makes this method particularly useful for the synthesis of ortho-metalated benzylamide complexes. The only potential limitation of this method of amide synthesis arises from the weak Lewis basicity of the imine nitrogen. There are only a few examples of N-bound imine ligands that are not stabilized by ortho-metalation or heteroatom coordination.[18] The generalization of this chemistry to the synthesis of monodentate amide complexes may be limited by starting material availability, which awaits further research.

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Supplementary Material Available: Tables of anisotropic thermal parameters and bond lengths and angles for **1a** and **2a** (12 pages); tables of observed and calculated structure factors for **1a** and **2a** (27 pages). Ordering information is given on any current masthead page.

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Titanocene(III) Phosphides: Trapping and Structure of Mononuclear Intermediates in the Formation of $[Cp_2Ti(\mu\text{-}PR_2)]_2$

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Intermediates in the reactions of Cp_2TiCl_2 with phosphides have been previously inferred by EPR studies. In this report two intermediates are trapped, isolated, and structurally characterized. Reaction of $LiPR_2$ (R = Et, Ph) with Cp_2TiCl_2 in the presence of PMe_3 yields the compounds $Cp_2TiPR_2(PMe_3)$ (**3**). The compound $Cp_2TiPPh_2(PMe_3)$ (**3b**) crystallizes in the space group $P2_1/c$ with $a = 8.716$ (3) Å, $b = 25.914$ (13), $c = 10.225$ (5) Å, $Z = 4$, and $V = 2276$ (2) Å^3. With the employment of excess phosphide and TMEDA, the compounds $[Li(TMEDA)_2][Cp_2Ti(PR_2)_2]$ (**4**) are obtained. The compound $[Li(TMEDA)_2][Cp_2Ti(PPh_2)_2]$ (**4b**) crystallizes in the space group $P2_1/c$ with $a = 13.058$ (5) Å, $b = 19.312$ (5) Å, $c = 18.441$ (6) Å, $Z = 4$, and $V = 4613$ (4) Å^3. The synthesis, isolation, and structural studies of these compounds serve not only to confirm the nature of the intermediates and the mechanism of formation of $[Cp_2Ti(\mu\text{-}PR_2)]_2$ but also to represent the first structural studies of mononuclear titanium phosphide complexes.

Introduction

Our interest in early-metal phosphide species has arisen from their utility as synthetic precursors for the preparation of early/late heterobimetallic (ELHB) complexes.[1] For example, we[2-6] and others[7-9] have described the use of species of the form $Cp_2M(PR_2)_2$ (R = Ph, Cy, Et; M = Zr, Hf) as metalloligands in the formation of mixed-metal, diphosphide-bridged products. The monophosphido-bridged ELHB complexes $Cp_2Zr(\mu\text{-}PR_2)(\mu\text{-}\eta^1,\eta^2\text{-}OC)M(CO)Cp$ are also accessible via redox reactions involving the zirconium(IV) phosphido precursors $Cp_2Zr(PR_2)_2$[10] or the zirconium(III) phosphido species $[Cp_2Zr(\mu\text{-}PR_2)]_2$.[11] Analogous reactions employing the Ti(III) species $[Cp_2Ti(\mu\text{-}PR_2)]_2$ afford the ELHB species $Cp_2Ti(THF)(\mu\text{-}OC)M(CO)_2Cp$.[11] While the chemistry of the derived ELHB complexes is a subject of ongoing investigations, further development in synthetic strategies to such complexes hinges on the development of new early-metal phosphide reagents.

The reactions of Cp_2TiCl_2 with phosphides affording diamagnetic Ti(III) and Zr(III) complexes were first reported in 1966 by Issleib and Hackert.[12] These species have been recently confirmed crystallographically to be the dimeric complexes $[Cp_2M(\mu\text{-}PR_2)]_2$ (a) (R = Me, M = Ti,[13] Zr;[14] R = Ph, M = Ti;[15a] R = Et, M = Ti[15b]). The preparation of the first zirconocene(IV) diphosphide species

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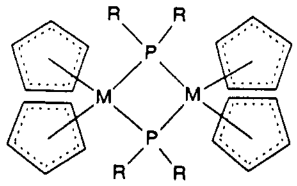
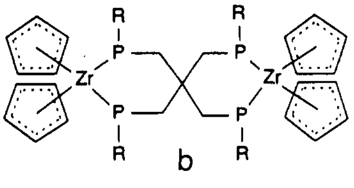


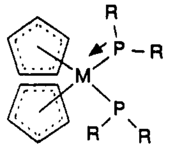
a

M = Ti, Zr R = Me, Et, Ph

(b) was reported by Ellerman and Poersch in 1967.[16]



