Organometallics 1993, *12*, 486–495

Generation and Reactivity of $Cp_2Ti(CH_2Ph)(L)^+$ Complexes. Oxidation and Protonolysis Chemistry of $Cp_2Ti(CH_2Ph)_2$

Samuel L. Borkowsky, Norman C. Baenziger, and Richard F. Jordan*

Department of Chemistry, University of Iowa, Iowa City, Iowa 52242

Received October 22, 1992

The reaction of $Cp_2Ti(CH_2Ph)_2$ (**5**) with $Ag[BPh_4]$ in CD_3CN yields bibenzyl, $Cp_2Ti^{IV}\{N{=}C(CH_3)(CH_2Ph)\}(NCCH_3)^+$ (**6a,b**), and $Cp_2Ti^{III}(NCCH_3)_2^+$ (**7**) as the BPh_4^- salts. Recrystallization of **7** from hot THF yields $Cp_2Ti^{III}(THF)(NCCH_3)^+$ (**8**), which has been characterized by X-ray crystallography. Labeling studies show that reaction of **5** with $Ag[BPh_4]$ proceeds via a stepwise mechanism, involving initial generation of the reactive cationic monobenzyl species $Cp_2Ti(CH_2Ph)(NCCH_3)^+$ (**12**) followed by competitive insertion to yield **6a,b** or Ti–benzyl bond homolysis to yield **7**. Intermediate **12** has also been generated by (i) one-electron oxidation of $Cp_2Ti^{III}(CH_2Ph)$ with $AgBPh_4$, (ii) reaction of **5** with Cp'_2Fe^+ ($Cp' = C_5H_4Me$), (iii) protonolysis of **5** with $HNMe_3^+$, and (iv) reaction of $Cp_2Ti(CH_2Ph)(Cl)$ with $NaBPh_4$ in CH_3CN. The reaction of **5** with either Cp'_2Fe^+ or $HNMe_3^+$ in THF yields the cationic Ti(III) complex $Cp_2Ti(THF)_2^+$ (**19**), most likely via an intermediate $Cp_2Ti(CH_2Ph)(THF)^+$ species. The metastable, base-free ion pair $Cp_2Ti(CH_2Ph)(CB_{11}H_{12})$ (**22**) has been observed spectroscopically. Complex **22** reacts with CD_3CN to form **6a,b**-d_6 as the $CB_{11}H_{12}^-$ salts. The chemistry of these reactive $Cp_2Ti(CH_2Ph)(L)^+$ species is contrasted with that of related group 4 metal complexes.

Introduction

It is believed that cationic, group 4 metal alkyl complexes $Cp_2M(R)(L)^+$ (L = labile ligand) and $Cp_2M(R)^+$ are the active species in Cp_2MX_2-based Ziegler–Natta olefin polymerization catalysts.[1] For several years we have studied the chemistry of 16-electron $Cp_2Zr(R)(L)^+$ systems in an effort to model the structures and reactivity of cationic species in catalytic reactions and to develop new synthetic reagents.[1-3] There is also a major current effort, which has been stimulated by the seminal work of the Exxon group[4] to prepare 14-electron base-free $Cp_2M(R)^+$ species for application as high-activity catalysts.[5] Cationic $Cp_2M(R)(L)^+$ and $Cp_2M(R)^+$ complexes have been obtained by M–R oxidative cleavage or protonolysis reactions, or R^- abstraction reactions, of neutral $Cp_2M(R)(R')$ complexes with Ag^+,[1c,6] Cp_2Fe^+,[7] HNR_3^+,[4,5,8] Ph_3C^+,[9] $B(C_6F_5)_3$,[10] and related reagents.

We reported earlier that reaction of $Cp_2Zr(CH_2Ph)_2$ (**1**) with $AgBPh_4$ in CH_3CN yields the cationic η^2-benzyl complex $Cp_2Zr(\eta^2\text{-}CH_2Ph)(NCCH_3)^+$ (**2**; Scheme I).[7a,11] Complex **2** does not insert acetonitrile even upon thermolysis (5 h, 60 °C), presumably because the Zr–Ph interaction precludes a cis arrangement of the migrating Zr–C bond and the coordinated CH_3CN.[12] The reaction of **1** with Cp_2Fe^+ in THF yields $Cp_2Zr(CH_2Ph)(THF)^+$ (**3**), which contains a normal η^1-benzyl ligand. This species undergoes significant THF dissociation in CD_2Cl_2 at −78 °C to yield the THF-free species $Cp_2Zr(\eta^2\text{-}CH_2Ph)^+$ (**4** or its CD_2Cl_2 adduct), which is stabilized by an η^2-benzyl interaction. Complex **4** is an active ethylene polymerization catalyst under mild conditions (1 atm pressure of ethylene, 23 °C).

Previous studies have shown that five-coordinate $Cp_2M(X)(L)_2^+$ and $Cp_2M(L)_3^{2+}$ complexes are often preferred for Zr systems but that four-coordinate $Cp_2M(X)(L)^+$ and $Cp_2M(L)_2^{2+}$ species are observed for the Ti analogues. This trend results from the difference in metal ionic radii (Zr (0.98 Å) vs Ti (0.88 Å) in eight-coordinate geometries).[13]

---

(1) (a) For a recent review with extensive references see: Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325. (b) Eisch, J. J.; Piotrowski, A. M.; Brownstein, S. K.; Gabe, E. J.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 7219. (c) Jordan, R. F.; Bagjur, C. S.; Willett, R.; Scott, B. *J. Am. Chem. Soc.* **1986**, *108*, 7410. (d) Gassman, P. G.; Callstrom, M. R. *J. Am. Chem. Soc.* **1987**, *109*, 7875.

(2) (a) Jordan, R. F. *J. Chem. Educ.* **1988**, *65*, 285. (b) Jordan, R. F.; Bradley, P. K.; Baenziger, N. C.; LaPointe, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 1289.

(3) (a) Jordan, R. F.; Taylor, D. F. *J. Am. Chem. Soc.* **1989**, *111*, 778. (b) Jordan, R. F.; Bradley, P. K.; LaPointe, R. E.; Taylor, D. F. *New J. Chem.* **1990**, *14*, 505. (c) Jordan, R. F.; Taylor, D. F.; Baenziger, N. C. *Organometallics* **1990**, *9*, 1546. (d) Jordan, R. F.; Guram, A. S. *Organometallics* **1990**, *9*, 2116. (d) Guram, A. S.; Jordan, R. F. *Organometallics* **1990**, *9*, 2190. (e) Guram, A. S.; Jordan, R. F.; Taylor, D. F. *J. Am. Chem. Soc.* **1991**, *113*, 1833. (f) Guram, A. S.; Jordan, R. F. *Organometallics* **1991**, *10*, 3470.

(4) (a) Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728. (b) Turner, H. W.; Hlatky, G. G. Eur. Patent Appl. 0 277 003, 1988. (c) Turner, H. W. Eur. Patent Appl. 0 277 004, 1988.

(5) (a) Bochmann, M.; Jagger, A. J.; Nicholls, J. C. *Angew. Chem.* **1990**, *102*, 830. (b) Horton, A. D.; Orpen, A. G. *Organometallics* **1991**, *10*, 3910. (c) Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1991**, *10*, 840. (d) Ewen, J. A.; Elder, M. J.; Jones, R. L.; Haspeslagh, H.; Atwood, J. L.; Bott, S. G.; Robinson, K. *Makromol. Chem., Macromol. Symp.* **1991**, *48/49*, 253. See also: (e) Crowther, D. J.; Baenziger, N. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1991**, *113*, 1455. (f) Hlatky, G. G.; Eckman, R. R.; Turner, H. W. *Organometallics* **1992**, *11*, 1413. (g) Horton, A. D.; Orpen, A. G. *Organometallics* **1992**, *11*, 8.

(6) (a) Jordan, R. F.; Dasher, W. E.; Echols, S. F. *J. Am. Chem. Soc.* **1986**, *108*, 1718. (b) Jordan, R. F.; Bajgur, C. S.; Dasher, W. E.; Rheingold, A. L. *Organometallics* **1987**, *6*, 1041. (c) Borkowsky, S. L.; Jordan, R. F.; Hinch, G. D. *Organometallics* **1991**, *9*, 2574.

(7) (a) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 4111. (b) Jordan, R. F.; LaPointe, R. E.; Bradley, P. K.; Baenziger, N. C. *Organometallics* **1989**, *8*, 2892. (c) See also: Crowther, D. J.; Jordan, R. F.; Baenziger, N. C. *Organometallics* **1990**, *9*, 2574.

(8) (a) Bochmann, M.; Wilson, L. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1610. Eshuis, J. J. W.; Tan, Y. Y.; Teuben, J. H. *J. Mol. Catal.* **1990**, *62*, 277.

(9) Chien, J. C. W.; Tsai, W. M.; Rausch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570.

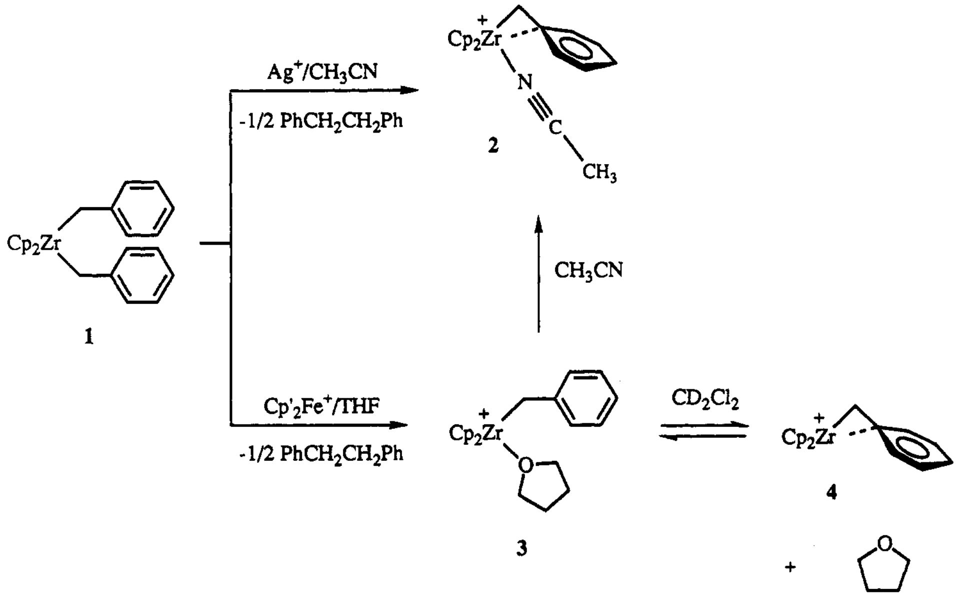
(10) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623.

(11) Jordan, R. F.; LaPointe, R. E.; Baenziger, N. C.; Hinch, G. D. *Organometallics* **1990**, *9*, 1539.

(12) Wang, Y.; Jordan, R. F.; Echols, S. F.; Borkowsky, S. L.; Bradley, P. K. *Organometallics* **1991**, *10*, 1406.

