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Formation of Titanium(III) Phosphide Dimers and Induction of Cyclopentadienyl C—H and P—C Bond Cleavage

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In 1966 Issleib and Hackert[1] established that diakylphosphides effect the reduction of Cp_2TiCl_2 affording dimeric Ti(III) species of the form $[Cp_2Ti(\mu\text{-}PR_2)]_2$. Since then, structural studies have confirmed the dimeric nature of the species $[Cp_2Ti(\mu\text{-}PR_2)]_2$ (R = Me,[2] Ph[4]), while spectroscopic studies of these reactions have implied mononuclear Ti(III) intermediates are formed en route to the dimers.[5-8] More recently, such mononuclear species have been intercepted and structurally characterized by ourselves[8] and Baker et al.[7] In related early metal phosphide systems, we have examined the reactions of a series of primary phosphine and phosphide derivatives with Zr species.[9-11] In several of these systems, C—H and P—C bond activation was observed when the lone substituent on phosphorus was extremely sterically demanding. Thus, we sought to determine if such steric effects could alter the course of the reduction of Cp_2TiCl_2 by phosphides. In the present report, we describe the reduction of Cp_2TiCl_2 with the primary phosphides K[PHR] (R = *t*-Bu, $SiPh_3$, C_6H_2-2,4,6-*t*-Bu_3) in the presence of the corresponding primary phosphine, PH_2R. In the first two cases, the products obtained were typical Ti(III) dimers of the form $[Cp_2Ti(\mu\text{-}PHR)]_2$ (R = *t*-Bu (**1**), $SiPh_3$ (**2b**)). However, in the case of the reaction of super-mesitylphosphide/phosphine, the product obtained is $[CpTi(\mu\text{-}PH_2)]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ (**3**). These reactions have been monitored spectroscopically, and the implications regarding the steric effects on the mechanism of the reaction are considered.

Experimental Section

General Data. All preparations were done under an atmosphere of dry, O_2-free N_2 by employing either Schlenk line techniques or a Vacuum Atmospheres inert atmosphere glovebox. Solvents were reagent grade, distilled from the appropriate drying agents under N_2 and degassed by the freeze–thaw method at least three times prior to use. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AC-300 operating at 300 and 75 MHz, respectively. Trace amounts of protonated solvents were used as references, and chemical shifts are reported relative to $SiMe_4$ and 85% H_3PO_4, respectively. X-band EPR spectra were recorded on a Bruker EPS-300e EPR spectrometer. DPPH was used as the external reference. Combustion analyses were performed by Galbraith Laboratories Inc., Knoxville, TN, and Schwarzkopf Laboratories, Woodside, NY. CP_2TiCl_2 was purchased from the Aldrich Chemical Co.

Table 1. Crystallographic Parameters for **3**

formula	$C_{20}H_{22}P_2Ti_2$
fw	420.14
cryst system	orthorhombic
space group	*Fdd*2 (No. 43)
a (Å)	20.440(9)
b (Å)	22.219(10)
c (Å)	7.760(2)
V (Å^3)	3524(3)
Z	4
μ (cm^{-1})	10.86
d(calc) (g/cm^3)	1.58
λ (Å)	0.710 69 (Mo Kα)
T (°C)	24
R (%)[a]	6.70
R_w (%)[a]	6.16

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum(|F_o| - |F_c|)^2|/\sum|F_o|^2]^{0.5}$.

Synthesis of K[PHR]/PH_2R (R = *t*-Bu, $SiPh_3$, C_6H_2-2,4,6-*t*-Bu_3). 2:1 mixtures of phosphide and phosphine were generated by the heterogeneous reaction of KH with primary phosphine in THF. The phosphide:phosphine ratio was monitored by ^{31}P NMR. These mixtures were typically stirred overnight and filtered before use.

Synthesis of $[Cp_2Ti(PH(t\text{-}Bu)]_2$ (1). Cp_2TiCl_2 (83 mg, 0.33 mmol) was dissolved in 2 mL of THF, and a THF solution of 2:1 mixture of K[PH(t-Bu)]/PH_2(*t*-Bu) (1.00 mmol total phosphorus) was added. The mixture was stirred for 1 h and allowed to stand overnight. The solution became purple-blue, and purple crystals were deposited after several days of standing. **1**: Yield 65%; $^{31}P\{^1H\}$ NMR (THF, 25 °C, δ) 75.9 ppm ($|J_{P-H}|$ = 250 Hz); ^1H NMR (C_6D_6, 25 °C, δ) 6.04 (s, Cp, 10H), 1.55 (s, *t*-Bu, 9H), 3.48 (d, PH, 1H, $|J_{P-H}|$ = 250 Hz). Anal. Calcd for $C_{28}H_{40}P_2Ti_2$: C, 62.94; H, 7.55. Found: C, 62.00; H, 7.50.

