Table I. IR Vibrations of Triplet 1,3-Perinaphthadiyl and Their Polarizations

	exptl				calcd^a	
compd	$\bar{\nu}$, cm^{-1}	$K(y)$	$K(z)$	sym	$\bar{\nu}$, cm^{-1}	sym
1A	2742	0.36	0.44	x	2824	x
	2761	0.33^b	0.22	z	2885	z
	3056	0.28	0.39	y	3011	y
	3066	0.35	0.19	z	3016	z
	$K_y(y) = 0.26$	$K_x(y) = K_z(y) = 0.37^c$				
	$K_z(z) = 0.23$	$K_x(z) = K_y(z) = 0.39^c$				
1C	2046	0.38	0.41	x	2081	x
	2061	0.35	0.26	z	2088	z
	2237	0.22	0.36	y	2208	y
	2253	0.39	0.23	z	2212	z
	$K_y(y) = 0.24$	$K_x(y) = K_z(y) = 0.41^c$				
	$K_z(z) = 0.22$	$K_x(z) = K_y(z) = 0.38^c$				

[a] MNDO, corrected by a multiplicative factor of 0.885, obtained by fitting the CH_2 *as* stretch in propane. [b] Subject to a large experimental uncertainty. [c] From the dichroic ratios of about 20 IR bands. Some of the small difference between $K_x(y)$ and $K_z(y)$ and between $K_x(z)$ and $K_y(z)$ is probably due to slightly mixed polarization of the absorption at 496.5 and 488 nm. This has no effect on the proposed assignments and C_{2v} symmetry.

of **2** at 10 K. The orientation of **2** was known from its UV dichroism.

Dichroic ratios of the approximately 20 IR bands of oriented **1A** and **1C** yielded the six orientation factors for each, $K_u(y)$ and $K_u(z)$, $u = x,y,z$. These are only compatible with C_{2v} symmetry and give an unequivocal assignment of the four stretching vibrations (Table I).[12]

It has been proposed[4] that the CH_2 group in **1A** is tilted out of the aromatic plane (C_s symmetry), although the two β protons are equivalent in the (poorly resolved) ESR spectrum. Such a geometry has been claimed to result from MNDO and molecular mechanics calculations.[4] Our polarization results clearly establish C_{2v} as the symmetry of both **1A** and **1C**, and this agrees with the absence of peak doubling and with our UHF MNDO geometry optimization.

The observed α C–H stretches are virtually identical with that of the isopropyl radical,[13] which is split and occurs at 3058 and 3069 cm^{-1}. The β C–H stretches are at strikingly low frequencies. In particular, the CH_2 *as* stretch, ordinarily[14] at 2853 ± 10 cm^{-1}, occurs at 2742 cm^{-1} in **1A**. The 111-cm^{-1} hyperconjugation shift is thus considerably larger than expected from a comparison with the 40-cm^{-1} shift in the *n*-propyl[13] radical (2812.5 cm^{-1}), which has a full unpaired unit spin adjacent to the CH_2 group. In **1** only about half of a unit spin resides on each radical center, judging both by calculations and by the ESR coupling constants.[2] If the orientation of the CH_2 group relative to the $2p\pi$ orbital on CH were the same in both compounds, one might expect a comparable shift. Perhaps the conformations differ, or it is far more effective to have half a spin on each side of the CH_2 group than a full spin on one side, because of the allylic resonance in the no-bond structure (phenalenyl is particularly stabilized).

MNDO calculations (Figure 1, Table I) reproduce the order of the *s* and *as* combinations of both the α and the β C–H stretches in **1** but underestimate the difference between the α and the β stretches and do not reproduce the large shift of the CH_2 *as* stretch in **1** although they presumably take full account of the special stability of phenalenyl. A crude comparison also can be made with published ab initio calculations[15] on the parent edge-to-edge $\cdot CH_2CH_2CH_2\cdot$ triplet. The calculated *s* and *as* stretches of the central CH_2 group are now in the opposite order than found in **1**. With a multiplicative correction factor of 0.892, fitted to the *as* CH_2 stretch of cyclopropane, the CH_2 *as* stretch is predicted at 2824 cm^{-1}, so that the striking shift we observe in **1** is again not reproduced. Thus, the observed very low frequency of the β C–H stretch in **1** does not currently have a satisfactory quantitative interpretation.