0276-7333/93/2312-0486$04.00/0

Scheme I

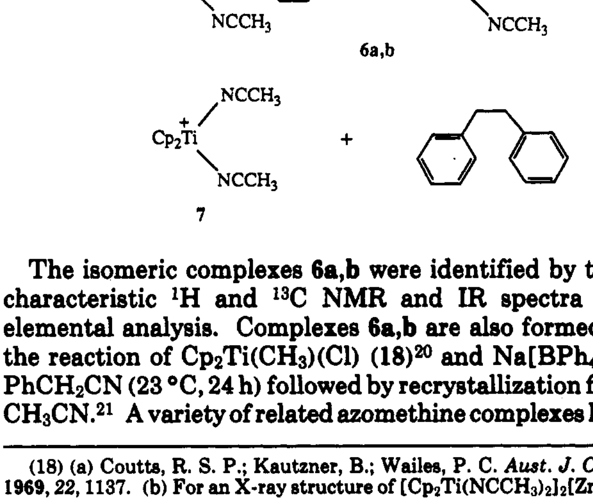


For example, the $Cp_2Zr(CH_3)^+$ ion coordinates two PMe_3 ligands to form the 18-electron $Cp_2Zr(Me)(PMe_3)_2{}^+$ complex, whereas the analogous Ti cation forms the stable 16-electron mono-PMe_3 complex $Cp_2Ti(CH_3)(PMe_3)^+$.[14] Similarly, the Ti(IV) analogues of the 18-electron Zr complexes $Cp_2Zr(L)_3{}^{2+}$ (L = CH_3CN, H_2O) are 16-electron $Cp_2Ti(L)_2{}^{2+}$ complexes.[15] On the basis of this general trend, and the observed lability of the THF ligand of $Cp_2Zr(CH_2Ph)(THF)^+$, we anticipated that the base free (η^2-benzyl)titanium complex $Cp_2Ti(\eta^2\text{-}CH_2Ph)^+$ might be stable. We therefore initiated an effort to explore the synthesis and reactivity of $Cp_2Ti(CH_2Ph)(L)^+$ and related base-free complexes.

Cationic $(C_5R_5)_2Ti(CH_3)(L)^+$ (C_5R_5 = Cp, indenyl, C_5Me_5) complexes have been studied extensively by Bochmann.[14,16] These species are formed by halide displacement from $Cp_2Ti(CH_3)X$ by coordinating solvents or by protonolysis of neutral $Cp_2Ti(CH_3)_2$ complexes and display a rich insertion chemistry. The base-free species $(C_5Me_5)_2Ti(CH_3)^+$ has been reported recently.[16c] Additionally, $Cp^*{}_2Ti(CH_3)(THF)^+$ has been prepared by one-electron oxidation of the Ti^{III} precursor $Cp^*{}_2Ti(CH_3)$.[17] In this paper, we describe related reactions which generate $Cp_2Ti(CH_2Ph)(L)^+$ complexes and the surprising reaction chemistry of these cationic species. We also report the crystal structure of the new cationic Ti(III) complex $Cp_2Ti(THF)(NCCH_3)^+$. All complexes were isolated/manipulated as the $BPh_4{}^-$ salts unless otherwise noted.

Results

Reaction of $Cp_2Ti(CH_2C_6H_5)_2$ (5) with $Ag[BPh_4]$. Synthesis and Characterization of $Cp_2Ti\{N{=}C(CH_3)(CH_2Ph)\}(NCCH_3)^+$ (6a,b) and $Cp_2Ti(NCCH_3)_2{}^+$ (7). The reaction of $Cp_2Ti(CH_2Ph)_2$ (5) and 1 equiv of $Ag[BPh_4]$ in CH_3CN did not yield the expected $Cp_2Ti(CH_2Ph)(CH_3CN)^+$ cation but instead yielded the cationic Ti(IV) azomethine complexes $Cp_2Ti\{N{=}C(CH_3)(CH_2Ph)\}(NCCH_3)^+$ (6a,b; 2/1 ratio, 9.3% isolated yield; eq 1), the known paramagnetic cationic Ti(III) complex $[Cp_2Ti(NCCH_3)_2][BPh_4]$ (7; 44% isolated yield),[18] and bibenzyl.[19] This reaction is complete within ca. 15 min at 23 °C and is unaffected by room light.



(1)

The isomeric complexes 6a,b were identified by their characteristic ^1H and ^{13}C NMR and IR spectra and elemental analysis. Complexes 6a,b are also formed by the reaction of $Cp_2Ti(CH_3)(Cl)$ (18)[20] and $Na[BPh_4]$ in $PhCH_2CN$ (23 °C, 24 h) followed by recrystallization from CH_3CN.[21] A variety of related azomethine complexes have

---

(13) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751.

(14) See ref 6a and: Bochmann, M.; Wilson, L. M.; Hursthouse, M. B.; Short, R. L. *Organometallics* **1987**, *6*, 2556.

(15) (a) Jordan, R. F.; Echols, S. F. *Inorg. Chem.* **1987**, *26*, 383. (b) Thewalt, R.; Klein, H. P. *J. Organomet. Chem.* **1980**, *194*, 297. (c) Thewalt, U.; Lasser, W. *J. Organomet. Chem.* **1984**, *276*, 341.

(16) (a) Bochmann, M.; Wilson, L. M.; Hursthouse, M. B.; Motevalli, M. *Organometallics* **1988**, *7*, 1148. (b) Taube, R.; Krukowka, L. *J. Organomet. Chem.* **1988**, *347*, C9. (c) Bochmann, M.; Jaggar, A. J. *J. Organomet. Chem.* **1992**, *424*, C5.

(17) Bochmann, M.; Jagger, A. J.; Wilson, L. M.; Hursthouse, M. B.; Motevalli, M. *Polyhedron* **1989**, *8*, 1838.

(18) (a) Coutts, R. S. P.; Kautzner, B.; Wailes, P. C. *Aust. J. Chem.* **1969**, *22*, 1137. (b) For an X-ray structure of $[Cp_2Ti(NCCH_3)_2]_2[ZnCl_4]$, see: Seewald, P. A.; White, G. S.; Stephan, D. W. *Can. J. Chem.* **1988**, *66*, 1148.

(19) ^1H NMR of bibenzyl (300 MHz, in CD_3CN): δ 7.3–7.2 (10 H, m, C_6H_5), 2.91 (4 H, s CH_2).

(20) Clauss, K.; Bestian, H. *Justus Liebigs Ann. Chem.* **1962**, *654*, 8.

(21) Cp_2TiCl_2 and several minor unidentified Cp_2Ti^{IV} and possibly Ti(III) product(s) are also formed.

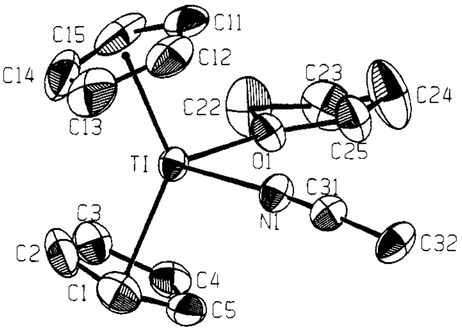


Figure 1. ORTEP view of the cation of 8.

been characterized previously.[1,16a,22] Complex 7 was identified by comparison of its IR spectrum with that reported by Coutts (ν_{CN} = 2268, 2278 cm^{-1} for 7, ν_{CN} = 2265, 2275 cm^{-1} reported).[18] The splitting of the ν_{CN} band was noted in the literature and is due to Fermi resonance. The ESR spectrum of 7 contains a single major peak (*g* value 1.979 μ_B) and satellite peaks from hyperfine coupling (9 G) to ^{47}Ti ($I = {}^5/_2$) and ^{49}Ti ($I = {}^7/_2$), consistent with a monomeric Ti(III) complex.[23] In addition, recrystallization of 7 from THF yielded the new cationic Ti(III) complex $Cp_2Ti(NCCH_3)(THF)^+$ (8; eq 2), which has been characterized by spectroscopy, analysis, and X-ray diffraction (Figure 1; vide infra).

(2)

The low isolated yields of the 6a,b and 7 in eq 1 are primarily due to the difficulty of separating these complexes from each other and from the Ag^0 and bibenzyl coproducts. As a prelude to mechanistic studies of this reaction, we determined accurate product yields by a combination of ^{1}H NMR and quantitative EPR spectroscopies. The reaction of 5 and Ag[BPh$_4$] in CD$_3$CN was performed on an NMR scale with a slight excess of 5; under these conditions Ag[BPh$_4$] is the limiting reagent and all of the BPh$_4^-$ salts are soluble at the end of the reaction. When the reaction was complete, a known amount of Si(CH$_2$CH$_3$)$_4$ was added as an internal standard and the yield of 6a,b determined to be 26% by comparison of the Cp and Si(CH$_2$CH$_3$)$_4$ ^{1}H NMR integrals. To determine the yield of paramagnetic 7, the EPR spectra of standard solutions of 7 in CH$_3$CN, and neat CH$_3$CN, were recorded. A linear calibration curve of peak area (determined by double integration) vs [7] was obtained from these spectra. The NMR reaction mixture was then diluted to an accurate volume and its EPR spectrum was obtained under identical conditions. The only observable peak was that for 7. The yield of 7 was determined to be 71% by interpolation using the peak area/[7] calibration curve. Thus, the product ratio for 7/6a,b is 71/26 or 2.7:1.[24] As identical product ratio was obtained by NMR integration assuming that the excess BPh$_4^-$ (vs 6a,b) is associated with NMR-silent 7. Furthermore, comparison of the BPh$_4^-$ para H integral with the total CH$_2$ integrals (Ti–C*H*$_2$ for 6a,b and bibenzyl) revealed an excellent mass balance of benzyl groups (>90%) for the reaction.

Table I. Summary of Crystallographic Data for 8

compd	$[Cp_2Ti(THF)(NCCH_3)][BPh_4]$
empirical formula	$C_{40}H_{41}BONTi$
fw	610.48
cryst size, mm	0.13 × 0.35 × 0.35
cryst color	blue
cryst shape	platelet
T, K	295
space group	$P2_1/n$
a, Å	13.432 (2)
b, Å	16.241 (6)
c, Å	15.393 (4)
β, deg	96.08 (2)
V, Å^3	3339.1 (2.7)
Z	4
d(calcd), g/cm^3	1.214
cell dimens	25 rflns; 30–40° (2θ)
radiation	Mo Kα (λ = 0.710 73 Å)
scan ratio, $2\theta/\omega$	1.0
scan limit, deg	$2 < 2\theta < 40$
scan speed, deg/min	0.66–5.0
scan range	0.8 + 0.35 tan (2θ)
data collected	$\pm h,-k,\pm l$
no. of rflns collected	6518
no. of unique rflns	3113
decay (F^2), %	0.9
agreement between equiv rflns	1% on *F*
no. of rflns $I > 2\sigma(I)$	1991
abs: μ, cm^{-1}	3.01
abs cor (emp on *F*)	none
soln method	Patterson and DIRDIF
refinement model	anisotropic on all non-H in cation, isotropic on non-H in anion, fixed H
data/param in LS	1991/272
R^a	0.058
$R_w{}^b$	0.088
wt (Killean and Lawrence)^c	$P = 0.06$, $Q = 1.0$
SDOUW^d	1.20
max param shift/esd	0.14
max residual electron density, e/Å^3	0.47

[a] $R = \sum\Delta F_H/\sum F_{o,H}$, where $H = hkl$ and F_o is scaled to F_c. ΔF is $||F_o| - |F_c||$. [b] $[R_w]^2 = \Delta w(\Delta F_H)^2/\Delta w(F_{o,H})^2$. [c] Killean and Lawrence weights are $1/(S^2 + (PF)^2 + Q)$, where *S* is the ESD in *F* from counting statistics. If several octants are averaged, *S* is the larger of the two estimates—one based on counting statistics and the other based on the agreement between equivalent reflections. esd = estimated standard deviation (Killean, R. C. G.; Lawrence, J. L. *Acta Crystallogr., Sect. B* **1969**, *B25*, 1750). [d] SDOUW = standard deviation in an observation of unit weight.