R = Ph



c

M = Zr, Hf
R = Ph, Cy, Et

However, it was not until the report of Baker et al., in 1982,[17] that a complete spectroscopic and structural study of a mononuclear metallocene(IV) diphosphides of the form (c) was presented. More recently, the species $Cp_2HfX(PRH)$,[18] as well as hemoleptic phosphide complexes of Ti, Zr, and Hf, have been prepared.[19] In the case of Ti, the complex $[Ti(PCy_2)_4]^-$, the unstable $Ti(PCy_2)_4$,[19a] and the species $Cp_2Ti(PR)_3$[20] represent the only isolable mononuclear phosphido species known to date. Mononuclear titanium(III) phosphide intermediates have been identified by EPR studies in the formation of titanium phosphido-bridged dimers (a, M - Ti); however, such species have not been isolated.[21-23] In this report we describe the isolation and characterization of two mononuclear derivatives of these Ti(III) intermediates. The synthesis, isolation, and structural studies of these compounds serve not only to confirm the nature of the intermediates and the mechanism of formation of $[Cp_2Ti(\mu\text{-}PR_2)]_2$ but also to represent the first structural studies of mononuclear Ti phosphido complexes.[19b]

Experimental Section

General Data. All preparations were done under an atmosphere of dry, O_2-free N_2 by employing 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. EPR spectra were recorded on a Varian E-12 EPR spectrometer employing DPPH as a reference. Combustion analyses were performed by Galbraith Laboratories Inc., Knoxville, TN, and Schwarzkopf Laboratories, Woodside, NY. Cp_2TiCl_2, Cp_2ZrCl_2, and tetramethylethylenediamine (TMEDA) were purchased from the Aldrich Chemical Co. $LiPEt_2$ was prepared by the literature method[11] from PEt_2H and PMe_3 obtained from the Pressure Chemical Co. The compounds $[Cp_2Ti(\mu\text{-}PR_2)]_2$ (R = Et (**2a**), Ph (**2b**))[12,15] were prepared by literature methods.

Generation of Cp_2TiPEt_2 (1a). A solution of **2a** in THF was placed in a quartz EPR tube, and the sample was warmed to 330 K affording $Cp_2TiPEt_2(THF)$. **1a**: EPR (THR, 330 K) $g = 1.983$, $\langle a, {}^{31}P\rangle = 33.4$ G.

Generation of Cp_2TiPPh_2 (1b). A solution of $LiPPh_2$·diox (diox = dioxane) (0.094 g, 0.337 mmol) in 10 mL of THF was added dropwise to a suspension of Cp_2TiCl_2 (0.040 g, 0.161 mmol) in 15 mL of THF. After 1 h of stirring, the THF solution was transferred to an EPR tube. **1b**: EPR (THF, 298 K) $g = 1.982$, $\langle a, {}^{47/49}Ti\rangle = 8.4$ G, $\langle a, {}^{31}P\rangle = 22.5$ G.

Generation of $Cp_2TiPEt_2(PMe_3)$ (3a). A solution of $LiPEt_2$ (0.032 g, 0.337 mmol) in 10 mL of THF was added dropwise to a suspension of Cp_2TiCl_2 (0.040 g, 0.161 mmol) in 15 mL of THF containing excess PMe_3 (0.120 g, 1.57 mmol). An aliquot of this solution was placed in an EPR tube and the spectrum taken within 5 min of mixing. The product **4a** is unstable and cannot be isolated: EPR (THF, 298 K) $g - 1.993$, $\langle a, {}^{47/49}Ti\rangle = 7.8$ G, $\langle a, {}^{31}P\rangle = 24.4$ G, $\langle a, {}^{31}P\rangle = 9.8$ G.

Synthesis of $Cp_2TiPPh_2(PMe_3)$ (3b). A solution of $LiPPh_2$·diox (0.094 g, 0.337 mmol) in 10 mL of THF was added dropwise to a suspension of Cp_2TiCl_2 (0.040 g, 0.161 mmol) in 15 mL of THF. After 1 h of stirring, THF was removed in vacuo and 20 mL of benzene was added. The solution was filtered, and the filtrate was reduced in volume to about 5 mL. Addition of PMe_3 (0.120 g, 1.57 mmol) and addition of pentane caused precipitation of the green crystalline product (0.058 g, 82%). Anal. Calcd for $C_{25}H_{29}P_2Ti$: C, 68.34; H, 6.65. Found: C, 68.20; H, 6.40. EPR (C_7H_8, 298 K): $g = 1.991$, $\langle a, {}^{47/49}Ti\rangle = 9.2$ G, $\langle a, {}^{31}P\rangle = 26.2$ G, $\langle a, {}^{31}P\rangle = 2.3$ G.

Generation of $[Li(TMEDA)_2][Cp_2Ti(PEt_2)_2]$ (4a). A solution of $LiPEt_2$ (0.027 g, 0.286 mmol) in 10 mL of THF was added dropwise to a suspension of Cp_2TiCl_2 (0.023 g, 0.091 mmol) in 15 mL of THF containing 0.5 mL of TMEDA. After 1 h of stirring, the THF was removed in vacuo and the product was extracted into 20 mL of hexane. EPR (C_7H_8, 298 K); $g = 1.991$, $\langle a, {}^{47/49}Ti\rangle = 9.8$ G, $\langle a, {}^{31}P\rangle = 10.9$ G.

