Contribution No. 2294 from the Central Research &
Development Department, Experimental Station,
E. I. du Pont de Nemours and Company,
Wilmington, Delaware 19898

Alkyl Complexes of Scandium(III), Titanium(III), and Vanadium(III) Derived from Phosphorus Ylide Anions

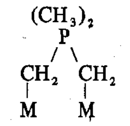
Leo E. Manzer

Received March 22, 1976 AIC602083

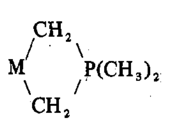
In recent years Schmidbaur and co-workers[1] have been investigating the coordination chemistry of phosphorus ylides, primarily that of $CH_2{=}P(CH_3)_3$ and its anion. Three types of bonding modes for the ylide and ylide anions **1–3** have been observed. Their studies have been mainly limited to main group and group 8 metals. Kurras et al. have extended this chemistry and have isolated ylide anion complexes of Cr(II),[2] Cr(III),[3] and Mo(II).[4] In view of the remarkable stability of these complexes we attempted to isolate stable phosphorus ylide anion complexes of Ti(III), Sc(III), and V(III) and present the results of our work in this paper.

$R_3PCH_2{\to}M$

1



2



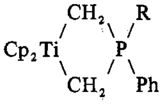
3

Results and Discussion

The addition of 2 equiv of BuLi to a suspension of $[Me_2PPh_2]^+I^-$ or $[Me_3PPh]^+I^-$ in ether gives off butane and $Li(CH_2)_2PR_2$ precipitates from solution. The LiI is ether soluble and may be removed by washing with ether. The lithium salts are stable indefinitely in the solid state at room temperature under an inert atmosphere and may be conveniently handled in a drybox.

The addition of 1 equiv of $Li(CH_2)_2PPh_2$ to a suspension of $Cp_2ScCl(THF)$[5] in ether gives a pale yellow solution. The lithium chloride is removed by filtration and the ether is concentrated by rotary evaporation to give colorless air-sensitive crystals. On drying they turn pale yellow. The NMR spectrum in benzene at room temperature shows a singlet for the cyclopentadienyl hydrogens at δ 6.0 and a doublet for the methylene hydrogens due to coupling with the ^{31}P nucleus. In a similar reaction $Cp_2V(CH_2)_2PPh_2$ was isolated as a red-brown crystalline solid.

The reaction between Cp_2TiCl and $Li(CH_2)PPhR$ (R = Me, Ph) gave the alkyl complexes **4** as purple-brown crystalline solids.



4a, R = Me
b, R = Ph

The mass spectrum of **4a** gave a parent ion peak at *m/e* 329.0934 and a metastable peak at *m/e* 212 corresponding to the loss of a cyclopentadienyl group ($M^+ - C_5H_5$). The magnetic moments of **4** were determined in benzene by the Evans method[6] and were in the range 1.6–1.7 μ_B. These values are close to the spin-only value of 1.73 μ_B for a d^1 configuration.[7] The electronic spectrum of $Cp_2Ti(CH_2)_2PPh_2$ shows a broadened doublet at 478, 586 nm. For a d^1 system of low symmetry a doublet is often observed.[8]

A strong signal is seen in the electron spin resonance spectra of the titanium compounds **4**. The main feature in the spectra (Figure 1a) is a doublet due to hyperfine coupling of the electron with only *one* phosphorus atom. Under high resolution and by using very dilute solutions (10^{-5}–10^{-6} M) each peak is split into a quintet, arising from hyperfine coupling of the electron with four equivalent hydrogen atoms. ^{47}Ti ($I = {}^5/_2$, 7.28% natural abundance) and ^{49}Ti ($I = {}^7/_2$, 5.51% natural abundance) satellites are also observed. The ESR data (Table I) are only consistent with a monomeric structure of type **3**.

