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# Novel Phosphorus Ylide Complexes of Zirconium(IV)

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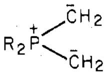
Novel ylide complexes of Zr(IV) were prepared by treatment of ($\eta^5$-$C_5H_5$)$_2$Zr(alkyl)(hydride) complexes with methylenetrimethylphosphorane and subsequent reactions. Spectroscopic data for these complexes are discussed and several reactions of them are presented.

## Introduction

Recent work has demonstrated that phosphorus ylides are versatile ligands for a wide variety of transition metals, and the chemistry of complexes of phosphorus ylides 1 and their anions, the phosphonium dimethylides 2, with group 6 and 8 metals and coinage metals has been extensively developed.[1,2] In these complexes three general binding modes (3–5) for the ylide ligand have been identified. However, few early transition-metal complexes of these ligands are known;[3–5] hence their potential as catalytic or stoichiometric reagents remains largely unexplored. In this paper we report the synthesis, characterization, and simple reactions of the first zirconium phosphorus ylide complex, a novel zirconium(IV) ylide hydride compound,[6] prepared by trimethylmethylenephosphorane-induced elimination of alkane from a zirconium(IV) alkyl hydride.[7]

$$R_3\overset{+}{P}—\overset{-}{C}H_2 \longleftrightarrow R_3P{=}CH_2$$

1, R = Me



2, R = Me

$$R_3P—CH_2\rightarrow M$$

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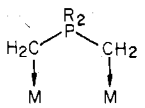

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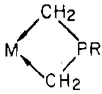

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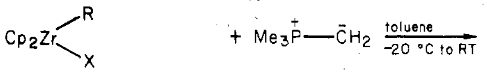
## Results

(Cyclohexylmethyl)bis($\eta^5$-cyclopentadienyl)hydridozirconium(IV)[8] (**6a**) reacts rapidly with 1 equiv of trimethylmethylenephosphorane ($Me_3PCH_2$) forming methylcyclohexane (80%) and a green, thermally unstable, air- and moisture-sensitive zirconium(IV) ylide hydride complex **7** which has been characterized by spectral methods (reaction 1). The corresponding reaction of the dideuterated compound **6b** in benzene-$d_6$ gives labeled methylcyclohexane (90% methylcyclohexane-*1*,$\alpha$,$d_2$) and **7** which is unlabeled. An alternative synthesis is from the Zr(II) complex $Cp_2Zr(dmpe)$[7c] which reacts very slowly with $Me_3PCH_2$ to produce **7**.



**6a**, R = $CH_2(CH_2)_4CHCH_2$, X = H

**b**, R = $CH_2(CH_2)_4CDCH_2$, X = D

$$Cp_2Zr[(CH_2)_2PMe_2]H + \text{methylcyclohexane} \quad (1)$$

7

In the $^1$H NMR of **7** the Cp resonance ($\delta$ 5.58) is a sharp singlet, indicating that phosphorus is not bound directly to Zr.[9] A terminal hydride ligand gives rise to a doublet of triplets ($^3J_{PH}$ = 42 Hz, $^3J_{HH}$ = 2 Hz) at characteristically low field ($\delta$ 3.82)[10] and in the IR produces a strong absorption, centered at 1465 cm$^{-1}$.[11] Whereas the two methyl groups on phos-

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[1] For recent reviews see: Schmidbaur, H. *Acc. Chem. Res.* **1975**, *8*, 62. Schmidbaur, H. *Pure Appl. Chem.* **1978**, *50*, 19.

[2] Several group 6 phosphorus ylide complexes are known: (a) Kurras, E.; Rosenthal, U.; Mennenga, H.; Oehme, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 854. (b) Kurras, E.; Rosenthal, U.; Mennenga, H.; Oehme, G.; Engelhardt, G. *Z. Chem.* **1974**, *14*, 160. (c) Kurras, E.; Mennenga, H.; Oehme, G.; Rosenthal, U.; Engelhardt, G. *J. Organomet. Chem.* **1975**, *84*, C13. (d) Kaska, W. C.; Reichelderfer, R. F.; Prizant, L. *Ibid.* **1977**, *129*, 97. (e) Knoll, L. *Ibid.* **1978**, *148*, C25. (f) Cotton, F. A.; Hanson, B. E.; Rice, G. W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 953. Cotton, F. A.; Hanson, B. E.; Ilsley, W. H.; Rice, G. W. *Inorg. Chem.* **1979**, *18*, 2713.

[3] Manzer, L. E. *Inorg. Chem.* **1976**, *15*, 2567.

[4] Schmidbaur, H.; Scharf, W.; Füller, H.-J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1977**, *32B*, 858.

[5] Scharf, W.; Neugebauer, D.; Schubert, U.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 601.