Synthesis of $[Li(TMEDA)_2][Cp_2Ti(PPh_2)_2]$ (4b). A solution of $LiPPh_2$·diox (0.106 g, 3.8 mmol) in 10 mL of THF was added dropwise to a suspension of Cp_2TiCl_2 (0.030 g, 1.21 mmol) in 15 mL of THF. The solution was stirred for 2 h and the solvent removed in vacuo. The residue was taken up into benzene (10 mL), and 0.5 mL of TMEDA was added. Vapor diffusion of hexane into the solution yielded crystals of **4b** (yield 48–60%). EPR (C_7H_8, 298 K): $g = 1.988$, $\langle a, {}^{47/49}Ti\rangle = 9.5$ G, $\langle a, {}^{31}P\rangle = 8.6$ G.

X-ray Data Collection and Reduction. X-ray-quality crystals of **3b** and **4b** were obtained directly from the preparations as described above. The crystals were manipulated and mounted in capillaries in a glovebox, thus maintaining a dry, O_2-free environment for each the crystal. Diffraction experiments were performed on a four-circle Syntex $P2_1$ or a Rigaku AFC6 diffractometer each equipped with graphite-monochromatized Mo Kα radiation. The initial orientation matrices were obtained from 15 to 20 machine-centered reflections selected from rotation photographs or by an automated peak search routine. These data were used to determine the crystal systems. Partial rotation photographs or automated Laue system check routines around each axis were consistent with monoclinic crystal systems. Ultimately, 60 and 23 reflections ($20° < 2\theta < 25°$) were used to obtain the final lattice parameters and the orientation matrices. Machine parameters, crystal data, and data collection parameters are summarized in Table I. The observed extinctions were consistent with the space group $P2_1/c$ in both cases. The data sets were collected in one shell ($4.5° < 2\theta < 45.0°$), and three standard reflections were recorded every 197 reflections. The intensities of the standards showed no statistically significant change over the duration of the data collection. The data were processed by using the SHELX-76 program package on the computing facilities at the University of Windsor for molecule **3b**. For molecule **4b**, the data was processed by employing 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 refinement.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[24,25]

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Table I. Crystallographic Parameters

	molecule **3b**	molecule **4b**
formula	$C_{25}H_{29}P_2Ti$	$C_{46}H_{62}LiN_4P_2Ti$
cryst color, form	green blocks	yellow blocks
a, Å	8.716 (3)	13.058 (5)
b, Å	25.914 (13)	19.312 (5)
c, Å	10.225 (5)	18.441 (6)
β, deg	99.74 (3)	97.27 (3)
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
V, Å^3	2276 (2)	4613 (4)
D(calcd), g cm^{-3}	1.28	1.13
Z	4	4
cryst dimens, mm	0.25 × 0.35 × 0.28	0.20 × 0.22 × 0.24
abs coeff μ, cm^{-1}	4.66	2.83
radiation (λ, Å)	Mo Kα (0.71069)	Mo Kα (0.71069)
temp, °C	24	24
scan speed, deg/min	2.0–5.0 ($\theta/2\theta$)	8.0 ($\theta/2\theta$)
scan range, deg	1.0 below Kα_1 1.0 above Kα_2	1.15 + 0.30 tan θ
bkgd/scan time ratio	0.5	0.5
no. of data collcd	3266	5059
2θ range, deg	4.5–45.0	4.5–45.0
index range	$\pm h,k,l$	$\pm h,k,l$
no. of data $F_o^2 > 3\sigma(F_o^2)$	1735	928
no. of variables	128	166
R, %	6.64	8.00
R_w, %	6.77	7.40
largest Δ/σ in final least squares cycle	0.011	0.03
max resid, e/Å^3	0.92 (Ti)	0.31 (Ti)

The Ti atom positions were determined by using direct methods employing SHELX-86 for molecule **3b**, while for **4b** the direct methods routine MITHRIL was employed. In each case, 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 of 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 all the Ti and P atoms were assigned anisotropic temperature factors. Carbon atoms were described isotropically. In the case of **4b** the cyclopentadienyl and phenyl rings were constrained to have pentagonal and hexagonal geometries, respectively, with C–C distances of 1.40 Å. Hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded by assuming a C–H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the carbon atom to which they are bonded. In all cases the hydrogen atom contributions were calculated but not refined. The final values of R and R_w are given in Table I. The maximum Δ/σ of 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 I. The residual electron densities were of no chemical significance. The following data are tabulated: positional parameters (Table II) and selected bond distances and angles (Table III). Thermal parameters (Table S1), hydrogen atom parameters (Tables S2 and S5), bond distances and angles associated with the cyclopentadienyl rings (Tables S3 and S6), bond distances and angles associated with the [Li(TMEDA)$_2$] cation (Table S7), and values of $10F_o$ and $10F_c$ (Tables S4 and S8) have been deposited as supplementary material.

