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Synthesis and Characterization of Alkylidene-Bridged Zirconium–Aluminum Complexes

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Examples of the title complexes have been prepared through two complementary routes. Spectral analysis indicate that they are best formulated as Zr analogues of Tebbe's reagent, $Cp_2\overline{TiCH_2AlCl}Me_2$. Single-crystal X-ray diffraction analysis of $Cp_2\overline{ZrCH(CH_2\text{-}t\text{-}Bu)AlCl}(i\text{-}Bu)_2$ at −100 °C confirms this result: space group C_{2h}^5—$P2_1/n$ (No. 14), a = 19.779 (3) Å, b = 14.055 (3) Å, c = 9.086 (2) Å, β = 90.12 (2)°, V = 2526 (2) Å, and Z = 4. The final conventional and weighted agreement indices on F_o for 4306 reflections with $F_o^2 > 3\sigma(F_o^2)$ are 0.035 and 0.040. Both Zr and Al show pseudotetrahedral coordination. The Zr—C bond length, 2.158 (2) Å, indicates significant Zr═C bonding.

Introduction

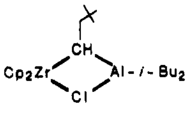
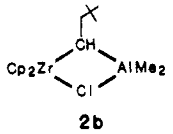
Alkylidene-bridged complexes of transition metals have been proposed as intermediates in several metal-catalyzed processes; a large number of such compounds have also been prepared, isolated, and studied with regard to stoichiometric reactions which they undergo.[1] Of these, as especially interesting example is the Tebbe compound[2] (**1a**), which serves as a starting point for studies of topics ranging from olefin metathesis[2-4] to novel "Wittig"-type reactivity with regard to carbonyl group containing organics.[2] In the latter context the "Tebbe reagent" has now been developed as a unique reagent in the repertory of the synthetic organic chemist,[5] and its ability and that of analogues[6-9] to methylenate esters or lactones has been exploited in a variety of interesting organic transformations.[10-12] Unfortunately, due to its mode of synthesis,[13] alkyl *chain* containing analogues of the "Tebbe" reagent have not been forthcoming with use of variations on the originally described synthetic scheme.

Tebbe's compound has been described as a organoaluminum-stabilized Ti carbene complex,[2,3] and reactions of note of this species have been discussed in terms of processes in which the organoaluminum residue of **1a** is either lost or removed, yielding a reactive Ti carbene compound.[3,4] The carbenoid nature of these compounds has been proposed but has not been demonstrated; due to CH_2, Cl disordering in **1b**, an analogue of **1a**, no meaningful structural analysis of this class of compounds has yet been obtained.[3] Zirconium compounds could behave in similar fashion to their Ti analogues, and details of structure of such alkylidene-bridged complexes, aimed at revealing the "carbenoid" nature of such species, are of general significance. In this paper we describe the first example of the preparation and structural characterization of a novel, long-chain alkylidene-bridged member of this class of compounds (**2**),[14] which demonstrate conclusively the carbenoid character of these species.

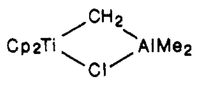
Results and Discussion

Attempts to prepare titanium-based long alkylidene chain bridged species from trialkylaluminum reagents fail due to formation of hydridic species.[15] An alternative route could involve the addition of a metal hydride to a metal alkenyl complex.[16] A reaction of this type was studied, but products could not be separated from Ti(III) byproducts.

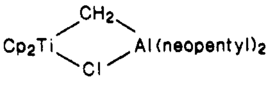
Table I. NMR Data for 2 Analogues of Tebbe's Reagent[a]

 **2a**	δ 7.02 (dd, $^3J_{HH}$ = 4.0, 11.4 Hz, 1), 5.78 (s, 5), 5.74 (s, 5), 3.18 (dd, $^3J_{HH}$ = 11.4, 14.9 Hz, 1), 2.79 (dd, $^3J_{HH}$ = 4.0, 14.9 Hz, 1), 2.15 (septet, $^3J_{HH}$ = 6.4 Hz, 2), 1.22 (d, $^3J_{HH}$ = 6.4 Hz, 12), 0.85 (s, 9), 0.40 (m, 4) [^{13}C δ 151 ($^1J_{CH}$ = 107 Hz)]
 **2b**	δ 6.96 (dd, $^3J_{HH}$ = 5.6, 8.9 Hz, 1), 5.74 (s, 5), 5.71 (s, 5), 3.07 (dd, $^3J_{HH}$ = 8.9, 15.0 Hz, 1), 2.84 (dd, J = 5.6, 15.0 Hz, 1), 0.87 (s, 9), −0.28 s, 6) [^{13}C δ 152]

[a] In C_6D_6.



1a



1b

Zirconium(IV) is considerably more stable than is Ti(IV) toward reduction to lower valent species. For example, the

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‡ Contribution No. 3636.

[1] For example, see: Holton, J.; Lappert, M. F.; Pearce, R.; Yarrow, P. I. W. *Chem. Rev.* **1983**, *83*, 135.