It is surprising that Ti(III) complex 7, which is generated by the oxidation of 5 with Ag[BPh$_4$], is not further oxidized to $Cp_2Ti(NCCH_3)_2{}^{2+}$.[18,25] In fact, control experiments show that there is no reaction between Ag[BPh$_4$] and 7. This may in part be due to the insolubility of Ag[BPh$_4$].

X-ray Structure of [Cp$_2$Ti(CH$_3$CN)(THF)][BPh$_4$]. To confirm the identity of the Cp$_2$Ti(L)$_2^+$ products, [Cp$_2$Ti(THF)(NCCH$_3$)][BPh$_4$] (8) was characterized by X-ray crystallography (Figure 1). Crystallographic data, positional parameters, and bond distances and angles are given in Tables I–IV.

---

(22) (a) den Haan, K. H.; Luinstra, G. A.; Meetsma, A.; Teuben, J. H. *Organometallics* **1987**, *6*, 1509. (b) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 1291. (c) Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443.

(23) (a) Green, M. L. H.; Lucas, C. R. *J. Chem. Soc., Dalton Trans.* **1972**, 1000. (b) Chaloyard, A.; Dormond, A.; Tirouflet, J.; el Murr, Nabil. *J. Chem. Soc., Chem. Commun.* **1980**, 214. (c) Samuel, E.; Vedel, J. *Organometallics* **1989**, *8*, 237.

(24) The uncertainty in this value is dominated by the uncertainty in the NMR integrals and is estimated to be ±10%.

(25) (a) The reaction of Cp$_2$TiI$_2$ with Tl[PF$_6$] in CH$_3$CN yields [Cp$_2$Ti(NCCH$_3$)$_2$][PF$_6$]$_2$; see: Bruce, M. R. M.; Tyler, D. R. *Organometallics* **1985**, *4*, 528. (b) For [Cp$_2$Ti(NCCH$_3$)$_2$][SbCl$_6$]$_2$ see: Billinger, P. N.; Claire, P. P. K.; Collins, H.; Willey, G. R. *Inorg. Chim. Acta* **1988**, *149*, 63. (c) For [Cp$_2$Ti(NCCH$_3$)$_3$][AsF$_6$]$_2$ see: Klapotke, T. *Polyhedron* **1989**, *8*, 315.

Table II. Positional Parameters for 8[a]

atom	*x*	*y*	*z*	*B*, Å^2
Ti	0.28194 (8)	–0.39449 (8)	0.33806 (8)	4.21 (3)
C1	0.3230 (7)	–0.4617 (6)	0.4709 (6)	8.2 (3)
C2	0.2247 (7)	–0.4407 (6)	0.4664 (5)	8.2 (2)
C3	0.1724 (6)	–0.4849 (5)	0.3998 (5)	7.2 (2)
C4	0.2411 (6)	–0.5368 (5)	0.3636 (5)	6.6 (2)
C5	0.3341 (6)	–0.5212 (5)	0.4075 (5)	7.2 (2)
C11	0.2580 (7)	–0.2716 (5)	0.2557 (6)	7.9 (2)
C12	0.3226 (6)	–0.2533 (5)	0.3249 (7)	8.0 (3)
C13	0.2800 (8)	–0.2627 (5)	0.4011 (7)	9.5 (3)
C14	0.1810 (7)	–0.2842 (6)	0.3742 (7)	9.4 (3)
C15	0.1689 (6)	–0.2917 (5)	0.2865 (7)	8.8 (3)
O1	0.2594 (3)	–0.4456 (3)	0.2066 (3)	5.3 (1)
C22	0.1603 (7)	–0.4665 (7)	0.1649 (6)	9.6 (3)
C23	0.1780 (8)	–0.5124 (7)	0.0853 (6)	9.4 (3)
C24	0.2748 (8)	–0.4864 (9)	0.0635 (6)	12.4 (4)
C25	0.3297 (6)	–0.4506 (6)	0.1433 (5)	7.7 (2)
N1	0.5604 (4)	0.4022 (4)	0.6805 (4)	5.2 (2)
C31	0.4783 (5)	0.4102 (4)	0.6869 (5)	5.0 (2)
C32	0.3717	0.4233 (5)	0.6932 (6)	6.4 (2)
B	0.6678 (5)	–0.1263 (4)	0.2649 (4)	3.2 (1)*
C1P	0.6047 (4)	–0.1831 (4)	0.1898 (4)	3.6 (1)*
C2P	0.5081 (5)	–0.1642 (5)	0.1579 (4)	5.3 (2)*
C3P	0.4518 (6)	–0.2117 (5)	0.0944 (5)	6.3 (2)*
C4P	0.4923 (6)	–0.2801 (6)	0.0632 (5)	7.0 (2)*
C5P	0.5858 (6)	–0.3043 (5)	0.0944 (6)	7.4 (2)*
C6P	0.6421 (5)	–0.2548 (5)	0.1580 (5)	5.4 (2)*
C11P	0.6381 (4)	–0.0282 (4)	0.2511 (4)	3.2 (1)*
C12P	0.6177 (5)	0.0057 (4)	0.1677 (4)	4.3 (1)*
C13P	0.6013 (5)	0.0908 (5)	0.1551 (4)	5.2 (2)*
C14P	0.6047 (5)	0.1414 (5)	0.2254 (5)	5.4 (2)*
C15P	0.6228 (5)	0.1132 (5)	0.3045 (5)	5.6 (2)*
C16P	0.6413 (5)	0.0279 (4)	0.3197 (4)	5.1 (2)*
C21P	0.7882 (4)	–0.1292 (4)	0.2602 (4)	3.5 (1)*
C22P	0.8552 (5)	–0.1122 (5)	0.3327 (4)	5.3 (2)*
C23P	0.9601 (6)	–0.1115 (5)	0.3299 (5)	6.4 (2)*
C24P	0.9972 (6)	–0.1274 (5)	0.2522 (5)	6.4 (2)*
C25P	0.9369 (6)	–0.1425 (5)	0.1808 (5)	5.7 (2)*
C26P	0.8327 (5)	–0.1440 (4)	0.1840 (4)	4.6 (1)*
C31P	0.6388 (4)	–0.1625 (4)	0.3581 (4)	3.6 (1)*
C32P	0.5589 (5)	–0.1368 (5)	0.3987 (4)	5.0 (2)*
C33P	0.5332 (6)	–0.1712 (5)	0.4796 (5)	6.5 (2)*
C34P	0.5886 (6)	–0.2324 (5)	0.5151 (5)	6.4 (2)*
C35P	0.6665 (6)	–0.2636 (5)	0.4788 (5)	6.6 (2)*
C36P	0.6930 (5)	–0.2276 (5)	0.4007 (5)	5.2 (2)*

[a] Starred values denote atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement 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 III. Selected Bond Distances (Å) for 8

Ti–(C1 centroid)	2.055	C1–C5	1.39 (1)
Ti–(C2 centroid)	2.041	C1–C2	1.36 (1)
Ti–N1	2.170 (6)	O1–C25	1.429 (9)
Ti–O1	2.175 (4)	C2–C3	1.38 (1)
N1–C31	1.124 (8)	C3–C4	1.41 (1)
O1–C22	1.456 (9)	C4–C5	1.38 (1)
C22–C23	1.48 (1)	C24–C25	1.48 (1)
C23–C24	1.44 (1)		

Table IV. Selected Bond and Dihedral Angles (deg) for 8

Ti–O1–C22	121.9 (5)
Ti–O1–C25	128.2 (5)
C22–O1–C25	109.0 (6)
(C1 centroid)-Ti-(C2 centroid)	135.6
O1–Ti–N1	84.2 (2)
Ti–N1–C31	175.7 (7)
C31–N1–C32	177.9 (8)
C22–O1–C25)/(O1–Ti–N1)	11.8
(O1–Ti–N1)/((C1 centroid)-Ti-(C2 centroid))	90.7

Complex 8 adopts a normal bent-metallocene/pseudotetrahedral structure similar to those of related $Cp_2Ti^{III}(L)_2^+$ complexes. The (Cp centroid)–Ti–(Cp centroid) angle (135.6°) is very similar to those of $[Cp_2Ti^{III}(acetone)(THF)]_2[Zn(B_{10}H_{12})_2]$ (9; 136.0, 135.2° for two independent cations),[26] $[Cp_2Ti^{III}(NCCH_3)_2]_2[ZnCl_4]$ (10; 134.8°),[18b] and $[Cp_2Ti^{III}(THF)_2][Co(CO)_4]$ (11; 131.3–134.2° for three independent cations).[27] The Ti–(Cp centroid) distances for 8–11 are all very similar (2.05–2.07 Å). The O1–Ti–N1 angle of 8 (84.2°) is close to the optimum value (85°) predicted by EHMO theory for d^1 Cp_2ML_2 complexes[28] and in the normal range observed experimentally for d^1 $Cp_2MX_2{}^{n+}$ halide complexes.[29] It is, however, larger than the observed O–Ti–O angles for 9 (76.9, 78.6°) and 11 (77–83°) and the N–Ti–N angle for 10 (80.6, 80.8°). The Ti–OC_4H_8 distance of 8 (2.175 (4) Å) is somewhat shorter than those for 9 (2.21 Å) and 11 (average 2.21 Å). These differences can reasonably be ascribed to the reduced crowding in 8. The Ti–N bond length of 2.170 (6) Å for 8 compares well with the average Ti–N bond length for 10 (2.16 Å), and the CH_3CN ligand is nearly linear. The dihedral angle defined by the O1–Ti–N1 and C22–O1–C25 (THF) planes is 11.8° and places the THF ligand in the sterically noncongested plane between the two Cp ligands. This geometry precludes any significant Ti–O dπ–pπ orbital overlap.[30]

Mechanism of Formation of 6a,b and 7. One reasonable mechanism for the formation of 6a,b and 7 in the reaction of 5 with $Ag[BPh_4]$ involves the stepwise cleavage/loss of benzyl groups from 5 as illustrated in Scheme II. In this scheme, initial oxidative cleavage of one Ti–CH_2-Ph bond by Ag$^+$ yields the reactive cationic monobenzyl complex $Cp_2Ti^{IV}(CH_2Ph)(NCCH_3)^+$ (12),[31] a benzyl radical, and Ag^0, analogous to Scheme I. Complex 12 then undergoes competitive CH_3CN insertion (path a) followed by trapping by CH_3CN, yielding Ti^{IV} azomethine products 6a,b *or* Ti–CH_2Ph homolysis (path b) followed by CH_3CN trapping to yield $Cp_2Ti^{III}(NCCH_3)_2^+$ (7). In CD_3CN or CH_3CN solvent, benzyl radicals are expected to undergo predominant dimerization to the observed coupling product $PhCH_2CH_2Ph$ rather than D/H abstraction from solvent.[32]

An alternative possible mechanism (Scheme III) for this reaction involves initial outer-sphere oxidation of 5 followed by intramolecular reductive elimination of bibenzyl (path c), yielding Ti^{III} product 7. Competitive with this path is loss of benzyl radical from the initial oxidation product to yield intermediate 12, which undergoes CH_3CN insertion, ultimately yielding 6a,b (path d). This mechanism is suggested by the recent observation of Burk, Tumas, and Ward that chemical/electrochemical oxidation of titanacyclobutane complexes results in reductive elim-

---

(26) Allman, R.; Batzel, V.; Pfeil, R.; Schmid, G. *Z. Naturforsch.* **1976**, *31B*, 1329.