Acknowledgment. This project was supported by the National Science Foundation, Grant CHE-84-21117, and by the awards of an NIH fellowship to J.H.P. and of a NATO fellowship to D.D.

---

(12) For molecules of **1** remaining after photoselection on an absorbing visible $\pi\pi^*$ transition moment oriented in the naphthalene plane along z, we have $K_z(z) < K_y(z) = K_x(z)$. For either C_{2v} or C_s symmetry $K_y(z)$ is determined unequivocally as 0.39 in **1A** and 0.36 in **1C**, requiring $K_x(z) = 0.39$, $K_z(z) = 0.22$ and $K_x(z) = 0.36$, $K_z(z) = 0.28$, respectively. The dichroism of the *s* and *as* CH_2 or CD_2 vibrations reflects the orientation of the methylene group relative to z and to the out-of-plane axis x; for a transition polarized in the xz plane at angle ϕ to z, $\tan^2 \phi = (K_z - K_x)/(K_y - K_x)$. Within the experimental error of 0.02–0.03, the data in Table I are only compatible with a z polarization of the CH_2 and CD_2 *s* stretches ($\phi = 0^0$) and x polarization of the *as* stretches ($\phi = 90°$).

(13) Pacansky, J.; Brown, D. W.; Chang, J. S. *J. Phys. Chem.* **1981**, *85*, 2562.

(14) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Halsted Press: London, 1975; Vol. 1, p 15.

(15) Yamaguchi, Y.; Osamura, Y.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1983**, *105*, 7506.

Preparatively Useful Dehydrogenative Method for Dodecahedrane Synthesis

Leo A. Paquette,* Yuji Miyahara, and
Christopher W. Doecke

*Evans Chemical Laboratories, The Ohio State
University, Columbus, Ohio 43210*

Received November 19, 1985

Considerable attention remains focused on dodecahedrane (**2**) and its functional derivatives because these spherical molecules represent potentially useful tools for probing varied chemical phenomena in a unique way. In 1982, a successful synthesis of the parent hydrocarbon was achieved by the Paquette group.[1] The pivotal final step consisted of heating an intimate mixture of secododecahedrane (**1**) with hydrogen-presaturated 10% palladium on carbon at 250 °C for several hours.[2] The undesirable features of this otherwise remarkable ring closure are its modest efficiency (40–50% yield), severe limitation on throughout (maximum of 2 mg of **1** per run), and intolerance of pendant groups.[3] We have now developed a superior, preparatively useful dehydrocyclization system. The exceptional promise offered by this new process projects us from the era of concern over dodecahedrane construction[4] to the next evolutionary stage involved with assessing the chemical reactivity of this class.

The earlier complications stem in large part from the presence of excess hydrogen, which proved necessary to curtail the propensity of Pd(0) for 1,2-dehydrogenative elimination. Optimal alternative conditions were regarded to be those wherein one transition metal would effect smooth transannular C–C bond formation in the presence of a second metal capable of absorbing the liberated H_2 at elevated temperatures. Zerovalent titanium

---

(1) (a) Ternansky, R. J.; Balogh, D. W.; Paquette, L. A. *J. Am. Chem. Soc.* **1982**, *104*, 4503. (b) Paquette, L. A.; Ternansky, R. J.; Balogh, D. W.; Kentgen, G. *Ibid.* **1983**, *105*, 5446.

(2) For analogous C–C forming reactions, consult: (a) Rylander, P. N. *Organic Synthesis with Noble Metal Catalysts*; Academic Press: New York, 1973; p 28. (b) Kazanskii, B. A.; Balenkova, E. S.; Khromov, S. I. *Russ. Chem. Rev. (Engl. Transl.)* **1967**, *36*, 866. (c) Burns, W.; McKervey, M. A.; Mitchell, T. R. B.; Rooney, J. J. *J. Am. Chem. Soc.* **1978**, *100*, 906. (d) Crawford, M.; Supanekar, V. R. *J. Chem. Soc.* **1964**, 2380. (e) Pozdmikina, S. G.; et al. *Chem. Abstr.* **1973**, *79*, 31564x.