[2] Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611.

[3] Klabunde, U.; Tebbe, F. N.; Parshall, G. W.; Harlow, R. L. *J. Mol. Cat.* **1980**, *8*, 37.

[4] Howard, T. R.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 6876. Straus, D. A.; Grubbs, R. H. *Organometallics* **1982**, *1*, 1658.

[5] Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3270.

[6] Lombardo, L. *Tetrahedron Lett.* **1982**, 4293.

[7] Bruin, J. W.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *Tetrahedron Lett.* **1983**, 3935. Seetz, J. W. F. L.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 248.

[8] Buchwald, S. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 5490.

[9] Eisch, J. J.; Piotrowski, A. *Tetrahedron Lett.* **1983**, 2043.

[10] For example, see: Stevenson, J. W. S.; Bryson, T. A. *Tetrahedron Lett.* **1982**, 3143.

[11] Stille, J. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 1664.

[12] Chou, T.-S.; Huang, S.-B. *Tetrahedron Lett.* **1983**, 2169.

[13] Ott, K. C.; de Boer, E. J. M.; Grubbs, R. H. *Organometallics* **1984**, *3*, 223.

[14] Hartner, F. W., Jr.; Schwartz, J. *J. Am. Chem. Soc.* **1981**, *103*, 4979.

[15] Tebbe, F. N.; Guggenberger, L. J. *J. Chem. Soc., Chem. Commun.* **1973**, 227.

[16] Such Ti(IV) complexes are best made in CH_2Cl_2. For example, see; Waters, J. A.; Mortimer, G. A. *J. Organomet. Chem.* **1970**, *22*, 417.

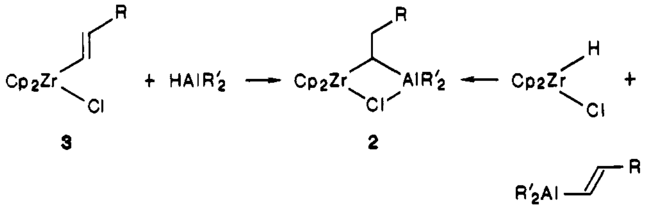
0276-7333/87/2306-1346$01.50/0

Table II. Summary of X-ray Diffraction Data

complex	$(\eta^5\text{-}C_5H_5)_2\overline{ZrCH[CH_2C(CH_3)_2]Al}Cl\text{-}[CH_2CH(CH_3)_2]_2$ (**2a**)
formula	$C_{24}H_{40}AlClZr$
fw	482.24
space group	C_{2h}^5—$P2_1/n$ (No. 14)
a, Å	19.779 (3)
b, Å	14.055 (3)
c, Å	9.086 (2)
β, deg	90.12 (2)
V, Å^3	2526 (2)
Z	4
ρ(calcd), g cm^{-3}	1.268
cryst dimens, mm	0.29 × 0.30 × 0.33
temp, °C	−100
radiatn	Mo Kα (0.71069 Å) from graphite monochromator
μ, cm^{-1}	5.75
absorptn correctn factors	0.84–1.13; average 0.99
2θ limits, deg	4.0–55.0
total no. of unique observns	6411
data, $F_o^2 > 3\sigma(F_o^2)$	4306
final no. of variables	271
R	0.035
R_w	0.040
error in observn unit wt, electrons	1.963

preparation of Zr(III) complexes from Cp_2ZrCl_2 requires the use of strong reducing agents such as alkali metals[17] whereas zinc, Grignard reagents, aluminum, and a variety of other reductants will readily transform Cp_2TiCl_2 into Ti(III) compounds.[18] Consequently the preparation of zirconium analogues of 1 was anticipated to be more facile than was that of their titanium counterparts.

Addition of 1 equiv of DIBAH to a benzene solution of chlorobis(cyclopentadienyl)(neohexenyl)zirconium (**3a**)[19] or addition of Cp_2ZrHCl to a solution of (neohexenyl)diisobutylaluminum gave a single product, **2a**, in essentially quantitative yield, which could be obtained as orange crystals. For this (and analogous) species, ^1H and ^{13}C NMR spectral analysis suggested a structural analogy with **1a** (see Table I). Other analogues of **2** could be obtained in similar fashion; however, as the steric bulk of substituents of the double bond decreased, isomeric products were also observed, and ^1H NMR spectroscopic analysis suggested the presence of a bimetallic (4) compound containing a bridging (ethylene) unit. In general, regioselectivity for formation of the bridged alkylidene species is higher when diisobutylaluminum hydride reacts with the alkenylzirconium compound than when the other mode of addition is utilized.