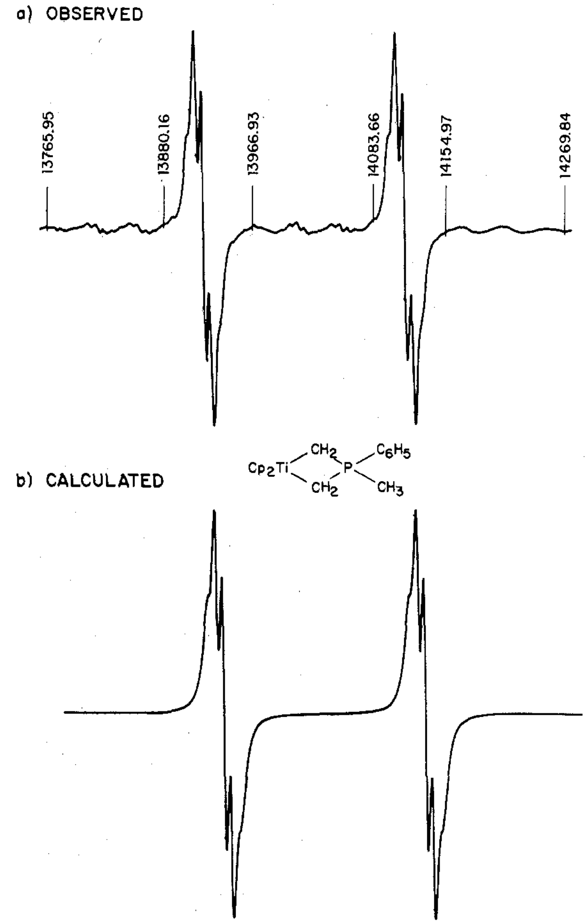
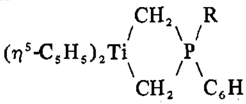


Figure 1. Electron spin resonance of $(\eta^5\text{-}C_5H_5)_2Ti(CH_2)_2PMePh$ in toluene at −60 °C. The proton NMR field markers are in kilohertz.

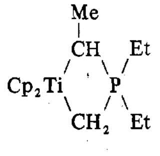
Table I. ESR Parameters[a] of



R	g	$\langle a_P\rangle$, G	$\langle a_H\rangle$, G	$\langle a_{Ti}\rangle$, G
CH_3	1.992	46.1	1.7	9.6
C_6H_5	1.986	43.0	1.9	9.8

[a] g values are accurate to ±0.001 and coupling constants are accurate to ±0.1 G. The spectra were recorded in very dilute toluene solutions at −60 °C.

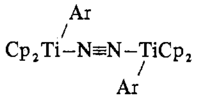
The reaction of $Li(CH_2)(CHMe)PEt_2$ (obtained by the reaction of BuLi with $[PMeEt_3]^+I^-$ in ether) with Cp_2TiCl gave a dark green crystalline solid. The analytical data are consistent with **5**. The ESR spectrum of **5**, even in very dilute solutions, showed only a doublet due to phosphorus coupling



5

($\langle a_P \rangle = 39.18$ G) with titanium satellites. No further splitting to the hydrogens was seen.

The stability of these titanium complexes is undoubtedly due to the chelating nature of the alkyl ligand. Other dicyclopentadienyl organometallic derivatives are relatively unstable[9] and tend to form adducts[10] with nitrogen, **6**. Also,

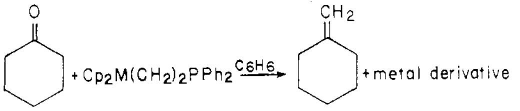


$Cp_2Ti(Ar)-N{\equiv}N-TiCp_2(Ar)$

6

$Cp_2Ti(o\text{-}C_6H_4CH_2NMe_2)$[11] which contains a built-in chelating amine group is quite stable. Attempts to observe Cp_2TiMe by ESR spectroscopy[12] showed only the presence of $Cp_2TiMe_2^-$.

Transition metal derivatives of phosphorus ylides are potentially useful reagents in organic synthesis. The reaction of $Cp_2M(CH_2)_2PPh_2$ (M = Ti, Sc, V) with cyclohexanone gave methylenecyclohexane according to eq 1. The products were analyzed by gas chromatography and mass spectrometry. Reaction 1 went to 70% conversion of the cyclohexanone using the titanium complex and was essentially quantitative for the vanadium complex. $Cp_2Sc(CH_2)_2PPh_2$ was more reactive and both methylene groups were quantitatively transferred to give methylenecyclohexane. The resultant organometallic product has not been identified.