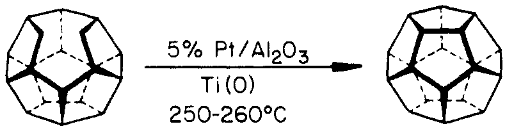
(3) Paquette, L. A.; Ternansky, R. J.; Balogh, D. W.; Taylor, W. J. *J. Am. Chem. Soc.* **1983**, *105*, 5441.

(4) (a) Eaton, P. E. *Tetrahedron* **1979**, *35*, 2189. (b) Baldwin, J. E.; Beckwith, P. L. M. *J. Chem. Soc., Chem. Commun.* **1983**, 279. (c) Eaton, P. E.; Bunnelle, W. H.; Engel, P. *Can. J. Chem.* **1984**, *62*, 2612.

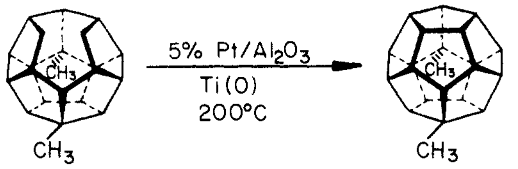
0002-7863/86/1508-1716$01.50/0

is well recognized to be amenable to conversion to a dihydride alloy stable to above 600 °C.[5] As a consequence, we were led preliminarily to heat cyclooctane with an intimate 1:1 mixture of 5% Pt on Al_2O_3 and Ti(O)[6] at 250 °C for 8 h. Under these conditions, predominant conversion to bicyclo[3.3.0]octane was observed and no cyclooctene was produced.

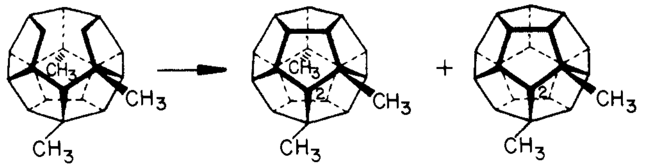
Analogous treatment of **1** (250–260 °C, 10 h) furnished dodecahedrane in a high state of purity. From 27 mg of **1**, 21.8 mg of **2** was isolated in a form admixed with less than 2% of its seco precursor.[7] That construction of the C–C bond proceeds without substituent migration[8] is evidenced by formation of the previously unknown **4**[9] from **3** in 74% yield (200 °C, 38 h).[10] The concurrent production of 10–15% of methyldodecahedrane attracted our attention. Although the mechanistic details of this demethylation are incompletely understood, the behavior of trimethyl-substituted hydrocarbon **5** clearly shows that a direct correlation exists with steric accessibility of the cleaved alkyl group to the catalyst. Thus, heating of this substrate with the Pt/Ti mixture[10] (200 °,C, 36 h), followed by isolation and reapplication to a new sample of catalyst for a second iteration of the thermal treatment, typically provided a mixture of **6** and **7**. Controlled crystallization from benzene–ethanol sufficed to separate the less soluble **7** (40%) from the more soluble **6** (23%). That dodecahdedrane derivatives had again been produced was evident from ^1H and ^{13}C NMR spectroscopy.[11] The lessened ability of eclipsing C–C bonds to deshield flanking hydrogen atoms happens to be particularly in evidence in these compounds. Both exhibit a doublet due to H-2 that is shifted substantially upfield (δ 2.50 in $CDCl_3$) from the other protons of the shell.