[6] To our knowledge this is a unique example of a compound containing both a phosphonium dimethylide and a hydride as ligands. A phosphonium ylide hydride complex has been reported: Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1121.

[7] (a) Yoshifuji, M.; Gell, K. I.; Schwartz, J. *J. Organomet. Chem.* **1978**, *153*, C15. (b) Gell, K. I.; Schwartz, J. *Ibid.* **1978**, *162*, C11. (c) Gell, K. I.; Schwartz, J. *J. Chem. Soc., Chem. Commun.* **1979**, 244. (d) Gell, K. I.; Schwartz, J., unpublished results.

[8] Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1978**, *100*, 3246.

[9] Bent sandwich phosphine complexes ($Cp_2M(L)X$, L = phosphine) normally show phosphorus coupling to the protons of the Cp ligands, with $^3J_{PH} \simeq 2$ Hz. For example, see: Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1324, and ref 7c.

[10] Hydride ligands in monomeric Zr complexes resonate in this region: Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 2716. In contrast, resonances of bridging hydride ligands are normally found at higher field, usually between $\delta$ 0 and −2.5. For example, see: Weigold, H.; Bell, A. P.; Willing, R. I. *J. Organomet. Chem.* **1974**, *73*, C23, and ref 8.

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**Table I.** $^1$H NMR (100 MHz), $^{13}$C NMR, and $^{31}$P NMR Data for Complexes **7**–**9**[a]

| | assignt | chem shift, $\delta$ | multiplicity | intens | $J$, Hz |
|---|---|---|---|---|---|
| **7** $^1$H | Cp | 5.58 | s | 10 | |
| | ZrH | 3.82 | d of t | 1 | $^3J_{PH} = 42$<br>$^3J_{HH} = 2^b$ |
| | PMe | 0.88 | d | 6 | $^2J_{PH} = 12$ |
| | PCH$_2$ ($\alpha$) | −0.42 | m | 2 | $^2J_{PH} = 5.6^d$<br>$^3J_{HH} = 2^c$ |
| | PCH$_2$ ($\beta$) | −0.65 | d | 2 | $^2J_{PH} = 13$ |
| $^1$H{$^{31}$P}[e] | 3 singlets | | | | |
| | | 3.82 (t, $^3J_{HH} = 2$ Hz), −0.42 (d, $^3J_{HH} = 2$ Hz) | | | |
| $^{13}$C{$^1$H}[f] | Cp | 102.13 | s | | |
| | PMe | 21.48 | d | | $^1J_{PC} = 30.9$ |
| | PCH$_2$ | −9.07 | d | | $^1J_{PC} = 41.0$ |
| | PCH$_2$ | −13.14 | d | | $^1J_{PC} = 43.6$ |
| $^{31}$P{$^1$H}[g] | | 29.8 | s | | |
| **8** $^1$H[h] | Cp | 5.76 | s | 10 | |
| | PMe | 0.74 | d | 6 | $^2J_{PH} = 12$ |
| | PCH$_2$ | 0.09 | d | 2 | $^2J_{PH} = 6.6$ |
| | PCH$_2$ | −0.68 | d | 2 | $^2J_{PH} = 13$ |
| $^1$H{$^{31}$P} | 4 singlets | | | | |
| $^{13}$C{$^1$H}[i] | Cp | 110.55 | s | | |
| | PMe | −22 | *l* | | |
| | PCH$_2$ | 0.61 | d | | $^1J_{PC} = 47.1$ |
| | PCH$_2$ | −2.90 | d | | $^1J_{PC} = 43.3$ |
| **9** $^1$H | Cp | 5.97 | s | 10 | |
| | PCH | 5.52 | d | 1 | $^2J_{PH} = 10$ |
| | PMe | 0.92 | d | 9 | $^2J_{PH} = 12$ |
| $^1$H{$^{31}$P} | 3 singlets | | | | |
| $^{13}$C{$^1$H}[j] | PCH | 122.62 | d | | $^1J_{PC} = 29.2$ |
| | Cp | 108.27 | s | | |
| | PMe | 17.62 | d | | $^1J_{PC} = 55.3$ |
| $^{31}$P | | 0.25 | d of 10 lines | | $^2J_{PH}$(methine) = 10<br>$^2J_{PH}$(methyl) = 12 |
| $^{31}$P{$^1$H} at Me group | | 0.25 | d | | $^2J_{PH} = 5.7^k$ |
| $^{31}$P{$^1$H} at CH group | | 0.25 | 6 lines of a 10-line pattern | | $^2J_{PH} = 7.5^k$ |