3

2

Description of the Structure of $Cp_2\overline{ZrCH[CH_2(t\text{-}Bu)]Al}Cl(i\text{-}Bu)_2$ (2a)

The crystal structure consists of the packing of four well-separated molecules in a cell having the dimensions shown in Table II. Selected bond distances and angles are listed in Table III, and non-hydrogen atom positional and equivalent isotropic thermal parameters are compiled in Table IV. Full non-hydrogen atom thermal parameters

Table III. Selected Distances (Å) and Angles (deg) and Estimated Standard Deviations

	Bond Distances		
Zr–C(1)	2.158 (2)	Zr–Cl	2.576 (1)
	Zr···Al	3.082 (1)	
Al–C(1)	2.087 (2)	Al–Cl	2.356 (1)
C(1)–C(2A)	1.444 (5)	C(1)–C(2B)	1.471 (5)
C(2A)–C(3)	1.629 (5)	C(2B)–C(3)	1.595 (5)
C(3)–C(4)	1.532 (3)		
C(3)–C(5A)	1.626 (6)	C(3)–C(5B)	1.383 (6)
C(3)–C(6A)	1.406 (6)	C(3)–C(6B)	1.622 (6)
Al–C(11)	1.970 (2)	Al–C(21)	1.977 (2)
C(11)–C(12)	1.528 (3)	C(21)–C(22)	1.538 (3)
C(12)–C(13)	1.512 (4)	C(22)–C(23)	1.500 (4)
C(12)–C(14)	1.514 (5)	C(22)–C(24)	1.522 (4)
Zr–C(31–35)	2.487–2.516 (3) (average 2.505 (3))		
Zr–C(41–45)	2.476–2.517 (3) (average 2.496 (3))		
C(31)–C(32)	1.390 (4)	C(41)–C(42)	1.311 (5)
C(31)–C(35)	1.410 (4)	C(41)–C(45)	1.336 (4)
C(32)–C(33)	1.371 (4)	C(42)–C(43)	1.356 (6)
C(33)–C(34)	1.385 (4)	C(43)–C(44)	1.417 (6)
C(34)–C(35)	1.384 (4)	C(44)–C(45)	1.381 (4)
	Bond Angles		
Cl–Zr–C(1)	90.69 (6)	Cl–Al–C(1)	98.89 (7)
Cl–Zr–3M[a]	105.0 (1)	Cl–Al–C(11)	109.06 (8)
Cl–Zr–4M[a]	105.5 (1)	Cl–Al–C(21)	106.21 (8)
C(1)–Zr–3M	107.6 (1)	C(1)–Al–C(11)	110.5 (1)
C(1)–Zr–4M	105.3 (1)	C(1)–Al–C(21)	111.7 (1)
3M–Zr–4M	124.3 (2)	C(11)–Al–C(21)	118.5 (1)
Zr–C(1)–Al	93.07 (9)	Zr–Cl–Al	77.20 (2)
Zr–C(1)–C(2A)	144.1 (2)	Zr–C(1)–C(2B)	146.0 (2)
Al–C(1)–C(2A)	108.3 (2)	Al–C(1)–C(2B)	108.0 (2)
C(1)–C(2A)–C(3)	116.5 (3)	C(1)–C(2B)–C(3)	117.0 (3)
C(2A)–C(3)–C(4)	110.5 (2)	C(2B)–C(3)–C(4)	108.7 (2)
C(2A)–C(3)–C(5A)	102.0 (3)	C(2B)–C(3)–C(5B)	117.3 (3)
C(2A)–C(3)–C(6A)	113.4 (3)	C(2B)–C(3)–C(6B)	103.3 (3)
C(4)–C(3)–C(5A)	108.2 (3)	C(4)–C(3)–C(5B)	110.4 (3)
C(4)–C(3)–C(6A)	112.7 (3)	C(4)–C(3)–C(6B)	105.7 (3)
C(5A)–C(3)–C(6A)	109.5 (4)	C(5B)–C(3)–C(6B)	110.7 (4)
Al–C(11)–C(12)	121.5 (2)	Al–C(21)–C(22)	120.4 (2)
C(11)–C(12)–C(13)	112.0 (3)	C(21)–C(22)–C(23)	112.3 (2)
C(11)–C(12)–C(14)	111.3 (3)	C(21)–C(22)–C(24)	111.7 (2)
C(13)–C(12)–C(14)	110.0 (3)	C(23)–C(22)–C(24)	110.3 (2)
C–C–C [C(31–35)]	106.8–109.1 (3)		
C–C–C [C(41–45)]	105.2–110.3 (3)		

[a] 3M and 4M = centroids of C(31–35) and C(41–45) rings, respectively.

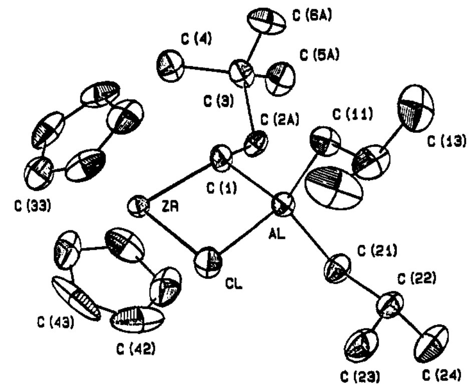


Figure 1. A perspective view of $Cp_2\overline{ZrCH(CH_2\text{-}t\text{-}Bu)Al}Cl(i\text{-}Bu)_2$ (**2a**). The vibrational ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Only one of the disordered neopentyl groups is included.