1 **2**

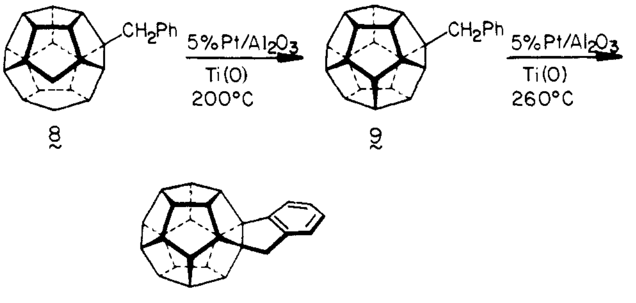


3 **4**



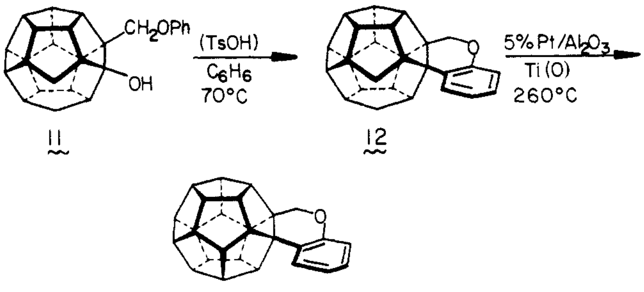
5 **6** **7**

A second serviceable aspect of this methodology resides in its efficiency toward controlled dehydrogenation. As an illustration, heating admixed **8** and catalyst at 200 °C for 40 h gave pure benzyldodecahedrane (**9**, 64%).[12] A modest increase in temperature to 260 °C (23 h) triggered further cyclization and afforded the indano-fused product **10**.[13] This conversion to **10**, which proceeds efficiently starting from either **8** or **9**, is of particular importance.[14] It provides a ready means for preparing 1,2-disubstituted dodecahedranes, derivatives of which are normally disadvantaged thermodynamically because of nonbonded steric compression.[15]



8 **9** **10**

We have also investigated the feasibility of hetero 1,2-annulation. Stirring the known alcohol **11**[1] with *p*-toluenesulfonic acid in benzene (70 °C, 3 h) results in intramolecular Friedel–Crafts cyclization to give cyclic ether **12** quantitatively. At this point, dehydrogenation (260 °C, 32 h) afforded **13**[16] (44%) and a second product that remains unidentified.



11 **12** **13**

For the future, our intention is to broaden still further the scope of this useful dehydrocyclization reaction and to commence de-

---

(5) (a) Libowitz, G. G. In *Critical Materials Problems in Energy Production*; Stein, C., Ed.; Academic Press: New York, 1976; Chapter 28. (b) Libowitz, G. G. *The Solid-State Chemistry of Binary Metal Hydrides*; Benjamin: New York, 1965; p 66. (c) Livanov, V. A.; Bukhanova, A. A.; Kolachev, B. A. "Hydrogen in Titanium", Israel Program for Scientific Translations, Jerusalem, 1965. (d) Clark, R. J. H. *Comprehensive Inorganic Chemistry*; Wiley: New York, 1973; Vol. 3, Chapter 32. (e) Fanelli, A. J.; Maeland, A. J.; Rosan, A. M.; Crissey, R. K. *J. Chem. Soc., Chem. Commun.* **1985**, 8.

(6) The powdered Ti was prepared at Allied Corporation by means of a hydriding–dehydriding cycle. The final stage consists simply of heating finely divided TiH_2 to 600 °C at 10^{-7} torr until all of the hydrogen has evolved. The resulting highly reactive metal was handled under argon at all times.

(7) Analysis was achieved by capillary gas chromatography (15 m DBN-5, H_2 carrier gas, 35 cm^3/s, 190 °C).

(8) (a) Paquette, L. A.; Balogh, D. W.; Usha, R.; Kountz, D.; Christoph, G. G. *Science (Washington, D.C.)* **1981**, *211*, 575. (b) Paquette, L. A.; Balogh, D. W. *J. Am. Chem. Soc.* **1982**, *104*, 774. (c) Paquette, L. A.; Ternansky, R. J.; Balogh, D. W. *Ibid.* **1982**, *104*, 4502.

(9) ^1H NMR (300 MHz, $CDCl_3$) δ 3.41 (m, 12 H), 2.90 (m, 6 H), 1.14 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) ppm 75.06, 74.94, 74.85, 67.43, 66.99, 66.66, 66.24, 32.54; *m/z* calcd (M^+) 288.1878, obsd. 288.1891.

(10) In this and subsequent experiments, a Pt/Ti ratio of 2:1 was utilized.

(11) For **6**: ^1H NMR (300 MHz, $CDCl_3$) δ 3.52–3.34 (m, 9 H), 3.0–2.87 (m, 7 H), 2.51 (d, *J* = 10.8 Hz, 1 H), 1.15 (s, 6 H), 1.14 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) ppm 82.73, 75.20, 75.18, 75.13, 75.07, 74.74, 67.26, 66.94, 66.85, 66.57, 66.15, 65.99, 33.07, 32.49; *m/z* calcd (M^+) 302.2079, obsd 302.2029. For **7**: ^1H NMR (300 MHz, $CDCl_3$) δ 3.34 (m, 13 H), 2.98 (m, 2 H), 2.88 (m, 2 H), 2.49 (d, *J* = 10.6 Hz, 1 H), 1.15 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) ppm 82.57, 75.64, 74.94, 74.51, 67.45, 67.30, 67.01, 66.94, 66.75, 66.51, 66.24, 65.86, 33.12; *m/z* calcd (M^+) 288.1878, obsd 288.1850.