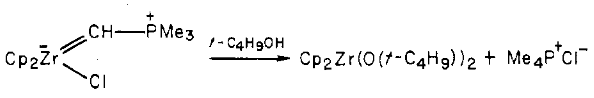
[a] The NMR solvent is toluene-$d_8$ unless otherwise stated. [b] Confirmed by single-frequency $^1$H decoupling at $\delta$ −0.42. [c] Confirmed by single-frequency $^1$H decoupling at $\delta$ 3.82. [d] On single-frequency $^1$H decoupling at $\delta$ 3.82, this multiplet becomes a doublet from which $^2J_{PH}$ is measured. [e] Decoupling at $^{31}$P $\delta$ 29.8. [f] Benzene-$d_6$ (15 °C). [g] Benzene-$d_6$. [h] 0 °C. [i] −8 °C. [j] In 1,2-dimethoxyethane (DME), using chloroform-$d$ (concentric tube) as a locking solvent. [k] $J_{residual}$. [l] Obscured by toluene-$d_8$.

phorus are equivalent, the two methylene groups are inequivalent at room temperature, and no equivalencing process is detected by variable-temperature $^1$H NMR spectroscopy up to a maximum of 85 °C, where thermal decomposition of **7** is rapid. Selective proton decoupling establishes that the downfield methylene group is more strongly coupled to the hydride on Zr than is the other methylene group. Irradiation at the unique phosphorus ($\delta$ 29.8) collapses the $^1$H NMR spectrum as required by these structural assignments. The $^{13}$C NMR spectrum shows a Cp resonance at relatively high field ($\delta$ 102) for a Zr(IV) complex and two inequivalent methylene carbons of the phosphonium dimethylide ligand at extremely high field ($\delta$ −9.07, −13.64).

A white chloride complex **8** forms in quantitative yield on treatment of **7** with methyl chloride (reaction 2). Methane

$$\underset{\mathbf{7}}{Cp_2Zr[(CH_2)_2PMe_2]H} \xrightarrow{CH_3Cl} \underset{\mathbf{8}}{Cp_2Zr[(CH_2)_2PMe_2]Cl} + CH_4 \quad (2)$$

(1 equiv) is evolved, verifying that **7** is a reactive metal hydride species.[12] Although the NMR spectral properties of **8** and **7** are analogous at 0 °C, **8** is fluxional and the methylene groups on phosphorus equivalence at approximately 50 °C ($\Delta G_c^{\ddagger} \approx 15.5$ kcal mol$^{-1}$).[13] At this temperature decomposition of **8** is rapid, and a smooth rearrangement to a bright yellow isomeric species **9** is complete in 12 h. Complex **9** reacts instantly and quantitatively with *tert*-butyl alcohol (2 equiv), producing $Cp_2Zr(O(t\text{-}Bu))_2$ and tetramethylphosphonium chloride (reaction 3).



**9**

(3)

The $^1$H NMR spectrum of **9** is temperature independent (−55 to +35 °C), showing three equivalent methyl groups bound to phosphorus and a unique downfield proton coupled to phosphorus. The $^{13}$C{$^1$H} NMR spectrum shows a Cp group and two chemically inequivalent carbons bound to phosphorus. These spectral data and the products of the reaction of **9** with *tert*-butyl alcohol suggest that **9** contains a CHPMe$_3$ group. This is confirmed by the $^{31}$P NMR spectrum, a doublet of 10-line patterns at $\delta$ 0.25, which collapses on selective $^1$H irradiation at each of the two proton resonances as required by the CHPMe$_3$ formulation.

The reactions of the ylide complexes **7** and **8** with carbonyl compounds have been briefly investigated. Both of these complexes transfer one of their methylene groups to ketones (acetone, cyclohexanone), producing the corresponding olefin;

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(11) Monomeric zirconium hydride complexes usually show a strong band between 1500 and 1600 cm$^{-1}$ [10] whereas some hydride-bridged dimers (e.g., **6a**) absorb at lower frequencies (1380 cm$^{-1}$).[8,10] However, a strong Zr–H band is reported at 1590 cm$^{-1}$ in the hydride-bridged dimer [{Cp$_2$Zr[CH(SiMe$_3$)$_2$]($\mu$-H)}$_2$]: Jeffrey, J.; Lappert, M. F.; Luong-Thi, N. T.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1978**, 1081.

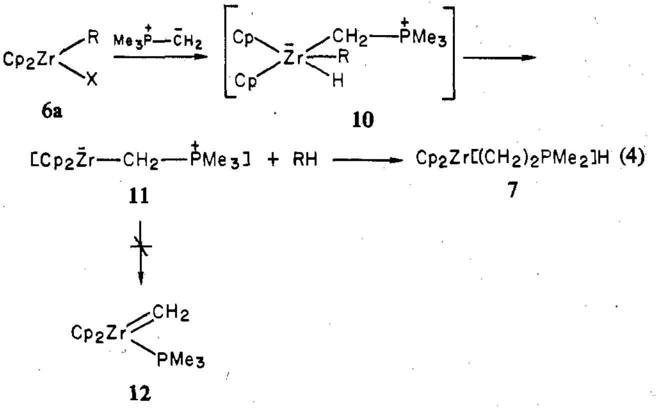
(12) Schunn, R. A. *Transition Met. Hydrides* **1971**, Chapter 5.