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[17] For example, see: Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1981**, *103*, 2687.

[18] Wailes, P. C.; Coutts, R. S. P.; Weigold, H. *Organometallic Chemistry of Titanium, Zirconium, and Hafnium*; Academic: New York, 1974.

[19] Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1979**, *101*, 3521.

Table IV. Positional Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
ZR	0.09909(1)	0.22059(2)	0.46305(3)	1.745(4)	C(14)	-0.1077(3)	0.0459(4)	0.1094(6)	7.2(1)
CL	-0.01459(4)	0.13156(6)	0.4498(1)	3.05(2)	C(21)	-0.0995(2)	0.3398(2)	0.3592(4)	2.71(7)
AL	-0.02917(4)	0.25512(6)	0.2774(1)	1.93(2)	C(22)	-0.1744(2)	0.3107(3)	0.3536(4)	2.69(6)
C(1)	0.0668(1)	0.3163(2)	0.2910(3)	2.34(6)	C(23)	-0.1883(2)	0.2225(3)	0.4417(5)	4.57(9)
C(2A)	0.0613(3)	0.4152(4)	0.2497(7)	2.0(1)	C(24)	-0.2205(2)	0.3912(3)	0.4027(5)	4.6(1)
C(2B)	0.0829(3)	0.3579(5)	0.1467(6)	2.3(1)	C(31)	0.1399(2)	0.1077(3)	0.2686(4)	4.19(8)
C(3)	0.1215(2)	0.4575(2)	0.1467(3)	2.39(6)	C(32)	0.1407(2)	0.0565(3)	0.3996(5)	4.19(8)
C(4)	0.1903(2)	0.4446(3)	0.2219(4)	3.09(7)	C(33)	0.1882(2)	0.0951(3)	0.4922(4)	4.30(9)
C(5A)	0.1039(3)	0.5705(5)	0.1443(8)	3.3(1)	C(34)	0.2181(2)	0.1710(3)	0.4202(5)	4.19(9)
C(5B)	0.0879(4)	0.5348(5)	0.2057(8)	3.5(2)	C(35)	0.1897(2)	0.1790(3)	0.2814(4)	3.82(8)
C(6A)	0.1205(4)	0.4218(6)	0.0021(8)	3.9(2)	C(41)	0.0537(2)	0.3490(3)	0.6280(5)	4.95(9)
C(6B)	0.1379(3)	0.4750(5)	-0.0261(7)	3.0(1)	C(42)	0.0473(2)	0.2701(4)	0.7040(5)	6.1(1)
C(11)	-0.0440(2)	0.1994(2)	0.0811(4)	2.81(7)	C(43)	0.1095(3)	0.2342(3)	0.7339(4)	7.1(1)
C(12)	-0.1087(2)	0.1450(3)	0.0440(4)	4.05(8)	C(44)	0.1572(2)	0.2982(3)	0.6728(4)	5.12(9)
C(13)	-0.1207(2)	0.1394(3)	-0.1202(5)	5.4(1)	C(45)	0.1191(2)	0.3691(3)	0.6079(4)	4.01(9)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

(Table V) and idealized hydrogen atom positions (Table VI) are available as supplementary material as is a listing of observed and calculated structure amplitudes.[20] Figure 1 contains a diagram of the molecule and includes the atom labels used in the text and tables. Only one of the disordered neopentyl orientations (vide infra) is included in Figure 1. Figure 2 shows both orientations of the disorder and is available as supplementary material.[20]

The neopentyl side chain of the neohexylidene ligand is disordered about a pseudomirror defined by the metallacyclic plane. The two orientations are equally populated. The positions of C(1), C(3), and C(4) are common to both orientations and have been given full weight while A and B components of atom C(2), C(5), and C(6) have been included at 50% occupancy and successfully refined. The model is inadequate as nonrepresentative bond distances, e.g., C(2A)–C(3) = 1.629 (6) Å and C(3)–C(6B) = 1.622 (6) Å, are observed. These probably result from inclusion of only a single atom for C(3), but little additional information is expected from a more sophisticated model and none has been forthcoming. A consequence of the disorder is the lack of definition of the alkylidene hydrogen atom, HC(1), whose position might have been informative as to the nature of the Zr–C(1)–Al bonding. This disorder may also result in the large thermal parameters observed, e.g., those of the *i*-Bu methyl carbon atoms and those of ring 4, and in the associated nonrepresentative distances, e.g., C(41)–C(42) = 1.311 (5) Å. Dynamic disorder of these relatively unconstrained units, even at −100 °C, could also produce the apparent vibrational motion. Despite these difficulties, bonding information is available from the metrical details of the metallacyclic system.

The Zr atom adopts the expected pseudotetrahedral wedge structure with the Cl–Zr–C(1) plane bisecting the Cp(3)–Cp(4) dihedral angle. The parameters of the Cp_2Zr fragments are unexceptional, as is the pseudotetrahedral coordination about the Al center. The Zr–C(1)–Al–Cl ring is almost planar; the largest displacement from the best plane is 0.03 Å for C(1).