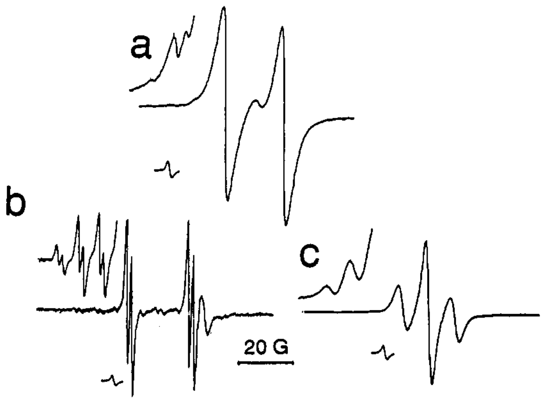
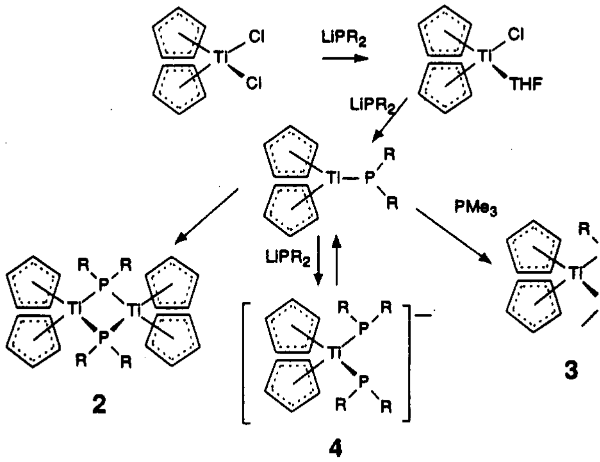


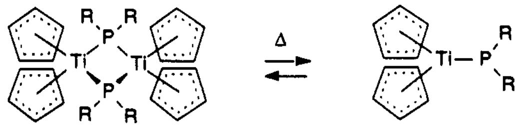
Figure 1. (a) EPR spectrum of **1b** in THF, (b) EPR spectrum of **3b** in toluene, and (c) EPR spectrum of **4b** in THF.

Scheme I



Results and Discussion

The reaction of Cp_2TiCl_2 with $LiPR_2$ proceeds smoothly accompanied by the color changes from red to green to purple, ultimately affording the dimeric species $[Cp_2Ti(\mu\text{-}PR_2)]_2$[12,15] and the byproduct P_2R_4. On the basis of EPR data, two mononuclear intermediates, Cp_2TiPR_2 and $[Cp_2Ti(PR_2)_2]^-$, were proposed to exist in solution; however, these formulations were neither confirmed by isolation nor structurally characterization. In our examination of such reactions we monitored the reaction of Cp_2TiCl_2 and $LiPPh_2$ in THF by EPR spectroscopy. As was previously reported, one observes a single clean doublet resonance at $g = 1.982$ with $\langle a,{}^{31}P\rangle$ and $\langle a,{}^{47/49}Ti\rangle$ values of 22.5 and 8.4 G (Figure 1a) attributable to the species Cp_2TiPPh_2 (**1b**). The analogous species Cp_2TiPEt_2 (**3a**) could not be generated in a similar manner at 298 K. However, we observed a similar doublet EPR signal attributable to **1a** via thermal dissociation of the dimer $[Cp_2Ti(\mu\text{-}PEt_2)]_2$ (**2a**).



The intermediate 1 can be trapped as the PMe_3 adduct. Performing the reaction of Cp_2TiCl_2 and $LiPEt_2$ in the presence of PMe_3 affords the species $Cp_2TiPEt_2(PMe_3)$ (**3a**) (Scheme I). This compound exhibits a doublet of doublets in the THF solution EPR spectrum. The g value of 1.993 with $\langle a,{}^{47/49}Ti\rangle = 7.8$ G and the two $\langle a,{}^{31}P\rangle$ values of 24.4 and 9.8 G, respectively, are consistent with this formulation. This complex is not stable. On standing, in solution, it gradually loses PMe_3, ultimately giving the dimer **2a**.

The analogous compound $Cp_2TiPPh_2(PMe_3)$ (**3b**) can be prepared in a manner similar to that used for **3a** by employing $LiPPh_2$. However, this compound is stable in the absence of oxygen and moisture and readily crystallizes from THF/pentane. The EPR spectrum of **3b** is also

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Table II. Positional Parameters