(12) ^1H NMR (300 MHz, $CDCl_3$) δ 7.2–7.0 (m, 5 H), 3.24 (br s, 19 H), 2.65 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 141.30, 129.89, 127.78, 125.53, 72.04, 67.09, 66.99, 66.55, 66.50, 49.19 (quaternary C not observed); *m/z* calcd (M^+) 350.2034, obsd 350.2084.

(13) ^1H NMR (300 MHz, $CdCl_3$) δ 7.24–7.03 (m, 4 H), 3.7–3.2 (series of m, 18 H), 3.24 (s, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) ppm 153.60, 141.26, 127.28, 126.12, 123.61, 123.45, 93.97, 84.96, 77.73, 75.44, 67.67, 67.58, 67.37, 66.95, 66.88, 66.75, 66.59, 53.67, 29.69; *m/z* calcd (M^+) 348.1878, obsd 348.1873.

(14) Since experiments conducted with Ti(O) alone led to no chemical change, it is reasonable as expected that the platinum acts as the dehydrogenating agent.

(15) Schulman, J. M.; Disch, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 5677.

(16) ^1H NMR (300 MHz, $CdCl_3$) δ 7.2–6.8 (m, 4 H), 3.75 (s, 2 H), 3.65 (br s, 2 H), 3.44 (br s, 14 H), 3.26 (narrow m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) ppm 154.59, 138.31, 126.85, 125.58, 122.45, 116.66, 79.67, 78.02, 77.50, 77.30, 71.50, 67.59, 67.34, 67.07, 66.99, 66.68, 64.85 (2C not observed); *m/z* calcd (M^+) 364.1827, obsd 364.1830.

tailed chemical investigation of the resulting dodecahedranes.

Acknowledgment. This research was made possible by the generous financial support of the National Institutes of Health (Grant AI-11490). Special thanks go to Dr. A. Rosan (Allied Corporation) for helpful advice and several zerovalent titanium samples. The 500-MHz NMR and mass spectra were recorded by Dr. C. Cottrell and C. Weisenberger, respectively, at The Ohio State University Campus Instrumentation Center.

Reactive Cationic Dicyclopentadienylzirconium(IV) Complexes

Richard F. Jordan,* William E. Dasher,† and Scott F. Echols

Department of Chemistry, Washington State University
Pullman, Washington 99164

Received November 4, 1985

Electron deficient early-transition-metal complexes are highly reactive with a variety of small molecules and organic substrates as exemplified by the now classic studies of dicyclopentadienylzirconium(IV) and -titanium(IV) compounds.[1] Attempts to extend this chemistry by increasing the electrophilicity of the metal center have involved replacement of (6-e$^-$ donor) cyclopentadienyl ligands with 2-e$^-$ donor ligands as well as investigation of related dicyclopentadienyl compounds of group III (3),[25] lanthanide, and actinide metals.[1i] Notable recent work includes the alkylation of carbonyl compounds by TiR_nX_{4-n},[2] the complete scission of CO by CpZrCl(diene),[3] intramolecular oxygen transfer in $[(Me_3C)_3CO]_2ZrR_2$,[4] and olefin polymerization and C–H activation by $(C_5Me_5)_2LuR$.[5] In an alternate approach to this problem we began an investigation of cationic dicyclopentadienyl Zr(IV) complexes of the type Cp_2ZrR^+. Previously the 14-electron fragment $Cp_2ZrCH_3^+$ had been incorporated in a variety of heterobimetallic compounds of both metal–metal bonded and isocarbonyl structures.[6] As initial observations indicate that reactions involving both metal centers will play a major role in the chemistry of such bimetallic compounds,[7] we sought simpler monometallic systems incorporating unreactive noncoordinating anions.[8] We report here the preparation of Cp_2ZrR^+ complexes via X^- or R^- abstraction from Zr(IV) by Ag^+ and several reactions which demonstrate the high electrophilicity of these complexes.