The most striking feature in the structure is the short Zr–C(1) distance, 2.158 (2) Å, which reflects a major contribution to the bonding in the title complexes from form A. This is consistent with the alkylidene-like deshielding of the α-proton in the ^1H NMR spectra described above. Three equivalent short Zr–C bonds have recently been reported for the complexes $Cp_2ZrClCHPPh_3$[21] [2.152 (8) Å], $\{[Zr(\mu\text{-}CPMe_3)[(CH_2)_2PMe_2]_2\}_2$[22] [2.158 (4) Å], and $\{ZrCHSiMe_2NSiMe_3[N(SiMe_3)_2]\}_2$[23] [2.16 (2) Å]. The first two complexes certainly involve Zr–C double-bond character while in the third the short Zr–C distance is ascribed to contraction of the metal's radius resulting from the relatively low coordination number. An alternative bonding description in which alkylidene units bridge two Zr atoms was disfavored by the authors but cannot be excluded. For comparison, $d[Zr–C(sp^3)]$ in $Cp_2ZrX(alkyl)$ complexes have been reported in the range 2.25–2.20 Å.[24] Zirconium–carbon (sp^2) bond lengths of 2.18–2.20 Å have been observed for zirconocene complexes of η^2-acyl, ketene, and enolate complexes.[25-27] Delocalized bonding schemes incorporating Zr–C bonds of order greater than one have been advanced for these complexes. The contribution to the bonding in complex **2a** from form A is also evident in the unusually large Zr–C(1)–C(2A,2B) angles, which average 145°. Schrock has commented extensively on the distended angles observed in terminal alkylidene complexes.[28] In zirconocene–hydrocarbyl complexes Zr–C–X ($X \neq H$) angles range from 117 to 143°.[24] The anomalously large value of 142.7 (5)° is reported for $Cp_2Zr(CH_2CMe_3)_2$,[29] in which nonbonded repulsions involving

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[20] See paragraph at end of paper regarding supplementary material.

[21] Baldwin, J. C.; Keder, N. L.; Strouse, C. E.; Kaska, W. C. *Z. Naturforsch., B: Anorg. Chem. Org. Chem.* **1980**, *35B*, 1289–1297.

[22] Rice, G. W.; Ansell, G. B.; Modrick, M. A.; Zentz, S. *Organometallics* **1983**, *2*, 154–157.

[23] Planalp, R. P.; Andersen, R. A.; Zalkin, A. *Organometallics* 1983, 2, 16–20.

[24] See for examples ref 14 of ref 23.

[25] Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1977**, 1946–1950.

[26] Bristow, G. S.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1982**, 462–464. Moore, E. J.; Straus, D. A.; Armantrout, J.; Santarsiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2068–2070.

[27] Ho, S. C. H.; Straus, D. A.; Armantrout, J.; Schaefer, W. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 2211–2213. Waymouth, R. M.; Santarsiero, B. D.; Grubbs, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 4050–4051.

[28] Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98–104.

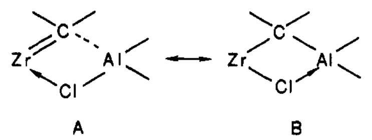
the bulky t-Bu group are severe. Angles of ca. 160° are reported for η^2-acyl, ketene, and enolate complexes.[25-27]

The Zr–Cl bond length, 2.576 (1) Å, is longer than that observed in Cp_2ZrClX complexes, 2.42–2.46 Å,[24] as predicted from form A. We are aware of no structurally characterized Cp_2Zr^{IV} complexes that contain simple bridging chloride ligands. The two coordination complexes that have such bridging atoms are $(Zr(\mu\text{-}Cl)Cl_2[P(n\text{-}Bu)_3]_2)_2$[30] and $[(\eta^6\text{-}C_6Me_6)Zr(\mu\text{-}Cl)_2]_3[Al_2Cl_7]_2$,[31] which have Zr–Cl(bridge) distances of 2.54–2.56 Å. Both of these complexes contained reduced Zr, and we expect Zr(IV) bridge bonds to be shorter. The structures of $ZrCl_4$ shows two bridging Zr–Cl lengths 2.498 (2) and 2.655 (2) Å.[32] Unusually long Zr–Cl bonds have been observed in bridges to Al in the complexes $Cp_2ZrC_2H_3(AlEt_2)_2Cl$ (2.60 Å) and $[Cp_2ZrClAlEt_2]_2C_2H_4$ (2.40 Å).[33]