(27) Merola, J. S.; Campo, K. S.; Gentile, R. A.; Modrick, M. A. *Inorg. Chim. Acta* **1989**, *165*, 87.

(28) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

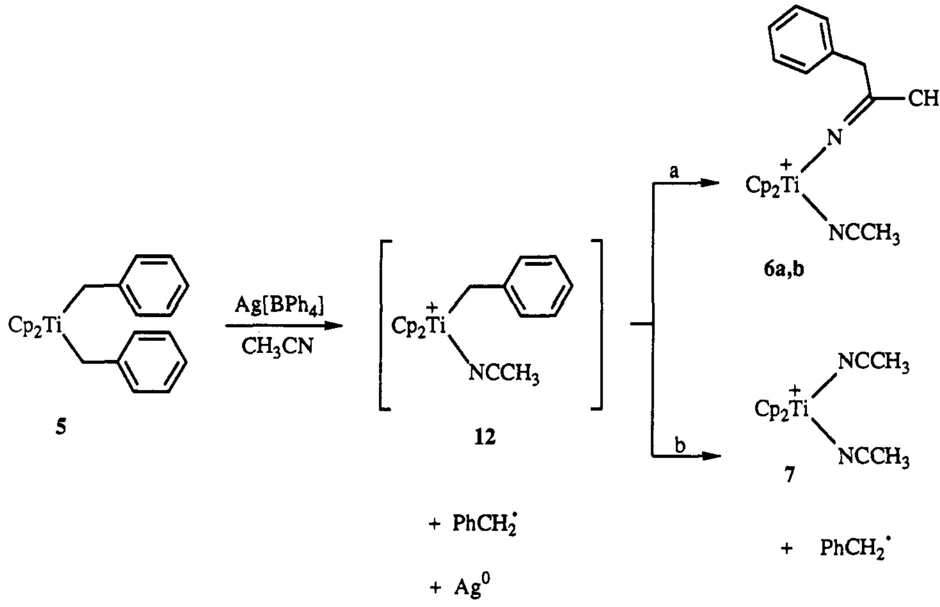
(29) Prout, K.; Cameron, T. S.; Forder, R. A.; Critchley, S. R.; Denton, B.; Rees, G. V. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2290.

(30) In contrast, the THF ligand of the d^0 complex $Cp_2Zr(CH_3)(THF)^+$ lies nearly in the (Cp centroid)–Zr–(Cp centroid) plane, which allows for Zr–O dπ–pπ ovelap. Chemical reactivity results are consistent with Zr–O π bonding in this case.[6b]

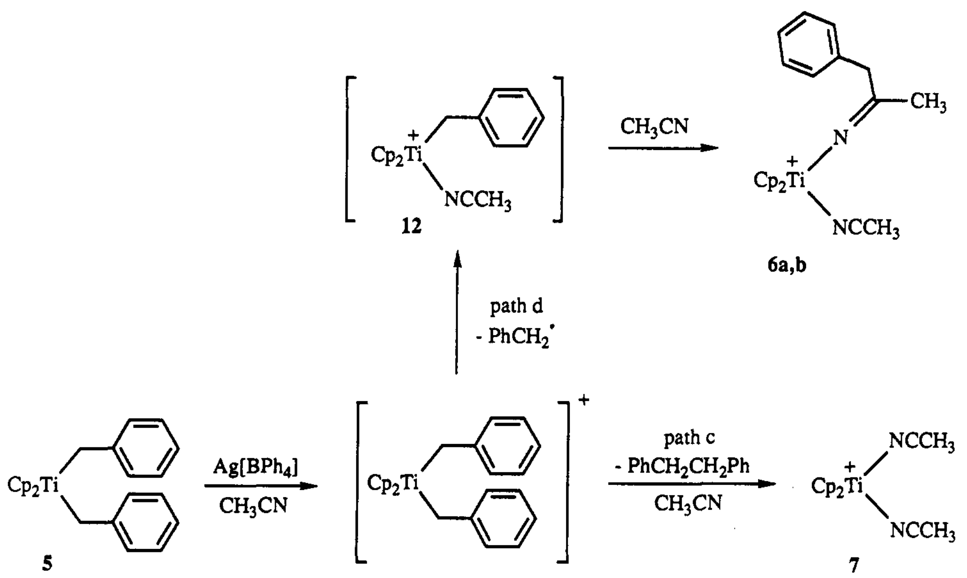
(31) This cleavage may involve –CH_2Ph abstraction by Ag$^+$ to yield $[AgCH_2Ph]$, which is expected to decompose to Ag^0, and $PhCH_2CH_2Ph$, or initial outer-sphere electron transfer as in Scheme III (vide infra), followed by loss of CH_2Ph radical. Attempts by others to prepare $AgCH_2$-Ph or to observe it at –78 °C have been unsuccessful and have yielded Ag^0 and bibenzyl: (a) Glockling, F.; Kingston, D. *J. Chem. Soc.* **1959**, 3001 (Part 3). (b) Beverwijk, C. D. M.; van der Kerk, G. J. M.; Leusink, A. J.; Noltes, J. G. *Organomet. Chem. Rev. A* **1970**, *5*, 215.

(32) (a) The photodecarbonylation of dibenzyl ketone in CH_3CN yields bibenzyl, not toluene; see: Robbins, W. K.; Eastman, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 6077. (b) In CH_3OH; see: Meiggs, T. O.; Grossweiner, L. I.; Miller, S. I. *J. Am. Chem. Soc.* **1972**, *94*, 7686.

Scheme II



Scheme III



ination of cyclopropanes with a high degree of retention of configuration.[33]

The key difference between these two mechanisms is that in Scheme II bibenzyl is formed by an intermolecular path (coupling of benzyl radicals), while in Scheme III bibenzyl is formed by intramolecular reductive elimination. To distinguish these mechanisms several labeling experiments were conducted.

The reaction of a 1:1 mixture of **5** and $Cp_2Ti(CD_2C_6D_5)_2$ (**5**-d_{14}) with $Ag[BPh_4]$ in CD_3CN yielded a 1:2:1 mixture of scrambled bibenzyls $C_6H_5CH_2CH_2C_6H_5$, $C_6H_5CH_2CD_2C_6D_5$, and $C_6D_5CD_2CD_2C_6D_5$ by GC-MS. This statistical scrambling favors Scheme II. However, the observed scrambling may also have resulted from a Ag^+-mediated exchange of benzyl groups between **5** and **5**-d_{14}. To investigate the facility of such benzyl exchange reactions in $Cp_2Ti(benzyl)_2$ systems, we studied the reactions of **5** with the chemically labeled complex $Cp_2Ti(p\text{-}CH_2C_6H_4CH_3)_2$ (**13**).[34]

On the basis of ^1H NMR data for related mixed $Cp_2Zr(R)(R')$ and $Cp_2Ti(R)(R')$ compounds,[35,36] we anticipated that the ^1H NMR Cp resonance of the mixed-benzyl complex $Cp_2Ti(CH_2Ph)(p\text{-}CH_2C_6H_4CH_3)$ (**14**) would lie between the resonances for **5** and **13**. In fact, ^1H NMR analysis of a 1:1 mixture of **5** (δ 5.54, Cp) and **13** (δ 5.59, Cp) in C_6D_6 after 1.5 h at 23 °C revealed the appearance of a single new Cp resonance at δ 5.57, which is assigned to **14** (eq 3).[37] Complex **14** grew in with time relative to **5** and **13** (**5**:**14**:**13** = 3:1:3 after 7 h), but thermal decomposition also occurred, as evidenced by the appearance of

---

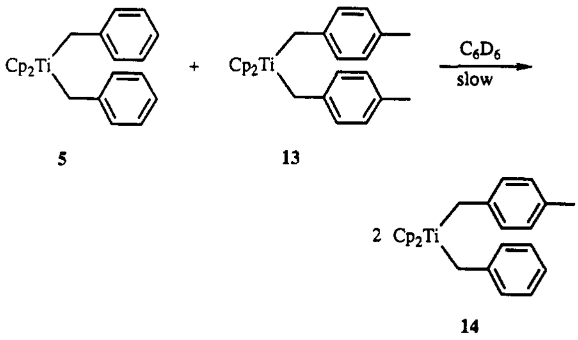
(33) Burk, M. J.; Tumas, W.; Ward, M. D.; Wheeler, D. R. *J. Am. Chem. Soc.* **1990**, *112*, 6133.

(34) Chemical labeling is required here, as parent ions are not observed in the mass spectra of $Cp_2Ti(CH_2Ph)_2$ complexes.

(35) (a) ^1H NMR of sample Zr compounds (Cp in C_6D_6): $Cp_2Zr(CH_2Ph)_2$, δ 5.51; $Cp_2Zr(Ph)_2$, δ 5.77; $Cp_2Zr(CH_2Ph)(Ph)$ ^1H NMR δ 5.65. (b) ^1H NMR in CD_3CN: $Cp_2Zr(CH_3)_2$, δ 6.12; $Cp_2Zr(CH_2Ph)_2$, δ 5.96; $Cp_2Zr(CH_3)(CH_2Ph)$, δ 6.00. (c) For $Cp_2Zr(CH_3)_2$, $Cp_2Zr(CH_3)X$, and Cp_2ZrX_2 compounds see: Jordan, R. F. *J. Organomet. Chem.* **1985**, *294*, 312.

(36) ^1H NMR of Ti compounds (Cp): (a) Cp_2TiCl_2, δ 6.60; $Cp_2Ti(CH_3)_2$, δ 5.90; $Cp_2Ti(CH_3)(Cl)$, δ 6.19 (in CCl_4) (Beachell, H. C.; Butter, S. A. *Inorg. Chem.* **1965**, *4*, 1133). (b) $Cp_2Ti(CH_2Ph)_2$, δ 6.01; Cp_2TiCl_2, δ 6.70 (Bruce, P. M.; Kingston, B. M. ; Lappert, M. F.; Spalding, T. R.; Srivasta, R. C. *J. Chem. Soc. A* **1969**, 2106), $Cp_2Ti(CH_2Ph)(Cl)$, δ 6.17.

(37) The other resonances of **14** are coincident with those for **5** or **13**.