Reaction of $Cp_2Zr(CH_3)Cl$ with $AgPF_6$ or of $Cp_2Zr(CH_3)I$ with $TlPF_6$ in CH_3CN followed by filtration and concentration of the filtrate produced $[Cp_2Zr(CH_3)(CH_3CN)][PF_6]$ (**1**-PF_6) in 75% yield as a pale yellow solid after vacuum drying (eq 1).

$$\begin{array}{l} Cp_2Zr(CH_3)X \;+\; M[PF_6] \xrightarrow{CH_3CN} \\ X = Cl,\ M = Ag \\ X = I,\ M = Tl \qquad \underset{\mathbf{1}\text{-}PF_6}{[Cp_2Zr(CH_3)(CH_3CN)][PF_6]} + MX \quad (1) \end{array}$$

This compound was characterized spectroscopically;[9] in particular a singlet in the ^1H NMR (CD_3CN) spectrum at δ 1.95 integrating for 3 H and IR ν_{CN} bands at 2310 and 2283 cm^{-1} shifted from 2287 and 2251 cm^{-1} for free CH_3CN indicate the presence of a coordinated CH_3CN ligand.[10] In CD_3CN the ^1H NMR resonances for the Cp and Zr–CH_3 groups of **1**-PF_6 appear at δ 6.11 and 0.09, values that are nearly identical with those observed for the heterobimetallic compounds $Cp_2ZrCH_3(\mu\text{-}OC)M(CO)_2Cp$ (M = Cr, Mo, W) which exhibit substantial conductivity in this solvent.[6b]

While stable as a solid, **1**-PF_6 decomposed instantaneously in THF and in CH_2Cl_2 to $Cp_2Zr(CH_3)F$ via F^- abstraction from PF_6^- (eq 2). PF_5 was not detected in this reaction but its formation

$$\begin{array}{l} [Cp_2Zr(CH_3)(CH_3CN)][PF_6] \xrightarrow[THF]{CH_2Cl_2\text{ or}} \\ \qquad\qquad Cp_2Zr(CH_3)F + PF_5 \rightarrow Cp_2ZrF_2 \quad (2) \end{array}$$

was implicated by the observed polymerization of the solvent in the THF experiment. Cp_2ZrF_2, presumably formed by CH_3/F exchange between $Cp_2Zr(CH_3)F$ and PF_5,[11] was observed as a secondary reaction product. A similar but much slower (days) decomposition was observed in CH_3CN.[12]

Previously we had observed that while CH_3/F exchange between $Cp_2Zr(CH_3)_2$ and Cp_2ZrF_2 was fast, phenyl/F exchange between Cp_2ZrPh_2 and Cp_2ZrF_2 was extremely slow.[11] This suggested that use of BPh_4^- as a counterion might provide a more stable compound for study. $[Cp_2Zr(CH_3)(CH_3CN)][BPh_4]$ (**1**-BPh_4) was prepared most conveniently by reaction of $Cp_2Zr(CH_3)_2$ with $AgBPh_4$ in CH_3CN followed by filtration, recrystallization from CH_3CN, and vacuum drying (yield 80%, eq 3).[13] The ^1H and

$$\begin{array}{l} Cp_2Zr(CH_3)_2 + Ag[BPh_4] \xrightarrow{CH_3CN} \\ \qquad \underset{\mathbf{1}\text{-}BPh_4}{[Cp_2Zr(CH_3)(CH_3CN)][BPh_4]} + Ag^0 + C_2H_6 \quad (3) \end{array}$$

^{13}C NMR and IR spectra of **1**-BPh_4 are nearly identical with those of **1**-PF_6 except for characteristic BPh_4^- absorbances.[14] The other products of this reaction, Ag^0 and ethane (which was identified by its characteristic ^1H NMR signal at δ 0.86 but was not quantified), are those expected from the thermal decomposition of $AgCH_3$, a possible intermediate in this reaction.[15] In contrast to its PF_6^- analogue, **1**-BPh_4 is stable in THF solution. In this

---

† Visiting summer fellow from University of Puget Sound, Tacoma, WA.

(1) For leading references, see: (a) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *19*, 121. (b) Barger, P. T.; Santarsiero, B. D.; Armantrout, J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5178. (c) Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333. (d) Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103. Negishi, E. *Aldrichimica Acta* **1985**, *18*, 31. (f) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. (g) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729. (h) Tatsumi, K.; Nakamura, A.; Hofmann, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 4440. (i) See also: Marks, T. J.; Ernst, R. D. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Chapter 21.