The endocyclic bond lengths about the Al center are also of interest, although they are not definitive in regard to the bonding mode. The Al–C(1) distance, 2.087 (2) Å, is markedly longer than the terminal Al–C(11,12) distances, 1.970 (2) and 1.977 (2) Å, consistent with form A. A distance of 1.917 (3) Å has been observed in the methylene-bridge complex $Al_2(\mu\text{-}CH_2)Cl_4{\cdot}OEt_2$ in which an sp^3-carbon bridge is present.[34] The value in **2a** corresponds reasonably to the bridging Al–C(sp^2) data reported for $Al_2(c\text{-}C_3H_5)_6$ (2.087 (8) Å)[35] and $Al_2(\mu\text{-}CH{=}CH\text{-}t\text{-}Bu)_2(i\text{-}Bu)_4$ (2.11 Å).[36] Unfortunately the C/Cl disorder in $Cp_2\overline{TiCH_2AlCl}(neopentyl)_2$[3] prohibits meaningful comparison with **2a**. Churchill, Schrock, and co-workers have observed a bridging Al–C bond length of 2.223 (6) Å in the methylidyne complex $W({\equiv}CHAlMe_{2-x}Cl_x)Cl(PMe_3)_3$.[37] Aluminum to sp^3-carbon bridge bond lengths in alkyl-bridged complexes are also long: 2.124 (2) Å in Al_2Me_6.[38]

The Al–Cl bond, 2.356 (1) Å, is surprisingly long on the basis of form A. In supported Al–Cl–M, where M = a transition or a lanthanide metal, Al–Cl bridge bonds range from 2.15 to 2.20 Å.[39] A 2.31-Å Al–Cl bond has been reported for $Cp_2ZrC_2H_3(AlEt_2)_2Cl$.[33] Chloride-bridged dialuminum complexes exhibit Al–Cl bonds between 2.25 and 2.31 Å, but long bonds comparable to that found in **2a** have been found in $[(\eta^3\text{-}C_5Me_5)Al(\mu\text{-}Cl)Me]_2$ (average 2.388 (3) Å).[40] The Al–Cl bond length in **2a** is more in accord with form B than A but may result in part from steric repulsion across the metallacyclic ring. Because of the tight Zr–C binding the Zr–Al separation is only 3.082 (1) Å. With additional contraction of the Al–Cl bond excessive nonbonded repulsions would be expected.

We interpret these structural features to indicate a major contribution from canonical form A with a lesser admixture from form B. Of particular interest would be comparison of these data with those of a Ti analogue which, on the basis of NMR criteria, should have a structure even more in line with form A.



Experimental Section

General Details. Reactions of organometallic compounds were conducted under purified nitrogen, either with a Schlenk apparatus or in a Vacuum Atmospheres drybox. Solvents were distilled under nitrogen from sodium benzophenone ketyl. Dialkylalkenylaluminum and chlorobis(cyclopentadienyl)alkenylzirconium compounds were prepared and isolated according to a published procedure.[19]

Preparation of *ab*-Bis(cyclopentadienyl)-*c*-(μ-chloro)-*d*-(μ-neohexylidene)-*ef*-diisobutylzirconium(IV)aluminum (2a). Method B. To a suspension of 7.08 g (22 mol) of Cp_2ZrHCl in 60 mL of benzene was added dropwise, at room temperature, a solution of 4.48 g (20 mmol) of diisobutylneohexenylaluminum in 5 mL of the same solvent. The mixture was stirred in the dark for 5 h and was filtered to give a red-brown solution. Evaporation of the solvent yielded a waxy solid which was dissolved in a minimal amount of pentane, decanted, and cooled to −30 °C. Red-orange crystals could thus be obtained in 90% yield. NMR data are listed in Table I.

Anal. Calcd for $C_{24}H_{40}AlClZr$: C, 59.78; H, 8.36; Cl, 7.35; Zr, 18.92; Al, 5.59. Found: C, 59.69; H, 8.21; Cl, 7.53; Zr, 19.10; Al, 5.63. Mass spectrum (relative intensity), m/e 480 (38.86), 481 (8.48), 482 (25.51), 483 (2.75), 484 (17.24), 486 (6.37), and 488 (0.69).

Preparation of *ab*-Bis(cyclopentadienyl)-*c*-(μ-chloro)-*d*-(μ-neohexylidene)-*ef*-dimethylzirconium(IV)aluminum (2b). Method B. The procedure for the preparation of **2a** was followed, using Cp_2ZrHCl (1.97 g, 6.13 mmol) and dimethylneohexenylaluminum (0.86 g, 6.13 mmol) in 20 mL of benzene. This reaction mixture was stirred 18 h. The benzene was removed at reduced presure, and the residue was redissolved in 5 mL of toluene. Ten milliliters of hexane was added dropwise to the solution, which was then filtered. The filtrate was maintained at −33 °C for 18 h. The reddish brown crystals that formed were filtered, washed, and dried to give 0.65 g (27%) of products. No attempt was made to maximize the yield of this product.

Data Collection and Structure Solution and Refinement of Complex 2a. A suitable crystal was grown by slowly cooling a pentane solution to −30 °C. The crystal was encapsulated in a glass capillary under N_2 and subjected to preliminary photographic evaluation which indicated the space group and approximate cell parameters. Final versions of these and other crystallographic data are compiled in Table II. The crystal was placed in a Syntex P3 diffractometer and cooled to −100 °C, at which temperature it was shown to be acceptable on the basis of a typical ω-scan peak width at half-height of ca. 0.25°. The cell parameters were then refined to the reported values on the basis of 50 computer-centered reflections chosen from diverse regions of reciprocal space. As the β value closely approaches 90°, we conducted a careful examination of the photographic and intensity data to eliminate an alternative orthorhombic space group.