(1)

Experimental Section

All reactions and manipulations were performed in a Vacuum Atmosphere drybox under an atmosphere of dry nitrogen.

Solvents were dried by passage through molecular sieves (Linde 4A) and sparged with nitrogen prior to use.

Cp_2MCl complexes (M = Ti, V, Sc) were prepared by established procedures.[5]

Microanalyses were performed by the Physical and Analytical Section of this department.

Preparation of $[PhMeP(CH_2)_2]Li$. $[PMe_3Ph]I$ (39.4 g, 0.141 mmol) was suspended in ether and a solution of MeLi (164 ml of a 1.72 M solution in ether; 0.282 mol) was added dropwise. The phosphonium salt rapidly dissolved with evolution of methane. When the addition was half-finished, a clear yellow solution formed. Further addition of methyllithium precipitated a white solid and evolved methane. When the addition was completed, the solution was allowed to sit for 2 h and the white solid was then filtered off and washed with copious quantities of ether to remove the LiI. The yield of white solid was 18.0 g (81%).

Preparation of $Cp_2Ti(CH_2)_2PMePh$. Cp_2TiCl (1.35 g, 6.32 mmol) was suspended in ether and $Li(CH_2)_2PMePh$ was added. Two milliliters of THF was added and the solution was stirred for 1 h and filtered. The solvents were removed to give a purple-brown solid. Toluene was added, the solution was filtered, and pentane was added. The solution was cooled to −40 °C for 24 h and filtered to give 1.93 g (93%) of long, purple needles, mp 147–150 °C.

Anal. Calcd for $TiPC_{19}H_{22}$: C, 69.31; H, 6.74; P, 9.41. Found: C, 68.48; H, 6.78; P, 10.28. ESR (toluene): doublet quintet at $g = 1.992$; $\langle a_P \rangle = 46.1$ G; $\langle a_H \rangle = 1.7$ G; $\langle a_{Ti} \rangle = 9.6$ G. Mass spectrum: M^+ ion at m/e 329.0934; strong peaks at 264, 204, 191, 178; metastable at 212 ($329 \rightarrow 264$) ($M^+ \rightarrow C_5H_5$). Visible spectrum in toluene: 535 nm; (ϵ 155).

Preparation of $(C_5H_5)_2Ti(CH_2)_2P(C_6H_5)_2$. To a stirred solution of $[PMe_2Ph_2]I$ (4.8 g, 14.04 mmol) in ~200 ml of ether was added 17.5 ml of a 1.6 M solution of butyllithium. After being stirred for 2 h the solution was filtered and the solid was washed with 100 ml of ether to remove LiI. The white solid was dried, and the yield was 2.80 g (91%). This was then added to a stirred suspension of Cp_2TiCl (2.71 g, 12.71 mmol) in ether. The solids slowly dissolved to give a dark brown solution. After about 15 min a thick brown precipitate settled out. It was filtered and washed through the filter with toluene. The solvents were removed by rotary evaporation to give a brown crystalline solid which was washed from the flask with pentane; yield 4.70 g (95%); mp 152–153 °C.

Anal. Calcd for $TiC_{24}H_{24}P$: C, 73.66; H, 6.18; P, 7.91; Ti, 12.24. Found: C, 73.13, 72.74, 72.34; H, 6.18, 6.18, 6.21; P, 7.91, 7.90; Ti, 12.91. Electronic spectrum (benzene): 478 nm (ϵ 153), 586 nm (ϵ 120). ESR (toluene, room temperature): $g = 1.986$; $\langle a_{Ti} \rangle = 9.81$ G; $\langle a_P \rangle = 42.96$ G; $\langle a_H \rangle = 1.86$ G.

Preparation of $Cp_2Sc(CH_2)_2P(C_6H_5)_2$. To a stirred suspension of $Cp_2ScCl(THF)$ (3.59 g, 12.71 mmol) in ether was added $Li(CH_2)_2P(C_6H_5)_2$ (2.80 g). After being stirred for 1 h the solution was filtered and the ether concentrated by rotary evaporation to give white crystals. They were filtered off and dried. The filtrate was cooled to give a further crop of white crystals. Total yield was 4.22 g. On drying, the crystals turn pale yellow. The compound is very air sensitive.