Generation of $[Cp_2Ti(PH(SiPh_3)_2]^-$ (2a) and Isolation of $[Cp_2Ti(PH(SiPh_3)]_2$ (2b). Cp_2TiCl_2 (83 mg, 0.33 mmol) was dissolved in 2 mL of THF, and a THF solution of a 2:1 mixture of K[$PHSiPh_3$]/PH_2SiPh_3 (1.00 mmol total phosphorus) was added. The mixture was stirred for 1 h and allowed to stand overnight. Monitoring of the reaction mixture by EPR revealed an signal attributed to **2a**. After the solution was allowed to stand for several days, a small amount of purple crystals was deposited. **2a**: EPR (C_6H_6, 25 °C, *g*): 2.066 (t), $\langle a_P\rangle$ 9.5 G; $\langle a_{Ti}\rangle$ = 5.0 G; $\langle a_H\rangle$ = 0.5 G. **2b**: Yield 2%. Anal. Calcd for $C_{56}H_{52}P_2Si_2Ti_2$: C, 71.64; H, 5.58. Found: C, 71.16; H, 5.40.

Synthesis of $[CpTi(PH_2)]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ (3). Cp_2TiCl_2 (83 mg, 0.33 mmol) was dissolved in 2 mL of THF, and a THF solution of 2:1 K[PH(C_6H_2-2,4,6-t-Bu_3)]/PH_2(C_6H_2-2,4,6-*t*-Bu_3) (1.0 mmol total phosphorus) was added. The mixture was stirred for 1 h and allowed to stand overnight. The solution became dark brown-red. The solvent was removed, the residue extracted into THF, the mixture filtered, and the volume reduced. A small portion of pentane was added, and the mixture was allowed to stand for several days during which dark brown crystals were deposited: Yield 70%; EPR (THF, 25 °C, *g*) 1.991 (t), $\langle a_P\rangle$ 10 G; $\langle a_{Ti}\rangle$ = 5 G. Anal. Calcd for $C_{20}H_{24}P_2Ti_2$: C, 56.91; H, 5.73. Found: C, 56.30; H, 5.20.

X-ray Data Collection and Reduction. X-ray-quality crystals of **3** were obtained directly from the preparation as described above. The crystals were manipulated and mounted in capillaries in a glovebox, thus maintaining a dry, O_2-free environment for each crystal. Diffraction experiments were performed on a Rigaku AFC6 diffractometer equipped with graphite-monochromatized Mo Kα radiation. The initial orientation matrix was obtained from 20 machine-centered reflections selected by an automated peak search routine. These data were used to determine the crystal system. Automated Laue system check routines around each axis were consistent with the crystal system. Ultimately, 25 reflections (20° < 2θ < 25°) were used to obtain the final lattice parameters and the orientation matrices. Crystal data are summarized in Table 1. The observed extinctions were consistent with the space group *Fdd*2. The data set was collected in three shells (4.5° < 2θ < 50.0°), and three standard reflections were recorded every 197 reflections. Fixed scan rates were employed. Up to 4 repetitive scans of each reflection at the respective scan rates were averaged to ensure meaningful statistics. The number of scans of each reflection was

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Table 2. Positional Parameters for **3**

atom	x	y	z
Ti(1)	0.4111(1)	−0.0070(1)	0.2006
P(1)	0.4931(2)	0.0729(2)	0.1246(6)
C(1)	0.341(1)	0.0378(8)	0.001(3)
C(2)	0.384(1)	−0.002(1)	−0.092(2)
C(3)	0.369(1)	−0.0584(9)	−0.052(3)
C(4)	0.317(1)	−0.054(1)	0.074(3)
C(5)	0.300(1)	0.003(1)	0.104(3)
C(6)	0.3593(7)	−0.0398(7)	0.463(3)
C(7)	0.4257(7)	−0.0546(7)	0.471(2)
C(8)	0.4650(6)	−0.0019(7)	0.478(2)
C(9)	0.4206(7)	0.0473(7)	0.473(2)
C(10)	0.3581(7)	0.0235(7)	0.464(3)