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
			Molecule **3b**				
Ti	0.0535 (2)	0.1296 (1)	0.1996 (1)	C24	–0.1896 (11)	0.1356 (4)	0.0460 (10)
P1	0.2736 (3)	0.0597 (1)	0.2613 (2)	C25	–0.2025 (12)	0.0952 (4)	0.1305 (10)
P2	–0.0400 (3)	0.1028 (1)	0.4244 (2)	C31	–0.1748 (9)	0.1514 (3)	0.4753 (8)
C1	0.4385 (10)	0.0743 (4)	0.3916 (9)	C32	–0.2578 (9)	0.1876 (3)	0.3910 (8)
C2	0.2216 (10)	–0.0058 (4)	0.3076 (9)	C33	–0.3663 (10)	0.2208 (3)	0.4302 (9)
C3	0.3755 (11)	0.0448 (4)	0.1208 (10)	C34	–0.3938 (10)	0.2183 (3)	0.5611 (9)
C11	0.0512 (11)	0.2202 (3)	0.1616 (9)	C35	–0.3157 (10)	0.1825 (3)	0.6470 (9)
C12	0.1700 (10)	0.1995 (3)	0.0989 (9)	C36	–0.2068 (10)	0.1501 (3)	0.6065 (8)
C13	0.2846 (10)	0.1799 (3)	0.1987 (8)	C41	0.01157 (9)	0.1054 (3)	0.5715 (8)
C14	0.2375 (10)	0.1880 (3)	0.3230 (9)	C42	0.1764 (9)	0.1516 (3)	0.6313 (8)
C15	0.0942 (10)	0.2132 (3)	0.2976 (8)	C43	0.2967 (11)	0.1535 (4)	0.7392 (10)
C21	–0.1004 (11)	0.0579 (4)	0.1114 (10)	C44	0.3599 (12)	0.1059 (4)	0.7873 (10)
C22	–0.0194 (13)	0.0748 (4)	0.0140 (10)	C45	0.3003 (11)	0.0607 (4)	0.7354 (10)
C23	–0.0762 (12)	0.1235 (4)	–0.0270 (10)	C46	0.1782 (10)	0.0592 (4)	0.6296 (9)
			Molecule **4b**				
Ti1	0.2443 (5)	0.1345 (2)	0.2449 (4)	C53	0.234 (1)	0.1507 (8)	0.524 (1)
P1	0.2706 (6)	0.0288 (5)	0.1525 (5)	C54	0.328 (2)	0.136 (1)	0.5654 (7)
P2	0.2500 (6)	0.0296 (5)	0.3401 (4)	C55	0.396 (1)	0.089 (1)	0.539 (1)
C11	0.072 (1)	0.1119 (8)	0.185 (1)	C56	0.369 (1)	0.0568 (7)	0.471 (1)
C12	0.114 (1)	0.168 (1)	0.1521 (7)	C61	0.127 (1)	–0.0155 (7)	0.343 (1)
C13	0.129 (1)	0.2221 (8)	0.203 (1)	C62	0.079 (1)	–0.0425 (9)	0.2773 (8)
C14	0.096 (1)	0.199 (1)	0.2685 (9)	C63	–0.016 (1)	–0.0768 (8)	0.2754 (8)
C15	0.060 (1)	0.131 (1)	0.257 (1)	C64	–0.062 (1)	–0.0840 (8)	0.339 (1)
C21	0.422 (1)	0.153 (1)	0.228 (1)	C65	–0.013 (1)	–0.0569 (9)	0.4049 (8)
C22	0.420 (1)	0.1370 (8)	0.302 (1)	C66	0.081 (1)	–0.0227 (8)	0.4068 (8)
C23	0.367 (1)	0.190 (1)	0.3333 (7)	N1	0.628 (2)	0.283 (2)	0.476 (2)
C24	0.337 (1)	0.2393 (8)	0.279 (1)	N2	0.863 (3)	0.282 (2)	0.489 (2)
C25	0.371 (1)	0.216 (1)	0.2139 (9)	N3	0.753 (2)	0.134 (2)	0.387 (2)
C31	0.247 (2)	0.066 (1)	0.0576 (7)	N4	0.729 (2)	0.268 (2)	0.301 (2)
C32	0.295 (1)	0.126 (1)	0.035 (1)	C71	0.698 (4)	0.323 (3)	0.536 (3)
C33	0.264 (1)	0.1534 (7)	–0.034 (1)	C72	0.799 (4)	0.326 (3)	0.528 (3)
C34	0.187 (1)	0.121 (1)	–0.0811 (7)	C73	0.565 (3)	0.233 (2)	0.513 (2)
C35	0.140 (1)	0.061 (1)	–0.059 (1)	C74	0.565 (3)	0.336 (2)	0.436 (2)
C36	0.170 (1)	0.0338 (7)	0.010 (1)	C75	0.910 (4)	0.232 (3)	0.528 (3)
C41	0.4072 (9)	0.0039 (8)	0.160 (1)	C76	0.926 (3)	0.337 (2)	0.458 (2)
C42	0.469 (1)	0.0134 (7)	0.1048 (7)	C81	0.730 (3)	0.127 (2)	0.307 (3)
C43	0.572 (1)	–0.0074 (8)	0.1152 (9)	C82	0.744 (4)	0.196 (3)	0.263 (3)
C44	0.613 (1)	–0.0376 (8)	0.181 (1)	C83	0.858 (4)	0.108 (2)	0.387 (2)
C45	0.552 (2)	–0.0471 (7)	0.2368 (7)	C84	0.690 (3)	0.087 (2)	0.421 (2)
C46	0.448 (1)	–0.0264 (8)	0.2264 (8)	C85	0.633 (3)	0.285 (2)	0.264 (2)
C51	0.274 (2)	0.072 (1)	0.4305 (7)	C86	0.793 (3)	0.322 (2)	0.274 (2)
C52	0.206 (1)	0.119 (1)	0.457 (1)	Li	0.742 (4)	0.239 (3)	0.415 (3)