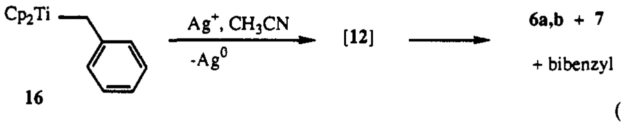
(3)

resonances for toluene and *p*-xylene. This establishes that **14** can be detected by NMR and that exchange of benzyl groups between **5** and **13** is slow in the absence of Ag^+ in C_6D_6. ^1H NMR monitoring of the reaction of **13** with $Ag[BPh_4]$ in CD_3CN revealed the formation of the substituted bibenzyl $(p\text{-}CH_3C_6H_4CH_2)_2$ (δ 2.84, 2.27), as the sole organic product and the insertion products $Cp_2Ti\{N{=}C(CH_3)(p\text{-}CH_3C_6H_4)\}(NCCH_3)^+$ (**15a,b**). Thus, complex **13** reacts in a manner analogous to that for **5**.[38]

To check for the scrambling of benzyl groups of neutral $Cp_2Ti(benzyl)_2$ complexes in the *presence of Ag^+ prior to Ti–CH_2Ph cleavage*, we reacted a 1:1 mixture of **5** and **13** with $^1/_2$ equiv of $Ag[BPh_4]$ in CD_3CN at 23 °C for 15 min (reaction complete) and then removed the solvent under vacuum. The ^1H NMR spectrum of a C_6D_6 extract of the residue indicated the presence of unreacted **5** and **13**, but no **14**.[39] Thus, scrambling of benzyl groups between **5** and **13** does not occur under the $Ag[BPh_4]$ reaction conditions. On this basis, we conclude that scrambling of benzyl groups between **5** and **5**-d_{14} also is unlikely under $Ag[BPh_4]$ reaction conditions and that the reaction of **5** with $Ag[BPh_4]$ proceeds via the mechanism in Scheme II.

Alternate Routes to $Cp_2Ti(CH_2Ph)(NCCH_3)^+$ (12). To confirm the conclusion above that cationic complex **12** is formed by the reaction of **5** and $Ag[BPh_4]$ and undergoes competitive CH_3CN insertion and Ti–CH_2Ph homolysis, we explored other routes to this species and *qualitatively* analyzed the resulting product distributions.

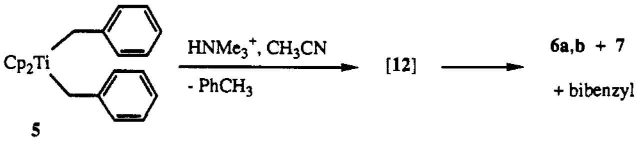
(i) Reaction of $Cp_2Ti(CH_2Ph)$ with $Ag[BPh_4]$. A solution of $Cp_2Ti(CH_2Ph)$[40] (**16**) in toluene was prepared by the reaction of Cp_2TiCl[41] with $K[CH_2Ph]$;[42] at −78 °C under N_2 this solution displayed the expected intense blue color of the N_2 adduct $Cp_2Ti(CH_2Ph)(N_2)$. The solution was transferred via cannula to a slurry of $Ag[BPh_4]$ in CH_3CN. The mixture was stirred for 1 h at −10 °C and then warmed and filtered, and the filtrate was evaporated to dryness. The ^1H NMR spectrum of the crude product mixture showed resonances for bibenzyl and insertion products **6a,b**. An IR spectrum of the product showed ν_{CN} bands for coordinated CH_3CN which matched those for **7**. Teuben has reported that the sole organic product of the thermal decomposition of **16** is toluene[43] and that $Cp_2Ti(R)$ complexes reductively couple rather than insert CH_3CN.[44] Thus, the observed products **6a,b**, **7**, and bibenzyl are not derived from thermolysis of **16** or the reaction of **16** with CH_3CN. We therefore conclude that **6a,b** and **7** are formed from cationic complex **12**, which is the expected product of one-electron oxidation of **16** (eq 4).



(4)

(ii) Reaction of $Cp_2Ti(CH_2Ph)_2$ (5) with $[Cp'_2Fe][BPh_4]$ ($Cp' = C_5H_4Me$). The reaction of **5** with the outer-sphere oxidant $[Cp'_2Fe][BPh_4]$ in CD_3CN is much slower (hours) and less clean than the reaction with $Ag[BPh_4]$. The ^1H NMR spectrum of the product mixture from this reaction included resonances for insertion products **6a,b** (2/1 ratio), Cp'_2Fe (δ 3.95, 1.95), bibenzyl, toluene, and several unidentified Cp_2Ti^{IV} species. The GC–MS of the product mixture included a peak at *m/e* 304 corresponding to dimethylbenzylferrocene, an expected coupling product of benzyl radicals and Cp'_2Fe^+.[45,46] When the reaction was performed on a preparative scale, the IR spectrum of the crude product mixture contained the characteristic ν_{CN} bands of **7**. These results are consistent with formation and further reaction of **12**.

(iii) Reaction of $Cp_2Ti(CH_2Ph)_2$ with $[HNMe_3][BPh_4]$. The NMR-scale reaction of **5** with $[HNMe_3][BPh_4]$ in CD_3CN yielded **6a,b** and **7** (eq 5), toluene and bibenzyl (2.5/1 ratio), and several other minor unidentified Cp-containing products. This reaction likely proceeds via initial protonation of **5** by $HNMe_3^+$ to form toluene and **12**, which then undergoes competitive insertion and homolysis to form **6a,b** and **7**, respectively.



(5)

(iv) Reaction of $Cp_2Ti(CH_2Ph)Cl$ with $Na[BPh_4]$ in CH_3CN. Bochmann has prepared $Cp_2Ti(CH_3)(CH_3CN)^+$ by reaction of $Cp_2Ti(CH_3)Cl$ with $Na[BPh_4]$ in CH_3CN; evidently Na^+ precipitates the Cl^- formed by dissociation from Ti. We anticipated that a similar reaction between $Cp_2Ti(CH_2Ph)Cl$ (**17**)[47] and $Na[BPh_4]$ in CH_3CN would provide a simple route to **12**. The reaction of **17** with $Na[BPh_4]$ in CD_3CN was monitored by variable-temperature ^1H NMR spectroscopy (eq 6). No reaction was apparent below 10 °C. However, when the temperature was raised to 23 °C, resonances for **6a,b**-d_6 and

---

[38] Presumably 7 is also formed in this reaction.

[39] C_6D_6 was used to simplify the spectrum due to overlapping resonances for 5 and one isomer of 6a,b. The ^1H NMR spectrum of the C_6D_6 extract also contained resonances for $PhCH_2CH_2Ph$, $PhCH_2CH_2Ph'$, and $Ph'CH_2CH_2Ph'$ ($Ph' = p\text{-}CH_3C_6H_4$). The ratio of these products was quite sensitive to the reaction conditions, but the last two complexes were always present in excess, indicating more facile cleavage of Ti–CH_2Ph' groups vs Ti–CH_2Ph groups. Consistent with this, there was always more unreacted 5 than 11 and more 13a,b than 6a,b in the product mixture.

[40] Teuben, J. H.; De Liefde Meijer, H. J. *J. Organomet. Chem.* **1972**, *46*, 313.

[41] Manzer, L. *J. Organomet. Chem.* **1976**, *110*, 291.

[42] (a) Schlosser, M. *J. Organomet. Chem.* **1967**, *8*, 9. (b) Schlosser, M.; Hartmann, J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 248. (c) Bulls, A. R.; Schaefer, W. P.; Serfas, M.; Bercaw, J. E. *Organometallics* **1987**, *6*, 1219.

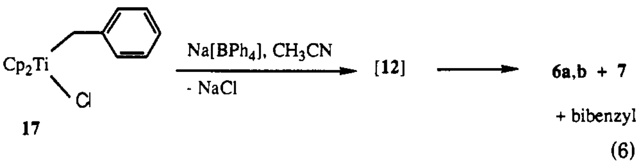
[43] Teuben, J. H. *J. Organomet. Chem.* **1974**, *69*, 241.

[44] (a) De Boer, E. J. M.; Teuben, J. H. *J. Organomet. Chem.* **1977**, *140*, 41. (b) De Boer, E. J. M.; Teuben, J. H. *J. Organomet. Chem.* **1978**, *153*, 53.

[45] (a) Little, W. F.; Clark, A. K. *J. Org. Chem.* **1960**, *25*, 1979. (b) Little, W. F.; Lynn, K. N.; Williams, R. *J. Am. Chem. Soc.* **1963**, *85*, 3055.

[46] The reaction of benzyl radicals with Cp_2Fe^+ yields benzylferrocene and H^+, which may protonate 5 to yield toluene: (a) Beckwith, A. L.; Leyden, R. J. *Tetrahedron* **1964**, *20*, 791. (b) Beckwith, A. L.; Leyden, R. J. *Aust. J. Chem.* **1966**, 1381.

[47] (a) Long, W. P.; Breslow, D. S. *J. Am. Chem. Soc.* **1960**, *82*, 1953. (b) Waters, J. A.; Mortimer, G. A. *J. Organomet. Chem.* **1970**, *22*, 417.

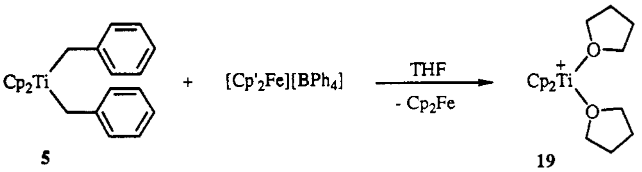


(6)

bibenzyl were observed. When the reaction of **17** with $Na[BPh_4]$ was performed on a preparative scale in CH_3CN, a blue paramagnetic solid was isolated whose EPR and IR spectra were identical with those for **7**. These observations are consistent with the generation of **12** via Cl^- dissociation from **17**.

During these studies we also noted that a reaction occurs between **17** and CD_3CN even in the absence of $Na[BPh_4]$. When a solution of **17** in CD_3CN was monitored by ^1H NMR, resonances for bibenzyl and two new sets of Cp and $N{=}C{-}CH_2$ resonances (2/1 ratio)[48] which are slightly shifted from those of **6a,b** were observed. The residual CD_2HCN solvent resonance appeared as a single, broad (>400 Hz) peak rather than the expected sharp pentet. After addition of $Na[BPh_4]$ to the sample, ^1H NMR resonances of **6a,b** were observed, and the residual solvent peak was sharp. When the solvent was evaporated, the IR spectrum of the resulting precipitate contained bands matching those for **7**. On the basis of these observations, we suggest that **17** reacts with CD_3CN by Cl^- dissociation, yielding **12**, followed by competitive insertion and homolysis, and ultimate trapping by Cl^- to yield $Cp_2Ti^{IV}\{N{=}C(CH_2Ph)(CD_3)\}(Cl)$ (**18a,b**) and the Ti(III) complex $Cp_2Ti(Cl)(CD_3CN)$, which undergoes rapid CD_3CN exchange with solvent. Consistent with this interpretation, the ^1H NMR spectrum of a solution of $[Cp_2TiCl]_2$ in CD_3CN contained a broad (>600 Hz at 360 MHz) CD_2HCN resonance. Addition of $Na[BPh_4]$ to this solution (to generate **7**)[18] resulted in a sharp pentet for CD_2HCN.