Table 3. Selected Bond Distances (Å) and Angles (deg) for **3**[a]

	Distances		
Ti(1)—P(1)	2.511(5)	Ti(1)—P(1)*	2.515(5)
Ti(1)—C(1)	2.33(2)	Ti(1)—C(2)	2.34(2)
Ti(1)—C(3)	2.42(3)	Ti(1)—C(4)	2.40(2)
Ti(1)—C(5)	2.40(2)	Ti(1)—C(6)	2.41(2)
Ti(1)—C(7)	2.36(2)	Ti(1)—C(8)	2.42(2)
Ti(1)—C(9)	2.44(2)	Ti(1)—C(10)	2.41(2)
	Angles		
P(1)—Ti(1)—P(1)*	80.6(2)	Ti(1)—P(1)—Ti(1)*	93.0(2)

[a] Asterisks indicate symmetry-related atoms.

determined by the intensity. The intensities of the standards showed no statistically significant change over the duration of the data collection. The data were processed using the TEXSAN crystal solution package operating on a VAX workstation 3520. The reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinements.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from literature tabulations.[12,13] The Ti atom positions were determined by employing the SHELX-86 direct methods routines. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least squares techniques on F, minimizing the function $w(|F_o| - |F_c|)^2$, where the weight w is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles of refinement the Ti and P atoms were assigned anisotropic temperature factors. The carbon atoms were assigned anisotropic thermal parameters so as to maintain a reasonable data:variable ratio. An empirical absorption correction was applied to the data on the basis of ψ-scan data and by employing the software resident in the TEXSAN package. Hydrogen atom positions were calculated and allowed to ride on the carbon to which they were bonded assuming a C—H bond length of 0.95 Å and a P—H bond length of 1.01 Å. Hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the carbon atom to which they are bonded. The hydrogen atom contributions were calculated but not refined. The final values of R and R_w are given in Table 1. The maximum Δ/σ on any of the parameters in the final cycles of the refinement and the location of the largest peaks in the final difference Fourier map calculation are also given in Table 1. The residual electron density was of no chemical significance. The following data are tabulated: selected positional parameters (Table 2) and selected bond distances and angles (Table 3). Crystallographic parameters, hydrogen atom parameters (Table S1), thermal parameters (Table S2), and bond distances and angles (Table S3) have been deposited as supplementary material.

Results

The reaction of Cp_2TiCl_2 with the primary phosphide KPH-*t*-Bu in the presence of the primary phosphine PH_2-*t*-Bu affords a dark purple-black solution. Monitoring the solution by ^{31}P NMR reveals a resonance at −61.0 ppm attributable to $(PHR)_2$ as well as a resonance at 75.9 ppm. Isolation of the crystalline product **1** was accomplished by addition of hexane. This species proved to be the source of the ^{31}P NMR resonance at 75.9 ppm as well as ^1H NMR resonances at 6.04, 1.60, 1.55, and 3.48 ppm. Repeated attempts to obtain single crystals of **1** met with only limited success.[14] The preliminary X-ray solution was consistent with the formulation of **1** as $[Cp_2Ti(\mu\text{-}PH\text{-}t\text{-}Bu)]_2$. In a similar manner, the reaction of $KPH(SiPh_3)/PH_2(SiPh_3)$ with Cp_2TiCl_2 was performed. Monitoring of the reaction revealed a triplet EPR signal at $g = 2.066$ (Figure 1). This same signal could be observed via the reaction of Cp_2TiCl_2 with excess $KPH(SiPh_3)$ suggesting the generation of the species $[Cp_2Ti(PH(SiPh_3))_2]^-$ (**2a**). The related structurally characterized species $[Cp_2Ti(PPh_2)_2]^-$ which exhibits a similar EPR resonance has been previously reported.[8] In addition, crystals of a second species were obtained from this reaction mixture. This compound **2b**, which was obtained in low yield, was sparingly soluble in common organic solvents and exhibited no EPR signal in the solid state at 25 °C. This product **2b** was formulated as $[Cp_2Ti(\mu\text{-}PH(SiPh_3))]_2$ on the basis of preliminary structural data. Poor crystal quality precluded precise structural analysis; nonetheless, the data are consistent with the dimeric formulation of **2b**.