Table III. Selected Bond Distances and Angles

Distances (Å) for Molecule **3b**					
Ti–P1	2.636 (3)	Ti–P2	2.681 (3)	Ti–C11	2.379 (9)
Ti–C12	2.399 (9)	Ti–C13	2.401 (9)	Ti–C14	2.407 (8)
Ti–C15	2.392 (8)	Ti–C21	2.381 (10)	Ti–C22	2.385 (10)
Ti–C23	2.427 (10)	Ti–C24	2.428 (10)	Ti–C25	2.397 (10)
P1–C1	1.834 (9)	P1–C2	1.841 (9)	P1–C3	1.867 (10)
P2–C31	1.858 (8)	P2–C41	1.860 (8)		
Angles (deg) for Molecule **3b**					
P2–Ti–P1	85.9 (1)	C1–P1–Ti	118.9 (3)		
C2–P1–Ti	119.7 (3)	C2–P1–C1	101.3 (4)		
C3–P1–Ti	112.1 (3)	C3–P1–C1	101.3 (4)		
C3–P1–C2	100.5 (4)	C31–P2–Ti	111.6 (3)		
C41–P2–Ti	114.3 (3)	C41–P2–C31	98.8 (4)		
Distances (Å) for Molecule **4b**					
Ti–P1	2.71 (1)	Ti–P2	2.67 (1)	Ti–C11	2.42 (2)
Ti–C12	2.35 (2)	Ti–C13	2.33 (2)	Ti–C14	2.39 (2)
Ti–C15	2.44 (2)	Ti–C21	2.41 (2)	Ti–C22	2.40 (2)
Ti–C23	2.39 (2)	Ti–C24	2.40 (2)	Ti–C25	2.41 (2)
P1–C31	1.88 (2)	P1–C41	1.84 (1)	P1–C51	1.84 (2)
P2–C61	1.83 (2)				
Angles (deg) for Molecule **4b**					
P2–Ti–P1	81.2 (3)	Ti–P1–C31	106.2 (7)		
Ti–P1–C41	110.3 (7)	C31–P1–C41	102 (1)		
Ti–P2–C51	104.3 (7)	Ti–P2–C61	115.3 (7)		
C51–P2–C61	103 (1)				

similar to that of **3a** with $b = 1.991$, $\langle a,{}^{31}P\rangle = 26.2$ and 2.3 G, and $\langle a,{}^{47/49}Ti\rangle = 9.2$ G (Figure 1b). The mononuclear nature and structure of **3b** was confirmed by a crystallographic analysis (vide infra).

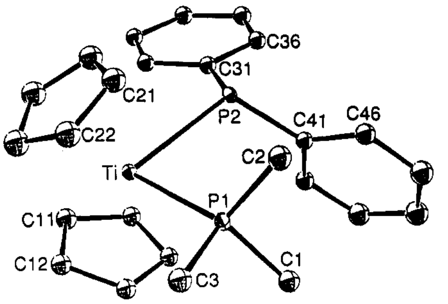

Figure 2. ORTEP drawing of molecule **3b**, with 30% thermal ellipsoids shown. Hydrogen atoms are omitted for clarity but are numbered such that the hydrogen atom numbers correspond to those of the carbon atoms to which they are bonded.

Structural Study of 3b. An ORTEP drawing of **3b** is shown in Figure 2. Two π-bonded cyclopentadienyl ligands, a diphenylphosphido moiety, and a trimethylphosphine ligand comprise the pseudotetrahedral coordination sphere of the Ti. The bond distances and angles within the Cp_2Ti and PMe_3 fragments are typical.[26-29] The

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titanium–phosphine distance (i.e., Ti–P1 = 2.636 (3) Å) is slightly longer than that found in $Cp_2TiCl(PMe_3)$ (2.599 (2) Å)[26] and substantially longer than those found in the related Ti(II) species $Cp_2Ti(CO)(PMe_3)$ (2.544 (1) Å) and $Cp_2Ti(PMe_3)_2$ (2.524 (4), 2.527 (3) Å).[28] Similarly the titanium–phosphide bond length (i.e., Ti–P2 = 2.681 (3) Å) is greater than those seen in the phosphide-bridged dimer **2a**. Presumably, the steric demands of the diphenylphosphido group, as well as the lesser basicity of PPh_2 ralative to PEt_2, account for the longer Ti–P bonds in **3b**. The P1–Ti–P2 angle of 85.9 (1)° is substantially greater than the Cl–Ti–P angle of 80.4 (1)° found in $Cp_2TiCl(PMe_3)$,[26] suggesting steric interactions between the phosphido group and the phosphine ligand in **3b**. This proposition is consistent with the close approach of H2B to H46 (2.412 Å). Similar steric effects presumably also account for the relatively long Ti–P bond length in $Cp_2Ti(C_2H_4)PMe_3$ (2.693 (2) Å).[29] The geometry about P2 is pyramidal with the lone pair of electrons oriented out of the TiP_2 plane. This is in contrast to the complex $Cp_2Hf(PEt_2)_2$, where alignment of a lone pair of electrons on one of the phosphorus atoms in the HfP_2 plane maximizes the overlap of the lone pair with the empty a_1 orbital on Hf(IV) affording substantial π-bonding.[17] While the geometry about P2 in **3b** is slightly flattened compared to PPh_3, the structural data does not suggest significant Ti–P2 π-bonding. The deformation of the geometry about P2 is attributed to steric interactions between phenyl rings and the Cp_2Ti fragment. The absence of π-bonding in the Ti(III) species **3b** is expected as the π-acceptor a_1 orbital on Ti is singly occupied.