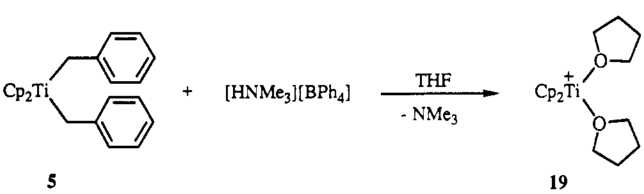
Reaction of 5 with $[Cp'_2Fe][BPh_4]$ and $[HNMe_3][BPh_4]$ in THF. Synthesis of $[Cp_2Ti(THF)_2][BPh_4]$. The results described above establish that $Cp_2Ti(CH_2Ph)(CH_3CN)^+$ (**12**) is unstable toward CH_3CN insertion and homolysis. We were unable to detect this species under a variety of conditions, even at low temperature. In an effort to prepare a more stable $Cp_2Ti(CH_2Ph)(L)^+$ species, we investigated the oxidation and protonolysis of **5** in THF. The reaction of **5** with $[Cp'_2Fe][BPh_4]$ in THF at room temperature yields the blue-green paramagnetic complex $[Cp_2Ti(THF)_2][BPh_4]$ (**19**; 27% isolated yield; eq 7).



(7)

The ^1H NMR spectrum of **19** in THF-d_8 includes broad C_4H_8O and $B(C_6H_5)_4^-$ resonances but no C_5H_5 resonances.[49] Comparison of the C_4H_8O and $B(C_6H_5)_4^-$ peak integrals confirms the presence of two THF ligands per BPh_4^- counterion. The ESR spectrum of **19** shows one major peak ($g = 1.973$) with hyperfine coupling (12 G) to ^{47}Ti and ^{49}Ti consistent with a monomeric Ti(III) complex. The IR spectrum contains bands for coordinated THF (1026, 850 cm^{-1}), which are shifted to lower energy relative to those of free THF (1065, 907 cm^{-1}).[50] Merola has prepared the analogous $Co(CO)_4^-$ salt $[Cp_2Ti(THF)_2][Co(CO)_4]$ (**20**) and has characterized it by single-crystal X-ray diffraction.[27,51]

Two mechanisms are again possible for the formation of **19** in eq 7: (i) initial oxidation of **5** followed by concerted reductive elimination of bibenzyl or (ii) initial oxidative cleavage of one $Ti{-}CH_2Ph$ bond to yield an intermediate $Cp_2Ti(CH_2Ph)(THF)^+$ (**21**) species followed by $Ti{-}CH_2Ph$ homolysis. To probe this question, we looked briefly at alternative routes to **21**. The reaction of **5** with $[HNMe_3][BPh_4]$ in THF is slow at room temperature but proceeds at 50 °C (overnight) to yield **19** (74% isolated yield) along with toluene and bibenzyl (approximately 2/1 ratio, eq 8).



(8)

As the first step in this reaction is almost certainly $Ti{-}CH_2Ph$ protonolysis to yield **21**, this experiment establishes that **21** does indeed decompose to **19** and that **21** is a reasonable intermediate in the oxidation of **5** by Cp_2Fe^+.

Synthesis and Reactivity of the Base-Free Ion Pair $Cp_2Ti(CH_2Ph)(CB_{11}H_{12})$ (22). Hlatky and Turner have prepared the base-free complexes $Cp^*_2Zr(Me)(C_2B_9H_{12})$ and $(C_5Me_4Et)_2Zr(Me)(C_2B_9H_{12})$ by reaction of $(C_5R_5)_2ZrMe_2$ with *nido*-$C_2B_9H_{13}$ in pentane.[4a] In these compounds, the $(C_5R_5)_2Zr(CH_3)^+$ cations are weakly ion-paired with the $C_2B_9H_{12}^-$ anion via Zr–H–B bridges. Reed has developed the chemistry of $CB_{11}H_{12}^-$, an alternative weakly coordinating carborane counterion which has the practical advantage (vs $C_2B_9H_{12}^-$) of not having an acidic hydrogen.[52] In other work we have prepared $(C_5H_4Me)_2Zr(CH_3)(\eta^1\text{-}CB_{11}H_{12})$, $Cp_2Zr(\eta^2\text{-}CH_2Ph)(\eta^1\text{-}CB_{11}H_{12})$, and $Cp^*Zr(CH_3)_2(\eta^3\text{-}CB_{11}H_{12})$ using $Ag(CB_{11}H_{12})$.[53] In these compounds $CB_{11}H_{12}^-$ is ion-paired with the Zr cations via one or three B–H–Zr bridges. In view of these results, we attempted to prepare $Cp_2Ti(CH_2Ph)(CB_{11}H_{12})$, a base-free analogue of **12**.

The reaction of **5** with $Ag[CB_{11}H_{12}]$ in C_6D_6 yielded the thermally sensitive, base-free species $Cp_2Ti(CH_2Ph)(CB_{11}H_{12})$ (**22**; eq 9), the composition of which was confirmed by NMR and chemical reactivity studies. The benzyl ligand likely adopts an η^1 structure, but this could

---

[48] ^1H NMR of **18a,b** (300 MHz, CD_3CN): δ 5.90 (major C_5H_5), 5.79 (minor C_5H_5), 3.41 (minor CH_2), 3.25 (major CH_2).

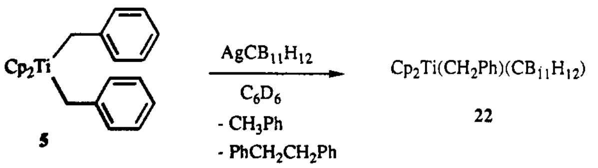
[49] Exchange of free and coordinated THF is rapid on the NMR time scale.

(50) (a) Clark, R. J. H.; Lewis, J.; Machin, D. J.; Nyholm, R. S. *J. Chem. Soc.* **1963**, 379. (b) Lewis, J.; Miller, J. R.; Richards, R. L.; Thompson, A. *J. Chem. Soc.* **1965**, 5850. (c) Clark, D.; Sattleberger, A. P.; Bott, S.; Vrits, R. N. *Inorg. Chem.* **1989**, *28*, 1771. (d) Galeffi, B.; Simard, M.; Wuest, J. D. *Inorg. Chem.* **1990**, *29*, 955.

(51) Merola, J. S.; Campo, K. S.; Gentile, R. A. *Inorg. Chem.* **1989**, *28*, 2950.

(52) (a) Shelly, K.; Finster, D. C.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1985**, *107*, 5955. (b) Shelly, K.; Reed, C. A.; Lee, Y. J.; Scheidt, W. R. *J. Am. Chem. Soc.* **1986**, *108*, 3117. (c) Liston, D. J.; Reed, C. A.; Eigenbrot, C. W.; Scheidt, W. R. *Inorg. Chem.* **1987**, *26*, 2740. (d) Gupta, G. P.; Lang, G.; Lee, Y. J.; Scheidt, W. R.; Shelly, K.; Reed, C. A. *Inorg. Chem.* **1987**, *26*, 3022. (e) Liston, D. J.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1989**, *111*, 6643.

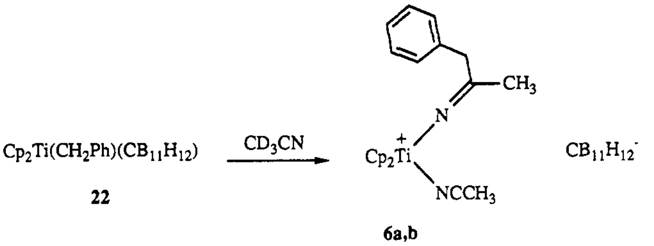
(53) Crowther, D. J.; Borkowsky, S. L.; Jordan, R. F.; Baenziger, N. C.; Swenson, D. Manuscript in preparation.



(9)

not be conclusively established. The ^1H NMR spectrum of **22** (C_6D_6) includes resonances for the Cp ligands (δ 5.66), the Zr–CH_2 group (δ 2.31), and the ortho phenyl hydrogens (δ 6.62, d, J = 7.4 Hz; remaining phenyl resonances obscured by the C_6D_6 peak). The ortho H resonance is shifted somewhat upfield from that of **5** (δ 6.82, in C_6D_6) which is suggestive of an η^2-benzyl structure;[54] however, the ipso ^{13}C resonance for **22** appears in the normal range (δ 154, toluene-d_8; vs 153.7 for **5**), which is inconsistent with an η^2-benzyl structure. The ipso C ^{13}C NMR resonances of η^2-benzyl complexes are usually shifted upfield compared to the resonances of similar η^1 species.

Complex **22** could not be isolated or characterized further as it decomposes at room temperature to a paramagnetic complex, possibly $Cp_2Ti(CB_{11}H_{12})$ (**24**) or a species derived therefrom, although this was not pursued further. Toluene and bibenzyl are formed, consistent with Ti–CH_2Ph homolysis. No ^{11}B NMR resonance is observed for **22**. Presumably this results from rapid exchange of $CB_{11}H_{12}^-$ between diamagnetic **22** and its paramagnetic decomposition product(s). The reaction of **22** with CD_3CN yields **6a,b**-d_6 as the $CB_{11}H_{12}^-$ salts.[55] These observations are consistent with the expected displacement of $CB_{11}H_{12}^-$ by CD_3CN and formation of reactive intermediate **12** (eq 10).



(10)

From the results described above, **7** is an expected coproduct of this reaction, but it was not detected by IR.[56]

Discussion

The neutral Ti(IV) complex $Cp_2Ti(CH_2Ph)_2$ (**5**) reacts with $Ag[BPh_4]$ in CH_3CN to yield bibenzyl, the cationic Ti(IV) azomethine complexes $Cp_2Ti\{N{=}C(CD_3)(CH_2Ph)\}(NCCD_3)^+$ (**6a,b**; 26%), and the cationic Ti(III) complex $Cp_2Ti(NCCH_3)_2^+$ (**7**; 71%). Several lines of evidence argue that this reaction proceeds by the mechanism in Scheme II. This mechanism involves initial net cleavage of one Ti–CH_2Ph bond to yield the reactive monobenzyl intermediate $Cp_2Ti(CH_2Ph)(NCCH_3)^+$ (**12**),[31] which undergoes rapid, competitive CH_3CN insertion leading to **6a,b**, or Ti–CH_2Ph homolysis leading to **7**. The formation of a statistical 1:2:1 mixture of scrambled bibenzyls in the reaction of a 1:1 mixture of **5** and **5**-d_{14} with $Ag[BPh_4]$, under conditions where benzyl scrambling between $Cp_2Ti(benzyl)_2$ complexes does not occur, is consistent with the coupling of benzyl radicals and inconsistent with mechanisms involving intramolecular C–C reductive elimination. Intermediate **12** can be generated in a variety of ways from **5** or other, monobenzyl, Cp_2Ti complexes. These include oxidation of **5** by Cp'_2Fe^+, protonolysis of **5** by $HNMe_3^+$, one-electron oxidation of the Ti(III) complex $Cp_2Ti(CH_2Ph)$ by Ag^+, and Cl^- dissociation from $Cp_2Ti(CH_2Ph)Cl$ in CH_3CN. In all these reactions the characteristic products of **12**, i.e. **6a,b**, and **7**, are observed.[57] The reaction of **5** with $Ag[CB_{11}H_{12}]$ in benzene yields the metastable, base-free monobenzyl species $Cp_2Ti(CH_2Ph)(CB_{11}H_{12})$ (**22**), which behaves similarly to **12**. The cleavage of a single Ti–CH_2Ph bond of **5** by Ag^+ and Cp_2Fe^+ and the formation of **12** parallel the chemistry observed for the analogous Zr system, although the Zr product $Cp_2Zr(CH_2Ph)(CH_3CN)^+$ is thermally stable.