Anal. Calcd for $ScC_{24}H_{24}P$: C, 74.22; H, 6.23; P, 7.97. Found: C, 73.46, 72.65, 72.41; H, 6.24, 6.13, 5.80; P, 7.60. NMR (C_6D_6/TMS): $\delta(C_5H_5)$ 6.0; $\delta(CH_2)$ 0.86, $^2J(PH) = 11$ Hz.

Preparation of $Cp_2V(CH_2)_2PPh_2$. A solution of 17.5 ml of a 1.6 M solution of butyllithium in hexane was added to a suspension of 4.8 g of dimethyldiphenylphosphonium iodide in ether. The solution was stirred for 2 h, filtered, and washed with ether. The solid was then added to a stirred solution of Cp_2VCl (2.80 g) in ether. The solution rapidly turned reddish brown and a red-brown solid separated from the solution. After being stirred for about $^1/_2$ h the solution was filtered and the solid was washed through the filter with toluene. The solvent was removed by rotary evaporation to give a red-brown crystalline solid that was washed from the flask with pentane. It was recrystallized from toluene and ether; yield 4.90 g; mp 129–130 °C.

Anal. Calcd for $VPC_{24}H_{24}$: C, 73.28; H, 6.13; P, 7.84. Found: C, 72.42, 72.85, 71.87; H, 6.33, 6.46, 6.42; P, 7.73, 7.42.

Reaction of $Cp_2Ti(CH_2)_2PPh_2$ with Cyclohexanone. A sample of 0.10 g of $Cp_2Ti(CH_2)_2PPh_2$ was dissolved in 1 ml of benzene, and 27 μl of cyclohexanone was added. After 1 h the solution was exposed to the air and filtered, and the filtrate was analyzed by mass spectroscopy. The analysis indicated 23% conversion of cyclohexanone to methylenecyclohexane which corresponds to 70% transfer of one $-CH_2$ unit.

Preparation of $Cp_2Ti(CH_2)(CHCH_3)PEt_2$. A solution of 17.5 ml of a 1.6 M solution of butyllithium in hexane was added to a suspension of methyltriethylphosphonium iodide in ether. The mixture was stirred 1 h and Cp_2TiCl (3.0 g, 14.04 mmol) was added. The mixture became very dark green and some bubbling was observed. After being stirred for 15 min the solution was filtered and the ether was removed to give a dark green solid. Toluene was added, the solution was filtered, and pentane was added. Lithium iodide separated so the solution was filtered and cooled to −40 °C overnight to give 1.80 g of large dark green crystals. They were filtered off and dried; mp 61–63 °C.

Anal. Calcd for $TiC_{17}H_{26}P$: C, 66.02; H, 8.47. Found: C, 65.08; H, 8.26. ESR (toluene): $g = 1.986$; $\langle a_P \rangle = 39.18$ G; $\langle a_{Ti} \rangle = 9.9$ G.

Acknowledgment. I am grateful to Dr. P. J. Krusic for recording the ESR spectra and for the computer simulation shown in Figure 1.

Registry No. $Cp_2Ti(CH_2)_2PMePh$, 59982-75-1; $Cp_2Ti(CH_2)_2PPh_2$, 59982-76-2; $Cp_2Sc(CH_2)_2PPh_2$, 59982-77-3; $Cp_2V(CH_2)_2PPh_2$, 59982-78-4; $Cp_2Ti(CH_2)(CHCH_3)PEt_2$, 59982-79-5; $[PhMeP(CH_2)_2]Li$, 59983-61-8; Cp_2TiCl, 1271-18-7; $Cp_2ScCl(THF)$, 59692-66-9; Cp_2VCl, 12701-79-0; $Li(CH_2)_2PPh_2$, 59983-62-9.