Implications regarding the structure of the reaction intermediate **1** are inferred from the structure of the PMe_3 adduct **3b**, as well as EPR parameters. On the basis of the structure of **3b**, a pseudotetrahedral geometry about Ti might be suggested in which a solvent molecule completes the coordination sphere. However, in related Ti–phosphorus species, the phosphorus hyperfine coupling has been shown to be strongly geometry dependent. For example, for the species $Cp_2Ti(SPPh_2)$ the $\langle a,{}^{31}P\rangle$ value is 20.7 G, while for $Cp_2Ti(S_2PPh_2)$ the hyperfine coupling is 38.9 G.[30] In $Cp_2Ti(SPPh_2)$ the phosphorus sits between the lobes of the singly occupied a_1 orbital on Ti, while in $Cp_2Ti(S_2PPh_2)$ the larger hyperfine coupling is attributed to the overlap of phosphorus-based orbitals with the torus of the a_1 orbital. Thus, on the basis of a comparison to the above compounds, a pseudotrigonal geometry might be suggested for **1**. Such coordination geometries have been confirmed for complexes of the form Cp_2TiOR where the R moiety is sterically demanding.[31] It is noteworthy that the $\langle a,{}^{31}P\rangle$ value for **1a** of 33.5 G is similar to those seen for the related titanium phosphido complexes Cp_2TiPR_2 (R = Ph, Cy).[35] In the case of Cp_2TiPCy_2 the trigonal coordination sphere about Ti has been recently confirmed by Baker et al.[35] Further, these results confirm that a larger $\langle a,{}^{31}P\rangle$ value is attributable to a planar, sp^2 nature of the P environment. This dependence of the $\langle a,{}^{31}P\rangle$ value on the P geometry is consistent with substantially lower $\langle a,{}^{31}P\rangle$ values for the phosphido ligands in **3b** (10 G) and **4b** (11 G) where the geometry about P has been confirmed to be pyramidal (vide supra and infra). On the basis of these assignments, the 24.4- and 26.2-G splittings in **3a** and **3b**, respectively, are attributed to the PMe_3 ligand.

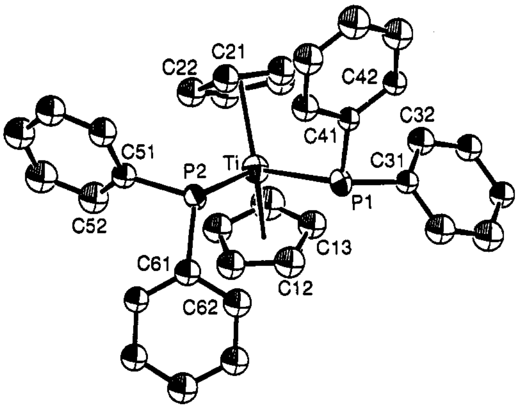

Figure 3. ORTEP drawing of the cation of **4b**, with 30% thermal ellipsoids shown. Hydrogen atoms are omitted for clarity but are numbered such that the hydrogen atoms numbers correspond to those of the carbon atoms to which they are bonded.

It has been previously shown that direct reaction of $LiPEt_2$ and Cp_2TiCl_2 at 298 K leads to the formation of a species exhibiting a triplet pattern in the EPR spectrum.[21-23] Similarly, on standing at 298 K the EPR signal of **3b** is replaced by a single triplet resonance. These resonances at g = 1.992 with $\langle a,{}^{31}P\rangle$ = 11.4 G and $\langle a,{}^{47/49}Ti\rangle$ = 10.9 G and at g = 1.985 with $\langle a,{}^{31}P\rangle$ = 11.8 G and $\langle a,{}^{47/49}Ti\rangle$ = 8.8 G have been previously attributed to the species $[Li(THF)_2][Cp_2Ti(PR_2)_2]$, R = Et (**4a**) and R = Ph (**4b**), respectively (Figure 1c). A zirconium analogue of **4** has been synthesized by Baker et al. via reduction of $Cp_2Zr(PR_2)_2$ with Na,[17] although in that case coordination of the phosphido groups to Na was inferred by the hyperfine coupling of the unpaired electron formally on Zr(III) to the P and Na nuclei. The intermediates **4** can be isolated. Excess phosphide was employed to maximize the conversion of Cp_2TiCl_2 to **4**, and excess TMEDA was added. This affords the isolation of the species $[Li(TMEDA)_2][Cp_2Ti(PR_2)_2]$ (**4**) (Scheme I). These salts **4a** (R = Et) and **4b** (R = Ph) exhibit triplet center-band signals in the EPR spectra at g = 1.991 and 1.988, with $\langle a,{}^{31}P\rangle$ values of 10.9 and 8.6 G and $\langle a,{}^{47/49}Ti\rangle$ values of 9.8 and 9.5 G, respectively. The formulation of these complexes were confirmed by a crystallographic study (vide infra).