The reaction of **5** with Cp_2Fe^+ or $HNMe_3^+$ in THF yields the Ti(III) cation $Cp_2Ti(THF)_2^+$. Both of these reactions most likely involve initial generation of the reactive intermediate $Cp_2Ti(CH_2Ph)(THF)^+$ (**19**), which undergoes rapid Ti–CH_2Ph homolysis.

The structures of **12** and **19** are not fully established, as these species could not be directly observed, even at low temperature. However, given the general tendency for Cp_2Ti systems to remain four-coordinate, **12** and **19** are almost certainly mono(solvento) species. NMR data suggest that the ion pair **22** adopts an η^1-benzyl structure.

The facile Ti–CH_2Ph homolysis chemistry of **12** and **19** contrasts with the thermal stability of the corresponding $Cp_2Ti(CH_3)(L)^+$ methyl complexes studied by Bochmann, but this difference is entirely reasonable given the relative bond strengths Ti–CH_2Ph < Ti–CH_3.[58] The neutral benzyl species $Cp_2Ti(CH_2Ph)_2$ (**5**) and $Cp_2Ti(CH_2Ph)Cl$ (**17**) are also comparatively stable toward homolysis at ambient temperature versus **12** and **19**. This difference is due in large part to the greater metal electron deficiency in the cationic systems, which favors reduction to Ti(III). The chloride complex **17** undergoes more rapid homolysis under conditions where Cl^- dissociation is favored, i.e. in CH_3CN solvent. Interestingly, Floriani noted many years ago that **17** reacts with cyclohexyl isocyanide to yield $Cp_2Ti^{III}(CNR)Cl$ and bibenzyl; in view of the results reported here this reaction may well proceed via Ti–CH_2Ph homolysis of an intermediate $Cp_2Ti(CH_2Ph)(CNR)^+$ cation.[59] The stability of ion pair **22** toward homolysis is intermediate compared to that of neutral complexes **5** and **17** and cationic species **12** and **19**. Similar Ti–R bond homolysis reactions of $Cp_2Ti(R)^+$ species in Cp_2TiX_2-based

---

[54] For η^2-benzyl complexes see the following: (a) $(ArO)_2Zr(CH_2Ph)_2$: Latesky, S. L.; McMullen, G. P. N.; Rothwell, I. P. *Organometallics* **1985**, *4*, 902. (b) $M(CH_2Ph)_4$ (M = Ti, Zr, Hf). Davies, G. R.; Jarvis, J. A. J.; Kilbourn, B. T.; Pioli, A. J. P. *J. Chem. Soc., Chem. Commun.* **1971**, 677. (c) Davies, G. R.; Jarvis, J. A. P.; Kilbourn, B. T. *J. Chem. Soc., Chem. Commun.* **1971**, 1511. (d) Bassi, I. W.; Allegra, G.; Scordamaglia, R.; Chioccola, G. *J. Am. Chem. Soc.* **1971**, *93*, 3787. (e) $Cp_2Zr(\eta^2\text{-}CH_2Ph)(L)^+$ complexes: ref 15 and 22. (f) Scholz, J.; Schlegel, M.; Thiele, K. H. *Chem. Ber.* **1987**, *120*, 1369.

[55] The counterion in these salts is free: ^1H NMR δ 2.4 ($HCB_{11}H_{11}$), ^{11}B NMR δ −6.1 (1 B), −12.5 (5 B), −15.4 (5 B).

[56] The IR spectrum of the crude reaction product contained a single ν_{CN} band for coordinated CH_3CN at 2272 cm^{-1} and did not include the characteristic ν_{CN} bands of **7**. The reaction of **12** in this case may be complicated by the unavoidable presence of **24** in **22**.

[57] These product distributions were not analyzed quantitatively. We anticipate that the **6a,b**/**7** ratio will vary due to the heterogeneity of some of these reactions, ligand and counterion effects, and temperature variations.

[58] Leading references: (a) Lappert, M. F.; Patil, D. S.; Pedley, J. B. *J. Chem. Soc., Chem. Commun.* **1975**, 830. (b) Davidson, P. J.; Lappert, M. F.; Pearce, R. *Chem. Rev.* **1976**, *76*, 219. (c) Skinner, H. A.; Connor, J. A. *Pure Appl. Chem.* **1985**, *57*, 79. (d) Dias, A. R.; Martinho-Simoes, J. A. *Polyhedron* **1988**, *16/17*, 1531. (e) Stoutland, P. O.; Bergman, R. G.; Nolan, S. P.; Hoff, C. D. *Polyhedron* **1988**, *16/17*, 1531. (f) Schock, L.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7701.

[59] Floriani, C.; Fachinetti, G. *J. Chem. Soc., Dalton Trans.* **1973**, 1954.

olefin polymerization catalysts may be important catalyst deactivation pathways.

The reactivity of **12** is quite different from that of related group 4 Cp_2M benzyl complexes. As mentioned above, the Zr analogue of **12**, $Cp_2Zr(\eta^2\text{-}CH_2Ph)(CH_3CN)^+$ (**2**), is resistant to CH_3CN insertion. This was ascribed to the η^2-benzyl bonding mode, which prevents the cis arrangement of coordinated CH_3CN and $Zr–CH_2Ph$ ligands which is required for migratory insertion. This rapid CH_3CN insertion of **12** suggests that this species may have an η^1 structure in which there are no geometric restrictions toward insertion. The neutral Ti(III) complex $Cp_2Ti(CH_2Ph)$ (**16**) coordinates nitriles but undergoes reductive RCN coupling rather than simple insertion. The difference in the RCN reactivity of **12** and **16**·RCN may be traced to back-bonding in the latter (d^1) system, which inhibits migration of the nucleophilic $PhCH_2^-$ ligand and promotes RCN coupling.[60] The neutral dibenzyl complexes $Cp_2M(CH_2Ph)_2$ (M = Ti, Zr) do not coordinate nitriles.

Experimental Section

All manipulations were performed under an inert atmosphere or under vacuum using a Vacuum Atmospheres drybox or a high-vaccum line. Solvents were purified by initial distillation from appropriate dehydrating/deoxygenating agents (ethers and hydrocarbons, Na/benzophenone; CH_2Cl_2, CaH_2; CH_3CN, P_2O_5), stored in evacuated bulbs over a drying agent, and vacuum-transferred into reaction vessels.[61] Deuterated NMR solvents were handled similarly (toluene-d_8, dried and stored over Na/benzophenone; benzene-d_6, predried over CaH_2, dried and stored over Na/K/benzophenone; CD_2Cl_2, dried over CaH_2; CD_3CN, dried over P_2O_5 and stored over 4-Å sieves) and vacuum-transferred into NMR tubes. NMR spectra were obtained on Bruker AMX-360, MSL-300, AC-300, or WP-360 instruments. ^1H and ^{13}C chemical shifts are reported versus Me_4Si and were determined by reference to the residual ^1H and ^{13}C solvent peaks. Elemental analyses were performed by E+R Microanalytical. IR spectra were obtained on a Mattson Cygnus 25 FT-IR spectrometer. EPR spectra were obtained on Varian E-4 EPR and Bruker ESP-300 spectrometers with a standard cavity. Cp_2TiCl_2 was purchased from Strem Chemicals and used without further purification. $Na[BPh_4]$ and $(C_5H_4Me)_2Fe$ were purchased from Aldrich and used without further purification. $[HN(CH_3)_3][BPh_4]$ was purchased from Aldrich, recrystallized from THF/hexane, and dried on a high-vacuum line. $Ag(CB_{11}H_{12})$ was prepared by Reed's method.[52]

$Cp_2Ti(CH_2Ph)_2$ (5).[62] A slurry of Cp_2TiCl_2 (3.81 g, 15.3 mmol) and $K[CH_2Ph]$ (4.19 g, 32.2 mmol, 5% excess) in toluene (50 mL) was prepared at −78 °C and warmed to 23 °C. The slurry was protected from light with Al foil, stirred for 5 h, and then filtered, leaving a purple filtrate and a purple precipitate. The precipitate was washed with 10 × 15 mL of toluene, and the combined filtrate and washes were evaporated to dryness. The resulting purple solid was washed with 4 × 10 mL of cold pentane and dried under high vacuum, yielding 4.42 g (80%) of deep purple **5**. The product may be recrystallized from toluene. ^1H NMR (300 MHz, C_6D_6): δ 7.21 (t, J = 7.7 Hz, 4 H, *m* Ph), 6.93 (t, J = 7.3 Hz, 2 H, *p* Ph), 6.82 (d, J = 7.3 Hz, 4 H, *o* Ph), 5.54 (s, 10 H, Cp), 1.88 (s, 4 H, $TiCH_2$). ^1H NMR (300 MHz, ppm in CD_3CN): δ 7.15 (t, J = 7.7 Hz, 4 H, *m* Ph), 6.82 (t, J = 7.3 Hz, 2 H, *p* Ph), 6.78 (d, J = 8.2 Hz, 4 H, *o* Ph), 5.99 (s, 10 H, Cp), 1.87 (s, 4 H, CH_2).

$Cp_2Ti(CD_2C_6D_5)_2$ (5-d_{14}). A slurry of Cp_2TiCl_2 (1.33 g, 5.36 mmol) and $K[CD_2C_6D_5]$ (1.50 g, 10.93 mmol, 2% excess) in toluene (50 mL) was prepared at −78 °C and warmed to 23 °C. The slurry was protected from light with Al foil and stirred for 2 h. The reaction mixture was filtered, leaving a purple filtrate and a purple precipitate. The precipitate was washed with 4 × 10 mL of toluene, and the combined filtrate and washes were evaporated to dryness, leaving a purple solid. This solid was washed with 2 × 10 mL of hexane and dried under high vacuum, yielding 1.42 g of crude **5**-d_{14}. This solid was dissolved in 35 mL of toluene, filtered, and cooled to −40 °C, producing deep purple crystals which were filtered, washed with 2 × 10 mL of cold pentane, and dried under vacuum to give 0.86 g (43%) of **5**-d_{14}. ^1H NMR (90 MHz, C_6D_6): δ 5.55 (s, 10 H).