References and Notes

(1) H. Schmidbaur, *Acc. Chem. Res.*, **8**, 62 (1975), and references therein.
(2) E. Kurras, U. Rosenthal, H. Mennenga, G. Oehme, and G. Engelhardt, *Z. Chem.*, **14**, 160 (1974).
(3) E. Kurras, U. Rosenthal, H. Mennenga, and G. Oehme, *Angew. Chem., Int. Ed. Engl.*, **12**, 854 (1973).
(4) E. Kurras, H. Mennenga, G. Oehme, U. Rosenthal, and G. Engelhardt, *J. Organomet. Chem.*, **84**, C13 (1975).
(5) L. E. Manzer, *J. Organomet. Chem.*, **110**, 291 (1976).
(6) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).
(7) B. N. Figgis and J. Lewis, *Prog. Inorg. Chem.*, **6**, 37 (1967).
(8) A. B. P. Lever, "Inorganic Electronic Spectroscopy", American Elsevier, New York, N.Y. 1968.
(9) J. H. Teuben and H. J. DeLiefde Meijer, *J. Organomet. Chem.*, **46**, 313 (1972).

(10) J. H. Teuben, *J. Organomet. Chem.*, **57**, 159 (1973).
(11) D. Ytsma, J. G. Hartsuiker, and J. H. Teuben, *J. Organomet. Chem.*, **74**, 239 (1974).
(12) H. H. Brintzinger, *J. Am. Chem. Soc.*, **89**, 6871 (1967).

Contribution from the Department of Chemistry,
Cornell University, Ithaca, New York 14853

Difluoroborane, an H–D Exchange Catalyst for the Preparation of *B*-Trideuterioborazines

Anthony J. DeStefano and Richard F. Porter*

Received March 22, 1976 AIC60229X

The purpose of this note is to describe a relatively simple procedure for preparing *B*-deuterioborazines. The method involves direct deuteration of a borazine derivative in the gas phase with a deuterium–HBF_2 mixture. In the reaction HBF_2 acts as an H–D exchange catalyst. The method appears to have advantages over conventional synthetic techniques which require specially deuterated starting materials.

Experimental Section

Mixtures of HBF_2–BF_3 were prepared by a method similar to that of Coyle, Cooper and Ritter.[1] In a typical synthesis a mixture of BF_3 and B_2H_6 in a molar ratio of 2:1 at a total pressure of 200 mm was heated to 200 °C for 0.5 h in a 1-l. stainless steel vessel. Under these reaction conditions HBF_2–BF_3 product mixtures contained 30–40% HBF_2 with less than 1% B_2H_6. Mixtures of DBF_2–BF_3 were prepared by reaction of HBF_2–BF_3 mixtures with deuterium gas.[2] Sample purities were checked by ir and mass spectra.

The preparation of borazine followed the procedure of Hohnstedt and Haworth.[3] *N*-Trimethylborazine and *N*-triethylborazine were prepared by the method used by Beachley.[4] Ether solvent remaining in the products after trap-to-trap distillation was removed by reaction with BCl_3. Sample purities were checked by ir and mass spectra.

Mass spectra were obtained on a CEC-21-103A mass spectrometer with probe temperature at 50 °C and on a previously described photon impact mass spectrometer employing the Lyman α line of hydrogen as the source of ionizing radiation.[5] Infrared spectra were obtained on Perkin-Elmer 337 and 521 grating spectrophotometers.

Results

Preparation of $D_3B_3N_3H_3$. Mixtures of $H_3B_3N_3H_3$ and DBF_2 containing some BF_3 were allowed to react for periods up to 1500 s in an 80-ml stainless steel vessel. The reaction was quenched by immersion of the reaction vessel into liquid nitrogen. The percent H–B converted to D–B in borazine was then determined by mass spectral analysis. Results of the analyses are shown in Table I. The data indicate that the deuteration reaction probably occurs through homogeneous and heterogeneous pathways, making the determination of specific rate constants difficult. It can be noted that the rate of formation of the deuterated borazine is comparable to the rate of DBF_2 formation from the reaction

$$HBF_2 + D_2 \rightarrow DBF_2 + HD \qquad (1)$$

under similar reaction conditions.[2]

