic U's = 0.063 Å^2. Least-squares refinement of all non-hydrogen parameters with anisotropic U's, the scale factor, and the coordinates and isotropic U for the bridging hydride H atom led to S = 2.80, R_F = 0.067, and R_F = 0.052;[56] final shift/errors <0.15. Two peaks of approximately

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(55) "Prudent Practices for Handling Hazardous Chemicals in Laboratories"; National Academy Press: Washington, DC, 1981.

(56) $R_F = \sum|F_o| - |F_c|/\sum|F_o|$, $S = [\sum_w\Delta^2/(n - v)]^{1/2}$, $R'_F = [\sum_w\Delta^2/\sum F_o^4]^{1/2}$, $w^{-1} = [s + r^2b + (0.02s)^2]k^4/(L_p)^2$, s = scan counts, r = scan-to-background time ratio, b = total background counts, k = 1.5539 (12) (scale factor on F_o), $\Delta = F_o^2 - (F_c/k)^2$, n = 3567, v = 379.

(57) Clark, E. P. *Ind. Eng. Chem., Anal. Ed.* **1941**, *13*, 820.

0.8 e Å^{-3} were found in the final difference Fourier map very near the methyl carbons of the diethylaluminum moiety. All other peaks were less than 0.6 e Å^{-3}. All calculations were carried out on a VAX 11/750 computer with the CRYRM system of programs.

$[Cp_2Zr(C,O-\eta^2-OCCHCH_2CMe_3)]_2(\mu-H)(\mu-AlEt_2)$ (X). A toluene solution of Ia (1.057 g, 1.58 mmol) was treated with several equivalents (0.400 mL, 3.77 mmol) of neat Et_2AlH. A deep yellow solution formed and was stirred for 24 h at 80 °C. Removal of solvent in vacuo afforded a dark brown waxy residue that was washed with four 15-mL portions of cold (−30 °C) hexane to yield X as a white powder (0.444 g, 0.589 mmol). The dark brown washings were evacuated to dryness, redissolved in toluene, and stirred at 80 °C for an additional 6 h. Workup in a similar manner provided an additional 0.094 g (0.125 mmol) of X. Recrystallization of 0.100 g of X from 5 mL of Et_2O–hexane (3/2) at −20 °C afforded crystals suitable for X-ray diffraction: IR (Nujol) 2800 (vs), 2750 (vs), 1630 (m) ($\nu_{C=C}$), 1630 (s), 1310 (m), 1290 (m), 1255 (w), 1195 (w), 1180 (w), 1155 (w), 1020 (m), 1110 (m), 975 (m), 940 (m), 900 (m), 875 (m), 820 (s), 780 (s) cm^{-1}.

X-ray Structure Determination of $[Cp_2Zr(C,O-\eta^2-OCCHCH_2CMe_3)]_2(\mu-H)(\mu-AlEt_2)$ (X). A crystalline block (0.35 × 0.30 × 0.25 mm) of X was mounted approximately along *a* in a glass capillary under N_2. A series of oscillation and Weissenberg photographs indicated monoclinic symmetry and the space group $C2/c$ (hkl absent for $h + k$ odd, $h0l$ absent for l odd); data were collected on a Enraf–Nonius CAD-4 diffractometer with a graphite monochromator and Mo Kα radiation (λ = 0.7107 Å). The unit cell parameters (Table II) were calculated from the setting angles of 25 reflections in the range $20 < 2\theta < 35°$. A total of 9443 reflections, comprising four symmetry-equivalent data sets, were averaged to give a total of 2845 reflections. The three check reflections, collected every 10000 s of exposure time, showed no significant deviations in their intensities. The correction for absorption was negligible (μ = 0.544 mm^{-1}). The form factors were taken from Table 2.2B, Vol. IV, "International Tables for X-Ray Crystallography" (1974) for all atoms.

The position of the Zr atoms was derived from the Patterson map, and the Fourier map phased on this atom revealed the remainder of the structure. All H atoms were introduced into the model with fixed coordinates at idealized positions and individual isotropic U's equal in magnitude to that of the adjacent heavy atom, plus 10–20%. Least-squares refinement of all non-hydrogen atoms with anisotropic U_{ij}'s, the scale factor, and the two parameters of the hydride H atom (y coordinate and U), minimizing $\sum_w[F_o^2 - (F_c/k)^2]^2$, with all the data (2845 reflections) led to $S = 1.76$, $R_F = 0.049$, and $R_{F'} = 0.033$;[56] final shift/errors <0.10. The maximum deviation found in the $\Delta\rho$ map is less than 0.8 e Å^{-3}. All calculations were carried out on a Vax 11/750 computer with the CRYRM system of programs.