Crystallographic Study of 4b. An ORTEP drawing of the anion of **4b** is shown in Figure 3. Two π-bonded cyclopentadienyl ligands and two diphenylphosphido moieties comprise the pseudotetrahedral coordination sphere about Ti. The bond distances and angles within the Cp_2Ti fragment and the cation are typical. The titanium–phosphide distances average 2.69 (1) Å, which is slightly longer than that found in **3b** and dramatically longer than the Ti–P distance of 2.396 Å found in Cp_2TiPCy_2.[35] The P–Ti–P angle in **4b** was found to be 81.3 (3)°. This is dramatically smaller than the P–Hf–P angles of 89.6 (3), 98.64 (3), and 99.4 (1)° found in $Cp_2Hf(PPh)_3$[20d] $Cp_2Hf(PEt_2)_2$,[17] and $Cp_2Hf(P(SiMe_3)_2)_2$,[32] respectively. This observation is consistent with a HOMO that is a singly occupied orbital derived from the $1a_1$ frontier orbital of the Cp_2Ti fragment.[33] Repulsive interactions with the formally anionic phosphido ligands results in the com-

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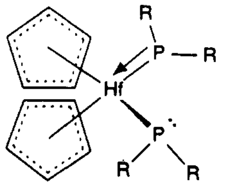
paratively small P–Ti–P angle. Presumably this effect also brings about steric interactions between the phosphide substituents, which accounts for the slight lengthening of Ti–P in **4b** compared to those in **3b**. Such stereochemical influences of unpaired electrons on the geometries of early metallocene dithiolates have been recently examined by Darensbourg et al.[34] As was observed for **3b**, the geometries about the phosphorus atoms in **4b** are pseudotetrahedral. This is marked contrast to that observed for $Cp_2Hf(PEt_2)_2$[17] and $Cp_2Hf(P(SiMe_3)_2)_2$,[32] where one of the two phosphido groups is flattened allowing significant Hf–P π-bonding.



The absence of such interaction in **4b** is yet another ramification of the presence of the singly occupied $1a_1$ orbital.

Summary. The earlier proposals[12,15,21-23] of the mechanism of the formation of the dimer species $[Cp_2Ti(\mu\text{-}PR_2)]_2$ (**2**) involved an initial step of nucleophilic substitution of phosphide for halide followed by rapid reduction to **1** (Scheme I). Dimerization of this species would afford **2**, while reaction with excess phosphide yields **4**. Our results are consistent with this view. The isolation and structural characterization of **3b** and **4b** support the notion of intermediacy of the mononuclear phosphido species **2**. Further the isolation of these species suggests that while the kinetic products of the reaction of Cp_2TiCl_2 and phosphide are mononuclear species, it is the attainment of equilibrium that yields the thermodynamic product, i.e. the dimer **2**.

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Supplementary Material Available: Tables S1–S3 and S5–S7, listing thermal and hydrogen atom parameters and bond distances and angles (11 pages); Tables S4 and S8, listing values of $10F_o$ and $10F_c$ (14 pages). Ordering information is given on any current masthead page.

Potential Energy Surfaces for Methyl Migration in Tetracarbonylmethylcobalt(I) and Dicarbonylcyclopentadienylmethyliron(II)

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Molecular orbital calculations were used to explore the potential energy surfaces in the methyl migration/carbonyl insertion reactions of tetracarbonylmethylcobalt(I)

$$(CO)_4CoCH_3 \rightarrow (CO)_3Co(COCH_3) \tag{1}$$

and dicarbonylcyclopentadienylmethyliron(II)

$$CpFe(CO)_2CH_3 \rightarrow CpFe(CO)(COCH_3) \tag{2}$$

Geometries were determined by using a fast but relatively accurate approximate method (PRDDO), coupled with the synchronous transit approach for estimating transition states. Ab initio calculations using significantly larger basis sets were then used to determine the energetics. In both cases we found low energy barriers to methyl migration as well as small ΔE's for the above reactions. The products of the above reactions, which are the coordinatively unsaturated intermediates in the overall carbonylation reactions, possess minimum energy conformations corresponding to both η^1- and η^2-bound acyl groups. Energetics for the addition of carbonyl will also be presented, as will substituent effects. The results are compared to our previous work involving pentacarbonylmethylmanganese(I), and we contrast these results with recent density functional calculations for the cobalt system.

Introduction

Group migration reactions such as

$$L_nXM\text{-}Y \rightarrow L_nM\text{-}Y\text{-}X$$

play an important role in organometallic chemistry because of their known involvement in homogeneous and heterogeneous catalysis and organic synthesis.[1,2] Group migration in pentacarbonylmethylmanganese(I), for example, has been particularly well-studied. Experimental evidence indicates that the mechanism of this reaction involves the intramolecular migration of the methyl group from the manganese atom to the neighboring carbonyl ligand.[3] This mechanism has been experimentally confirmed in carbonylation reactions using isotopically labeled ^{13}CO, where the labeled ^{13}C does not appear in the acyl position.[4,5] Furthermore, it has been shown that the methyl group in this reaction migrates to a carbonyl ligand cis to the

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