Figure 1. THF solution EPR spectrum of **2a**. The insert shows a horizontal and vertical expansion of the Ti hyperfine coupling.

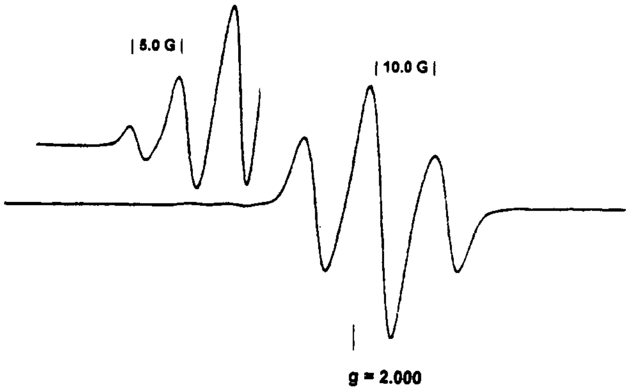

Figure 2. C_6H_6 solution EPR spectrum of **3**. The insert shows a horizontal and vertical expansion of the Ti hyperfine coupling.

The reaction of Cp_2TiCl_2, $K[PH(C_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)]$, and $PH_2(C_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)$ was undertaken. Despite the steric bulk the reaction appears to proceed in a similar manner with a color change to a dark solution. Addition of hexane and standing affords the crystalline, paramagnetic product **3**. This species also exhibits an EPR spectrum with $g = 1.991$ and an $\langle a_P \rangle$ value of 10.0 G (Figure 2); however, the observation of a half-field transition suggests a dimeric structure. An X-ray structural study of **3** indicated that P—C bond cleavage results in the loss

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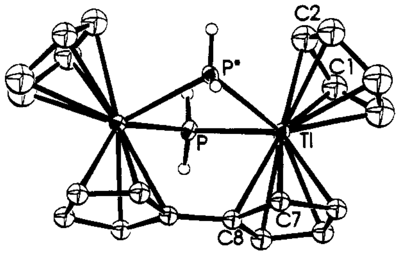
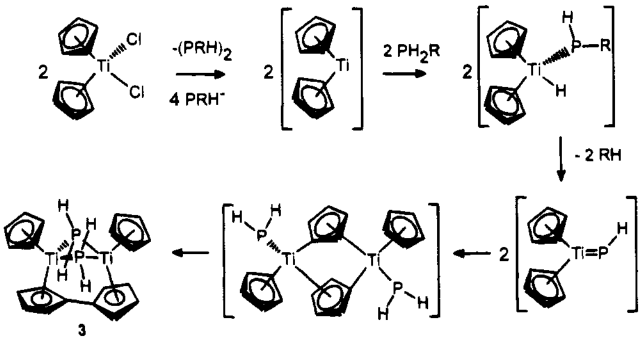


Figure 3. ORTEP drawing of **3**, with 30% thermal ellipsoids shown. All hydrogen atoms except for those on P are omitted for clarity.

Scheme 1



of the super-mesityl substituents and that the correct formulation of **3** is $[CpTi(PH_2)]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$. An ORTEP drawing of **3** is shown in Figure 3. The two Ti centers are each coordinated to π-bound cyclopentadienyl rings as well as half of the fulvalenide moiety which bridges the metal centers. The two phosphide (PH_2) moieties also bridge the two metal centers, thus completing the pseudotetrahedral coordination spheres of the Ti atoms. The Ti_2P_2 unit is not planar, being bent away from the fulvalenide moiety. The dihedral angle between the TiP_2 planes is 26.6(2)°, similar to that seen in related Zr—phosphide—fulvalenide dimers. The Ti—P—Ti angle is 93.0°. This is significantly larger than that seen for Zr-phosphide—fulvalenide dimers, where the corresponding angles range 80.3-(1)—87.5(2)°.[11] Similarly, the P—Ti—P angle of 80.6(2)° is much smaller than the corresponding angles in related Zr compounds, where P—Zr—P angles of about 90° are seen.[11] These differences in the Ti_2P_2 core reflect the diminished steric requirement of the P substituents in **3**. In addition while Zr—Zr bonding has been proposed for phosphide-bridged dimers,[15,16] the smaller covalent radius of Ti and observed Ti···Ti distance in **3** of 3.646(5) Å precludes such metal—metal interactions. The Ti—C distances are typical. The Ti—P distances in **3** of 2.511(5) and 2.515(5) Å are shorter than those seen in the related Ti(III) species $[Cp_2Ti(\mu\text{-}PEt_2)]_2$ (2.622(3), 2.616(3) Å),[3] $Cp_2Ti(PPh_2)(PMe_3)$ (2.681(3) Å),[8] or $[Cp_2Ti(PPh_2)_2]^-$ (2.71(1), 2.67(1) Å).[8] This is consistent with the greater basicity of the PH_2^- moiety. In fact, only the mononuclear Ti(III) species Cp_2TiPCy_2 contains a shorter Ti—P bond (2.396 Å).[7]