$[Cp_2Ti\{N{=}C(CH_3)(CH_2Ph)\}(NCCH_3)][BPh_4]$ (6a,b). A slurry of $Cp_2Ti(CH_2Ph)_2$ (5.06 g, 14.1 mmol) and $Ag[BPh_4]$ (6.00 g, 14.1 mmol) in CH_3CN (120 mL) was prepared at −30 °C. The reaction mixture was protected from light, warmed to room temperature, and stirred for 3.5 h. Some of the solvent was evaporated, and the mixture was cooled to −30 °C for 10 min. The reaction mixture was filtered, giving a black Ag^0 precipitate and a dark filtrate. The filtrate was concentrated to approximately 10 mL, cooled to −45 °C for 30 min, and filtered, leaving a blue precipitate and a red filtrate. The filtrate was extracted with 16 × 15 mL of hexane to remove bibenzyl. The CH_3CN layer was cooled to −45 °C and filtered, leaving a small amount of red precipitate and a red filtrate. The solvent was evaporated, yielding 0.96 g (9.3%) of brown **6a,b**. ^1H NMR (360 MHz, CD_3CN): δ 7.36 (t, J = 6.5 Hz, 2 H, aryl), 7.27 (br m, 11 H, aryl, *o* BPh_4^-), 6.99 (t, J = 7.4 Hz, 8 H, *m* BPh_4^-), 6.84 (t, J = 7.2 Hz, 4 H, *p* BPh_4^-), 6.00 (s, 10 H, Cp, **6a**), 5.91 (s, 10 H, Cp, **6b**), 3.50 (s, 2 H, CH_2, **6b**), 3.41 (s, 2 H, CH_2, **6a**), 1.86 (s, 3 H, CH_3, **6a**), 1.81 (s, 3 H, CH_3, **6b**). $^{13}C\{^1H\}$ NMR (360 MHz, CD_3CN): δ 174.1 (N=C, **6a**), 173.7 (N=C, **6b**), 164.8 (q, J_{BC} = 49.3 Hz, i BPh_4^-), 136.8 (*o* BPh_4^-), 134.0 (i aryl, **6a** and/or **6b**), 130.6 (*o* or *m* aryl, **6b**), 130.5 (*o* or *m* aryl, **6a**), 129.7 (*o* or *m* aryl, **6b**), 129.5 (*o* or *m* aryl, **6a**), 128.0 (*p* aryl, **6b**), 127.8 (*p* aryl, **6a**), 126.6 (*m* BPh_4^-), 122.8 (*p* BPh_4^-), 112.0 (C_5H_5, **6a**), 111.8 (C_5H_5, **6b**), 47.3 (CH_2, **6b**), 45.6 (CH_2, **6a**), 27.0 (CH_3, **6a**), 24.3 (CH_3, **6b**). Anal. Calcd for $C_{45}H_{43}N_2BTi$: C, 80.60; H, 6.46; N, 4.18. Found: C, 80.79; H, 6.62; N, 4.46.

$[Cp_2Ti(CH_3CN)_2][BPh_4]$ (7). A slurry of $Cp_2Ti(CH_2Ph)_2$ (1.00 g, 2.78 mmol) and $Ag[BPh_4]$ (1.19 g, 2.78 mmol) in CH_3CN (25 mL) was prepared at −78 °C and warmed to 23 °C. The slurry was protected from light with Al foil, stirred for 30 min, and filtered, leaving a black Ag^0 precipitate and purple filtrate. The filtrate was cooled with a dry ice/ethanol bath, resulting in formation of a blue crystalline solid. This new slurry was warmed to room temperature, stirred for 20 min, and filtered, leaving a blue precipitate. The precipitate was washed with 1 × 10 mL of CH_3CN and dried for several hours under vacuum, leaving 0.71 g of bright blue **7** (44%). IR (cm^{-1}, in KBr): 3111 (w), 3052 (s), 2996 (s), 2982 (s), 2913 (s), 2313 (m), 2301 (w), 2278 (m), 2268 (m), 2249 (w), 1945 (w), 1879 (w), 1819 (w), 1581 (m), 1478 (s), 1427 (s), 1379 (w), 1268 (w), 1181 (w), 1150 (w), 1067 (w), 1014 (s), 806 (vs), 743 (s), 731 (s), 702 (vs), 615 (m), 589 (s). ^1H NMR (360 MHz, CD_3CN): δ 7.28 (8 H, br s, *m* BPh_4^-), 7.00 (8 H, br s, *o* BPh_4^-), 6.85 (4 H, br s, *p* BPh_4^-). UV–vis: λ_{max} = 584 nm, ϵ_0 = 95. EPR (9.78 GHz, CH_3CN): g value 1.979 μ_B, satellite peaks from hyperfine coupling to ^{47}Ti ($I = {}^5/_2$) and ^{49}Ti ($I = {}^7/_2$), hyperfine coupling 9 G.

Preparation of 7 via Reaction of $Cp_2Ti(CH_2Ph)(Cl)$ with $NaBPh_4$. A slurry of $Cp_2Ti(CH_2Ph)(Cl)$ (0.42 g, 1.37 mmol) and $NaBPh_4$ (0.47 g, 1.37 mmol) in CH_3CN (25 mL) was prepared at −78 °C and warmed to 23 °C. The slurry was stirred overnight and then filtered, leaving a white NaCl precipitate and a green filtrate. The filtrate was evaporated to dryness, leaving a blue solid. This solid was recrystallized from CH_3CN at −35 °C and dried under high vacuum overnight, yielding 0.15 g (20%) of bright blue **7**.

$[Cp_2Ti(NCCH_3)(THF)][BPh_4]$ (8). A solution of $[Cp_2Ti(NCCH_3)_2][BPh_4]$ in warm THF was placed in a −40 °C freezer.

---

[60] De Boer, E. J. M.; Teuben, J. H. *J. Organomet. Chem.* **1978**, *153*, 53.

[61] Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: New York, 1980.

[62] (a) Boekel, C. P.; Teuben, J. H.; De Liefde Meijer, H. J. *J. Organomet. Chem.* **1975**, *102*, 317. (b) Razuvaey, G. A.; Latyaeva, V. N.; Vishinskaya, L. I. *Dokl. Akad. Nauk. SSSR* **1969**, *189*, 103.

After 2 days, 8 precipitated as blue crystals. IR (cm^{-1}, in KBr): 3054 (m), 3000 (m), 2984 (m), 2925 (w), 2897 (w), 2299 (m), 2268 (m), 1941 (w), 1885 (w), 1818 (w), 1751 (w), 1581 (m), 1479 (m), 1427 (m), 1019 (s), 868 (m), 816 (s), 742 (s), 735 (s), 709 (s), 607 (s). Anal. Calcd for $C_{40}H_{41}BNOTi$: C, 78.70; H, 6.77; N, 2.29. Found: C, 78.77; H, 6.61; N, 2.30.

$Cp_2Ti(p\text{-}CH_2C_6H_4CH_3)_2$ (13). A slurry of Cp_2TiCl_2 (1.37 g, 5.50 mmol) and $K[p\text{-}CH_2C_6H_4CH_3]$ (1.72 g, 11.9 mmol, 8% excess) in toluene (60 mL) was prepared at −78 °C and warmed to 23 °C. The slurry was protected from the light with Al foil and stirred for 3 h. The reaction mixture was filtered, and the solvent was evaporated, leaving a foam which was dried overnight: yield 1.2 g of 13 (56%). ^1H NMR (360 MHz, C_6D_6): δ 7.05 (d, J = 7.9 Hz, 4 H), 6.78 (d, J = 8.0 Hz, 4 H), 5.59 (s, 10 H), 2.25 (s, 6 H), 1.91 (s, 4 H).

$[Cp_2Ti(THF)_2][BPh_4]$ (19). A slurry of $Cp_2Ti(CH_2Ph)_2$ (1.00 g, 2.77 mmol) and $[Cp'_2Fe][BPh_4]$ (1.48 g, 2.77 mmol) in THF (30 mL) was prepared at −78 °C and warmed to 23 °C. The slurry was protected from light with Al foil and stirred for 9 h. The slurry was evaporated to dryness and then extracted with 2 × 50 mL of toluene, leaving a blue-green solid. This solid was recrystallized from THF (−40 °C) and dried under high vacuum overnight to yield 0.46 g (27%) of blue-green 19. ^1H NMR (THF-d_8): δ 7.29 (br s, 8 H, *m* BPh_4^-), 6.87 (br s, 8 H, *o* BPh_4^-), 6.72 (br s, 4 H, *p* BPh_4^-). IR (cm^{-1} in KBr): 3051 (s), 3031 (s), 2996 (s), 2981 (s), 2897 (m), 1941 (w), 1884 (w), 1818 (w), 1751 (w), 1580 (m), 1479 (m), 1457 (m), 1448 (m), 1438 (m), 1427 (m), 1364 (w), 1347 (w), 1266 (w), 1248 (w), 1181 (w), 1145 (w), 1067 (w), 1026 (m), 1014 (s), 916 (w), 860 (s), 847 (s), 810 (vs), UV–vis (THF). λ_{max} 706 nm. EPR (9.083 GHz in THF): $g = 1.973\ \mu_B$. Anal. Calcd for $C_{42}H_{46}BTi$: C, 78.63; H, 7.23. Found: C, 78.55; H, 7.30.

Preparation of 19 via Reaction of $Cp_2Ti(CH_2Ph)_2$ with $[HNMe_3][BPh_4]$. A slurry of $Cp_2Ti(CH_2Ph)_2$ (0.369 g, 1.02 mmol) and $[HNMe_3][BPh_4]$ (0.390 g, 1.02 mmol) in THF (40 mL) was heated to 55 °C for 36 h. The THF was evaporated, and the resulting precipitate was washed with 50 mL of toluene and 2 × 5 mL of pentane, leaving a dark blue solid. The solid was dried under high vacuum (1 day), yielding 0.45 g (74%) of powdery dark blue 19.

Spectroscopic Characterization of $Cp_2Ti(CH_2Ph)(CB_{11}H_{12})$ (22). A resealable NMR tube was charged with $Cp_2Ti(CH_2Ph)_2$ (0.004 g, 0.011 mmol) and $Ag(CB_{11}H_{12})$ (0.028 g, 0.011 mmol). Benzene-d_6 was added via vacuum transfer at −78 °C, and the tube was warmed to room temperature for several minutes and centrifuged upside down to collect the Ag^0 precipitate at the top of the tube. ^1H, ^{13}C, and ^{11}B NMR spectra were recorded and are discussed in the text. The solvent was removed under vacuum and the residue redissolved in CD_3CN, and NMR spectra were again recorded. Attempts to isolate 22 in larger scale reactions were unsuccessful due to its facile decomposition.

X-ray Structure of 8. Crystals of 8 were obtained by recrystallization of 7 from THF solution and mounted in capillaries which were sealed with a torch under N_2. X-ray data were collected on an Enraf-Nonius CAD-4 diffractometer system, and the crystallographic calculations were performed by using the SDP package for that system.[63]

Acknowledgment. This work was supported by NSF Grant CHE-9022700. We thank Prof. Harold Goff and John Pollack for assistance with the Varian E-4 spectrometer and Dr. Gary Buettner (University of Iowa) for assistance with the quantitative EPR experiments. We also thank Prof. Chris Reed for a detailed preparation for $AgCB_{11}H_{12}$.

Supplementary Material Available: Listings of all bond distances and angles, least-squares planes, anisotropic thermal parameters for the non-hydrogen atoms, and positional and isotropic thermal parameters for the hydrogen atoms (9 pages). Ordering information is given on any current masthead page.

OM920668P

---

[63] Frenz, B. A. The Enraf-Nonius CAD4 SDP System. In *Computing in Crystallography*; Delft University Press: Delft, Holland, 1978; p 64.