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Supplementary Material Available: Atom labeling schemes (Figures 1–4), bond lengths and angles (Tables X1, X4, X8, X12), anisotropic Gaussian amplitudes (Tables X2, X6, X10), hydrogen atom coordinates (Tables X3, X7, X11), and structure factor amplitudes (Tables X5, X9, X13) (71 pages). Ordering information is given on any current masthead page.

Cyclization Reactions of Electrochemically Generated *o*-(3-Butenyl)phenyl Anions and Radicals to 1-Methylindan

Miles D. Koppang, Gerald A. Ross, Neil F. Woolsey, and Duane E. Bartak*

Contribution from the Department of Chemistry, University of North Dakota, Grand Forks, North Dakota 58202. *Received September 12, 1985*

Abstract: Phenyl anions are electrochemically generated upon direct reduction of bromobenzene at mercury and platinum electrodes. Phenyl radicals are the result of the homogeneous reduction of bromobenzene using an electron-transfer mediator, the *m*-tolunitrile radical anion, which is electrochemically generated. Homogeneous reduction of *o*-(3-butenyl)bromobenzene (**3**) by the above mediator results in appreciable intramolecular cyclization of an intermediate to yield a product ratio of 8:1 for 1-methylindan (**1**)/3-butenylbenzene (**2**). Direct electrochemical reductions of **3** result in product ratios of 2:1 and 1:1 for **1**/**2** on platinum and mercury, respectively. In contrast, direct electrochemical reduction of **3** in the presence of D_2O or 2-propanol-*d* significantly decreases these product ratios to 0.2:1 and 0.05:1 on platinum and mercury, respectively. Furthermore, the deuterium incorporation results are consistent with trapping of the *o*-(3-butenyl)phenyl anion prior to reaction to form **1**. Product ratios for **1**/**2** are unaffected by the presence of D_2O or 2-propanol-*d* when **3** is reduced by homogeneous electron transfer from the *m*-tolunitrile radical anion. Cyclization of the *o*-(3-butenyl)phenyl radical can be affected by the addition of the H atom donating species, sodium isopropylate. This allowed a minimum rate constant of 1×10^7 s^{-1} to be estimated for cyclization of the *o*-(3-butenyl)phenyl radical. These data are consistent with intramolecular cyclization of both the *o*-(3-butenyl)phenyl radical and the *o*-(3-butenyl)phenyl anion to produce **1**.

Elucidation of an organic reaction mechanism often requires the deployment of various trapping schemes in order to detect reactive intermediates. Detection of aryl radicals as intermediates in reductive aryl halide reactions[1,2] has been accomplished by trapping the radicals with various anionic nucleophiles.[3,4] The resultant radical anions can propagate the aryl halide reduction via homogeneous electron transfer in a catalytic process by the $S_{RN}1$ mechanism.[3-5]

Unimolecular trapping processes involving intramolecular cyclizations between a free radical and double bond have been demonstrated for 5-hexenyl radicals,[6,7] in particular for 1-

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(1) For a review on reductive aryl halide reactions, see: Hawley, M. D. "Encyclopedia of Electrochemistry of the Elements"; Bard, A. J., Lund, H., Eds.; Marcel Dekker: New York, 1980; Vol. XIV, Chapter 3. Chapter 1 reviews reductive acyclic aliphatic halides reactions.

(2) Holy [Holy, N. L. *Chem. Rev.* **1974**, *74*, 243–277] reviews homogeneous electron-transfer reactions of aromatic halides.

(3) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413–420 and references cited therein.

(4) Saveant, J. M. *Acc. Chem. Res.* **1980**, *13*, 323–329 and references cited therein.

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(6) (a) Lamb, R. C.; Ayers, P. W.; Toney, M. K. *J. Am. Chem. Soc.* **1963**, *85*, 3483–3486. (b) Walling, C.; Pearson, M. S. *J. Am. Chem. Soc.* **1964**, *86*, 2262–2266. (c) Garst, J. F.; Ayers, P. W.; Lamb, R. C. *J. Am. Chem. Soc.* **1966**, *88*, 4260–4261. (d) Garst, J. F. *Acc. Chem. Res.* **1971**, *4*, 400–406. (e) Jenkins, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 843–855 and references cited therein. (f) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317–323 and references cited therein.

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