(2) (a) Weidmann, B.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 31. (b) Reetz, M. T. *Top. Curr. Chem.* **1983**, *106*, 1.

(3) Blenkers, J.; de Liefde Meijer, H.; Teuben, J. H. *Organometallics* **1983**, *2*, 1483.

(4) Lubben, T. V.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1985**, *107*, 701.

(5) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51.

(6) For leading references, see: (a) Casey, C. P.; Jordan, R. F.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 665. (b) Longato, B.; Martin, B. D.; Norton, J. R.; Anderson, O. P. *Inorg. Chem.* **1985**, *24*, 1389.

(7) (a) Marsella, J. A.; Huffman, J. C.; Caulton, K. G.; Longato, B.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 6360. (b) Casey, C. P.; Palermo, R. E.; Jordan, R. F.; Rheingold, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 4597.

(8) Several cationic Cp_2M (M = Ti, Zr) complexes have been reported. (a) $[\{Cp_2Ti(H_2O)\}_2O][S_2O_6]$: Thewalt, U.; Schleussner, G. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 531. (b) $[Cp_2Ti(H_2O_2][ClO_4]_2$: Thewalt, U.; Klein, H.-P. *J. Organomet. Chem.* **1980**, *194*, 297. (c) $[\{Cp_2Ti(H_2O)\}_2O][ClO_4]_2$: Thewalt, U.; Kebbel, B. *J. Organomet. Chem.* **1978**, *150*, 59. (d) $[Cp_2ZrCH_2CH(AlEt_2)_2][Cp]$: Kaminsky, W.; Kopf, J.; Sinn, H.; Vollmer, J. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 629. (e) $[Cp_2Ti(CH_3CN)_2][PF_6]_2$: Bruce, M. R. M.; Tyler, D. R. *Organometallics* **1985**, *4*, 528.

(9) **1**-PF_6 ^1H NMR (CD_3CN) δ 6.11 (s, 10 H), 1.95 (s, 3 H), 0.09 (s, 3 H, $ZrCH_3$); $^{13}C\{^1H\}$ NMR (CD_3CN) δ 112.6, 28.0 ($J_{^{13}C-^1H}$ = 121 Hz); ^{31}P NMR (CD_3CN) δ −143.4 (septet, $J_{^{31}P-^{19}F}$ = 707 Hz); IR (KBr) ν_{CN} 2310, 2283 cm^{-1}, $\nu_{PF_6^-}$ 835, 561 cm^{-1}.

(10) For a discussion of the IR spectrum of CH_3CN see footnote 11 in ref 8e.

(11) Jordan, R. F. *J. Organomet. Chem.* **1985**, *294*, 321.

(12) (a) **1**-BF_4, prepared from $Cp_2Zr(CH_3)_2$ and $HBF_4\cdot Et_2O$, decomposes similarly. (b) For a review of F^- transfer reactions, see: Reedijk, J. *Comments Inorg. Chem.* **1982**, *24*, 379.

(13) This reaction was suggested by the observation of minor amounts of ethane product in the reaction of $Cp_2Zr(CH_3)Cl$ with $AgNO_3$. Jordan, R. F., unpublished work.

(14) **1**-BPh_4 ^1H NMR (CD_3CN) δ 7.4–6.7 (m, 20 H, BPh_4^-) 6.07 (s, 10 H), 1.95 (s, 3 H), 0.079 (s, 3 H, $ZrCH_3$); ^{11}B NMR (THF) δ −6.31 s; ^{13}C NMR (CD_3CN) δ 165 (q, $J_{^{13}C-^{11}B}$ = 50 Hz), 136.6, 126.4, 122.6, 112.1 (Cp_2Zr), 30.8 ($ZrCH_3$); IR (KBr) ν_{CN} 2303, 2273 cm^{-1}.

(15) (a) Beverwijk, C. D. M.; van der Kerk, G. J. M.; Leusink, A. G.; Noltes, J. G. *Organometallic Chem. Rev. Sect., A.* **1970**, *5*, 215. (b) Experiments designed to probe the mechanism of this reaction are under way. (c) Reaction of boron alkyls with Ag^+ also gives alkyl coupling products. Brown, H. C.; Snyder, C. H. *J. Am. Chem. Soc.* **1961**, *83*, 1002.

0002-7863/86/1508-1718$01.50/0