Intensity data were collected by using the ω-scan technique (variable scan rate, 4.0–10.0° min^{-1}; total background counting time = scan time). The intensities of three standard reflections were measured every 200 reflections. No significant variations in the intensities of these reflections were observed. The data were corrected for absorption by using the Difabs routine.[41] The data were processed by using counting statistics and a p value of 0.02 to derive standard deviations.[42]

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(29) Jeffrey, J.; Lappert, M. F.; Loung-Thi, N. T.; Webb, M.; Atwood, J. L.; Hunter, W. *J. Chem. Soc., Dalton Trans.* **1981**, 1593–1606.

(30) Wengrovius, J. H.; Schrock, R. R.; Day, C. S. *Inorg. Chem.* **1981**, *20*, 1844–1849.

(31) Stollmaier, F.; Thewalt, U. *J. Organomet. Chem.* **1981**, *208*, 327–334.

(32) Krebs, B. *Z. Anorg. Allg. Chem.* **1970**, *378*, 263–272.

(33) Kaminsky, W.; Kopf, J.; Sinn, H.; Vollmer, H.-J. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 629–630.

(34) Messerle, L., unpublished results.

(35) Moore, J. W.; Sanders, D. A.; Scherr, M. D.; Oliver, J. P. *J. Am. Chem. Soc.* **1971**, *93*, 1035–1037.

(36) Albright, M. J.; Butler, W. M.; Anderson, T. J.; Glick, M. D.; Oliver, J. P. *J. Am. Chem. Soc.* **1976**, *98*, 3995–3996.

(37) Sharp, P. R.; Holmes, S. J.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 965–966. Churchill, M. R.; Rheingold, A. L.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 3392–3399.

(38) Huffman, J. C.; Streib, W. E. *J. Chem. Soc., Chem. Commun.* **1971**, 911–912.

(39) Watson, P. L.; Whitney, J. F.; Harlow, R. L. *Inorg. Chem.* **1981**, *20*, 3271–3278. Thewalt, U.; Stollmaier, F. *J. Organomet. Chem.* **1982**, *228*, 149–152. Thewalt, U.; Osterle, F. *J. Organomet. Chem.* **1979**, *172*, 317–324. Turner, R. W.; Amma, E. L. *J. Am. Chem. Soc.* **1966**, *88*, 1877–1882, 3243–3247.

(40) Schonberg, P. R.; Paine, R. T.; Campana, C. F. *J. Am. Chem. Soc.* **1979**, *101*, 7726–7728.

(41) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 159.

The solution and refinement of the structure were carried out on a PDP-11 computer using local modifications of the SDP-Plus structure determination package supplied by the Enraf-Nonius Corp. The zirconium atom was located in an origin-removed Patterson synthesis. The positions of the remaining non-hydrogen atoms were obtained by the usual combination of structure factor and Fourier synthesis calculations and full-matrix least-squares refinements. The function minimized in the least-squares runs was $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, respectively, $w = \sigma^{-2}(F_o)$. The scattering factors were taken from the compilation of Cromer and Waber[43a] and the anomalous dispersion terms from that of Cromer.[43b] During the refinement process we detected the disorder in the neopentyl group about the pseudomirror of the metallacyclic ring. Atoms C(1), C(3), and C(4), common in both orientations, were fully weighted. The C(2), C(5), and C(6) pairs were shown to be equally populated about the pseudomirror by occupancy factor refinement. The majority of hydrogen atoms were located. The positions of all H atoms other than those attached to C(1) were idealized with a C–H distance of 0.95 Å, and these atoms were included as a fixed contribution with $B_H = 5.0$ Å^2 and the appropriate occupancy factor. The highest peaks of residual electron density in a final difference Fourier synthesis are ca. 0.4 e Å^{-3} and correspond approximately to the expected H atom positions about C(1). These H atoms were not refined or included because of the proximity of the disordered atoms C(2A) and C(2B). Least-squares refinements converged to the values shown in Table III, where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|]^{1/2}$.

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Registry No. **2a**, 79061-88-4; **2b**, 79061-85-1; Cp_2ZrHCl, 79061-85-1; diisobutylneohexenylaluminum, 61382-44-3; dimethylneohexenylaluminum, 71058-46-3.

Supplementary Material Available: Non-hydrogen atom thermal parameters (Table V) and idealized H atom positions (Table VI), and a view of disordered neopentyl group (Figure 2) (6 pages); a listing of observed and calculated structure amplitudes (22 pages). Ordering information is given on any current masthead.

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[42] Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1976**, *6*, 197.

[43] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) Table 2.28B; (b) Table 2.3.1.