For qualitative determinations of the rate of borazine deuteration a number of mixtures with different DBF_2:$H_3B_3N_3H_3$:D_2:BF_3 ratios were allowed to react for periods of 1.0, 2.33, and 16 h. The results of mass spectral analysis of the products are shown in Table II. At short times the rate of deuteration of borazine is quite rapid and dependent, to a first approximation, on the DBF_2:$H_3B_3N_3H_3$ ratio. At longer times back-reactions became more important and the net rate of deuteration decreased markedly. A change from Pyrex to stainless steel reaction vessels did not appear to alter the results significantly. The final entry in Table II shows the result of allowing an $H_3B_3N_3H_3$–D_2 sample to react at 297 K for 16 h in the stainless steel container. This puts an upper limit of about 5% on the amount of borazine deuterated thermally[6,7] after 16 h under our experimental conditions.

Table I. Results of Isotope Exchange Experiments in Mixtures of $H_3B_3N_3H_3$, DBF_2, and BF_3 ($T = 297$ K)

Sample compn, $H_3B_3N_3H_3$:DBF_2:BF_3	Pressure, mm	Time, s	% H–B converted to D–B in borazine samples
1:0.24:0.40	40	1500	5.2
1:0.19:0.35	54	1500	6.9
1:0.14:0.26	45.5	1500	1.8
1:0.16:0.29	52	1500	5.5
1:0.10:0.18	73.5	1500	1.3
1:0.06:0.12	65	1500	1.4
1:0.04:0.08	56	1500	0.77
1:0.05:0.09	109.5	500	0.92

Table II. Results of Isotope Exchange Experiments in Mixtures of DBF_2, $H_3B_3N_3H_3$, D_2, and BF_3 ($T = 297$ K)

Sample compn, DBF_2:$H_3B_3N_3H_3$:D_2:BF_3	Pressure, mm	Time, h	% H–B converted to D–B in borazine samples	Vessel
1:1:28.7:1.8	192	1	34	Pyrex
1:2.1:28.7:1.8	130	1	16	Pyrex
1:1:23.7:1.9	268	1	31	Stainless
1:1.7:23.6:1.9	95	1	12	Stainless
1:2.4:28.7:1.8	113	2.33	31	Pyrex
1:0.8:24.5:1.8	183	2.33	23	Pyrex
1:0.8:23.6:1.9	155	2.33	56	Stainless
1:2.2:24.5:1.8	67	16	65	Pyrex
1:4.7:24.5:1.8	184	16	65	Stainless
0:1:33:0	274	16	5	Stainless

Table III. Parent Regions of the 70-eV Electron Impact Spectra of $H_3B_3N_3H_3$ and Deuterium-Enriched Borazines

Mass no.	D_3B_3-N_3H_3[a]	D_3B_3-N_3H_3[b]	D_3B_3-N_3H_3[c]	H_3B_3-N_3H_3
85	1.00	0.87	0.72	
84	50.0	51.1	50.0	
83	40.5	40.9	38.8	
82	100	100	100	0.51
81	66.7	68.9	68.3	39.3
80	19.8	20.0	17.0	100
79	9.0	8.9		62.4
78	7.4	7.4		21.4
77	6.2	6.2		11.3
76	4.8	5.0		8.5
75	2.1	2.3		4.0
74	0.48	0.60		0.85

[a] Prepared using DBF_2–D_2. [b] Prepared photochemically. [c] Calculated from the $H_3B_3N_3H_3$ spectrum (see text).

B-Trideuterioborazine of isotopic purity comparable to that produced photochemically[6] was obtained as follows. A mixture containing $H_3B_3N_3H_3$, DBF_2, BF_3, and D_2 at partial pressures of 7, 5, 9, and 453 mm, respectively, was allowed to react in an 80-ml stainless steel vessel. At intervals of 9, 14.5, and 5.5 h the H_2–HD–D_2 mixture in the products was removed and replaced with pure D_2 at pressures of 520, 430, and 456 mm, respectively. The final mixture was then allowed to react for 18 h prior to mass spectral and infrared analysis. The ir spectrum of the deuterated borazine was identical with that reported in the literature.[8,9] Shown in Table III are the 70-eV electron impact mass spectra of deuterated borazine samples prepared by the above procedure and by the photochemical