Discussion

Previous reports describe the reduction of Ti(IV) to Ti(II) by phosphide with the concurrent formation of diphosphine (P_2R_4).[1-5] Disproportionation of the Ti(IV) and Ti(II) leads to the subsequent formation of the Ti(III) phosphides $Cp_2Ti(PRH)$ which are known to dimerize or react with excess phosphide to generate monomeric anions of the form $[Cp_2Ti(PR_2)_2]^-$. This is the case for reactions affording **1** and **2a**,**b**. In the case of sterically demanding phosphides the course of such reactions is altered. For example, Baker et al.[7] have shown that, for the reaction of $LiPCy_2$ with Cp_2TiCl_2, the mononuclear species Cp_2TiPCy_2 is isolated and dimerization is not seen. The product presently described from the reaction of $LiPH(C_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)$ and Cp_2TiCl_2 is neither the mononuclear Ti(III) phosphide complex nor the simple Ti(III) dimer; rather **3** is derived. Efforts to monitor this reaction by both NMR and EPR spectroscopy were less than revealing although the ^{31}P NMR resonance attributable to the byproduct of Ti reduction, i.e. $P_2H_2R_2$, was observed at −63 ppm. Although mechanistic information in the present system is limited, speculation based on related Zr chemistry offers some insight. We have previously shown that oxidative addition of primary phosphines to Zr(II) affords Zr(III) phosphide dimers.[9,10] We suggest that a similar mechanism is operative in the present reactions. Reduction of Ti(IV) to Ti(II) results in the observed $P_2H_2R_2$. Oxidative addition of phosphine to Ti(II) yields a transient species $Cp_2TiH(PRH)$. This species may reductively dimerize, eliminating H_2 as in the reaction yielding **1** and **2b**. Alternatively, loss of RH affords a reactive Ti(IV)—phosphinidene intermediate, which induces C—H bond activation of a cyclopentadienyl ring and the subsequent formation of **3** (Scheme 1). Although efforts to observe phosphinidene intermediates in the present systems were unsuccessful, it is noteworthy that cyclopentadienyl C—H activation by a Zr—phosphinidene has been described.[10,11]

The chemistry described herein illustrates an effect of sterically demanding substituents, providing a novel route to a phosphide (PH_2^-) complex. Furthermore, the present results illustrate P—C bond activation and imply that the reactive nature of early metal phosphinidenes can induce C—H bond activation. Studies of systems in which early metal phosphinidenes are both transient and isolable are continuing.

Acknowledgment. Support from the PRF administered by the American Chemical Society is gratefully acknowledged. Additional support from the NSERC of Canada is also acknowledged.

Supplementary Material Available: Tables of crystallographic parameters, hydrogen atom parameters, bond distances and angles, and thermal parameters for **3** (6 pages). Ordering information is given on any current masthead page.

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(14) Repeated attempts to obtain crystals of **1** and **2** met with only limited success. Diffraction data were collected; however, the crystal qualities were consistently poor and thus the diffracted intensities weak. Consequently, while the solutions were consistent with the formulations, the solutions were not of acceptable quality for publication. The lattice parameters for compounds **1** and **2** are as follows: **1**, tetragonal space group $P4_2/mnm$, $a = 8.798(7)$ Å, $c = 17.351(9)$ Å, $V = 1343(1)$ Å^3; **2**, monoclinic space group $P2_1/n$, $a = 11.724(3)$ Å, $b = 14.213(5)$ Å, $c = 16.872(7)$ Å, $\beta = 93.80(3)$°, $V = 2805(2)$ Å^3.

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