Communications

Cationic Phosphonium Carbyne and Bis(phosphonium) Carbene Tungsten Complexes: $[Tp'(OC)_2WC(PMe_3)_n][PF_6]$ (n = 1, 2)

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Summary: Cationic phosphonium carbyne and bis(phosphonium) carbene complexes $[Tp'(OC)_2WC(PMe_3)_n][PF_6]$ (n = 1, 2) ($Tp' = [HB(N_2C_3Me_2H)_3]^-$, hydridotris(3,5-dimethylpyrazolyl)borate) have been prepared. The bis(phosphonium) carbene complex (n = 2) has been structurally characterized. The cationic carbyne complex reacts with MeLi or $K[HB(O\text{-}i\text{-}Pr)_3]$ to form $Tp'(OC)_2W{=}C(Me)PMe_3$ or $Tp'(OC)_2W{=}C(H)PMe_3$, respectively.

Angelici and co-workers have recently reported that carbyne–carbonyl coupling occurs when PEt_3 is added to $Tp(OC)_2W{\equiv}CSMe$ ($Tp = [HB(N_2C_3H_3)_3]^-$, hydridotris(pyrazolyl)borate) (**1**).[1] We wish to report formation of cationic phosphonium carbyne and bis(phosphonium)carbene tungsten complexes from reaction of the sterically congested analogue of **1**, $Tp'(OC)_2W{\equiv}CSMe$ ($Tp' = [HB(N_2C_3Me_2H)_3]^-$, hydridotris(3,5-dimethylpyrazolyl)borate) (**2**),[2] with excess PEt_3 and PMe_3, respectively. These reactions resemble those of $Tp'(OC)_2Mo{\equiv}CCl$ recently reported by Lalor and co-workers where Cl^- is the leaving group in nucleophilic displacement reactions (eq 1).[3,4]

$$Tp'(OC)_2M{\equiv}CX + Nu \rightarrow [Tp'(OC)_2M{\equiv}CNu]^+ + X^- \qquad (1)$$

Excess PEt_3 reacts slowly with **2** in CH_2Cl_2 at room temperature to replace the reagent dicarbonyl IR pattern (1975 (s), 1880 (vs) cm^{-1}) with higher energy absorptions (2020 (s), 1935 (vs) cm^{-1}). Slow addition of Et_2O precipitates white byproducts which include the $[MePEt_3]^+$ cation.[5] Further addition of Et_2O to the filtrate precipitates an orange solid which can be recrystallized from CH_3CN/H_2O with added $[NH_4][PF_6]$ to produce low yields (20%) of $[Tp'(OC)_2W{\equiv}CPEt_3][PF_6]$ (**3**) as air-stable, red-orange crystals. Informative NMR features[6] include a 2:1 ratio of pyrazolyl environments in the ^1H NMR, J_{HP} coupling constants suggestive of a PR_4^+ moiety rather than $M{-}PR_3$,[7] and a singlet in the ^{31}P spectrum at +30.1 ppm

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[1] Kim, H. P.; Kim, S.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1986**, *5*, 2481.

[2] **2** was prepared by using the reported procedure for **1**: Greaves, W. W.; Angelici, R. J. *Inorg. Chem.* **1981**, *20*, 2983.

[3] Desmond, T.; Lalor, F. J.; Ferguson, G.; Parvez, M. *J. Chem. Soc., Chem. Commun.* **1984**, 75.

[4] Angelici and co-workers have demonstrated that SMe^- is a good leaving group in the reactions of nucleophiles with thiocarbene complexes: Kim, H. P.; Angelici, R. J. *Organometallics* **1986**, *5*, 2489. Yu, Y. S.; Angelici, R. J. *Organometallics* **1983**, *2*, 1018. Yu, Y. S.; Angelici, R. J. *Organometallics* **1983**, *2*, 1583.

[5] The $[MePEt_3]^+$ cation was identified by comparison of its IR and ^1H NMR spectra with those of an authentic sample of $[MePEt_3][I]$.

[6] ^1H NMR (CD_2Cl_2): δ 6.07 (s, 2 H, Tp'C*H*), 5.86 (s, 1 H, Tp'C*H*), 2.49 (s, 6 H, Tp'CH_3), 2.42 (s, 6 H, Tp'CH_3), 2.40 (s, 3 H, Tp'CH_3), 2.33 (s, 3 H, Tp'CH_3), 2.2 (d of q, 6 H, $P(CH_2CH_3)_3$, $^2J_{HP} = 12.1$ Hz, $^3J_{HH} = 7.6$ Hz), 1.35 (d of t, 9 H, $P(CH_2CH_3)_3$, $^3J_{HP} = 19.0$ Hz, $^3J_{HH} = 7.6$ Hz).

[7] Schmidbaur, H.; Tronich, W. *Chem. Ber.* **1968**, *101*, 595. Weigart, F. J.; Roberts, J. D. *J. Am. Chem. Soc.* **1969**, *91*, 4940. Kreissl, F. R.; Stuckler, P.; Meineke, E. W. *Chem. Ber.* **1977**, *110*, 3040.

0276-7333/87/2306-1350$01.50/0