(13) $\Delta G_c^{\ddagger}$ = free energy of activation at the coalescence temperature calculated from $k_c = \pi(\Delta\nu)/2^{1/2}$, where $\Delta\nu$ is the line spearation in the absence of exchange: Pople, J. A.; Schneider, W. G.; Bernstein, H. J. "High-Resolution Nuclear Magnetic Resonance"; McGraw-Hill: New York, 1959.

for **7**, some trimethylphosphine oxide is also produced. The Zr-containing product of these reactions has not been characterized. Compounds **7** and **8** are decomposed by ethyl acetate; however, the methylene-transfer product, 2-ethoxypropene, is not formed (see Table I).

## Discussion

A plausible route to the zirconium(IV) ylide hydride species **7** is suggested in reaction 4. In the first step of this reaction



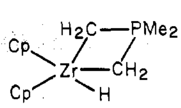
$R = CH_2(CH_2)_4CHCH_2$

[ ] = proposed intermediates

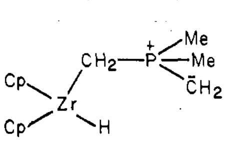
the strong nucleophile,[14] $Me_3PCH_2$, attacks the unsaturated zirconium(IV) alkyl hydride **6a**, producing an unstable 18-electron Zr(IV) species **10** which collapses to a Zr(II) intermediate **11** by reductive elimination of methylcyclohexane. The specific deuterium incorporation in the methylcyclohexane formed in the reaction of **6b** with $Me_3PCH_2$ is good evidence for this initial reductive elimination step, and we have observed similar reactions for several other donor ligands.[7] The labeling experiment using **6b** in benzene-$d_6$ shows indirectly that the hydride ligand in **7** is derived from $Me_3PCH_2$.[15] We suggest that **7** is generated from the unsaturated intermediate **11** by an insertion of Zr(II) into the C–H bond of a methyl group on phosphorus. Although we have not studied the reactions of zirconium(II) bis(phosphine) complexes, $Cp_2ZrL_2$ (L = mono(tertiary phosphine)) with activated sp$^3$ C–H bonds, we have observed[7c,d] that these complexes insert into sp$^2$ C–H bonds, presumably via the 16-electron complex $Cp_2ZrL$, an analogue of **11**.[16]

The zirconium(II)–methylene complex **12**, an isomer of **11**, is not a stable product of the reaction of **6a** with $Me_3PCH_2$ nor is it detected by $^1H$ NMR during the reaction.[17] Irreversible metalation of the phosphorus methyl group to give **7** may be rapid compared with the rearrangement of **11** to **12**, or, alternatively, this rearrangement may be reversible.

The ligand **2** is found in a symmetric environment in all of its complexes which have been previously described. For this reason, **7** is unusual. The phosphorus methylene groups of **2** are diastereotopic, clearly indicating that this ligand is bound unsymmetrically to the Zr(IV) center. From the spectral data, **7** is apparently monomeric.[18] Two extreme representations (**13**, **14**) satisfy the requirement of an unsymmetrically bound dimethylide ligand **2**. Instead of the coordinatively unsaturated structure **14**, we favor a chelating structure resembling **13**, in which there is at least some donation by the second methylene



**13**

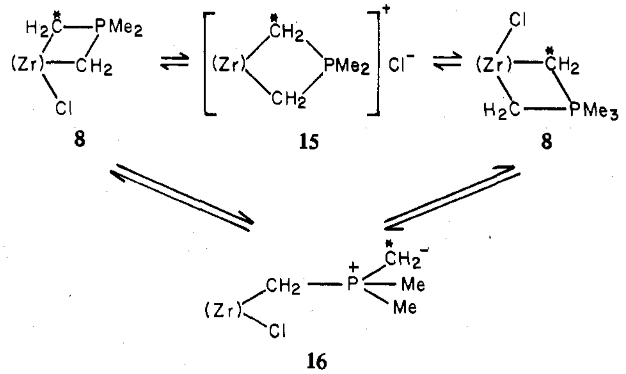


**14**

group on phosphorus into the vacant site on Zr.[19] (An analogy is suggested between the bonding in **13** and that in [$Cp_2Zr(BH_4)H$], with electron delocalization in the chelating ligand.[20]) NMR spectral data support this structural assignment: the methylene groups on phosphorus show similar one-bond carbon–phosphorus coupling ($^1J_{PC}$), a reasonable indication of similar hybridization and substitution of the methylene groups.[21,22]

The similarity of their NMR spectral data suggests that **7** and the chloride complex **8** have analogous structures, but **7** is stereochemically rigid within an accessible temperature range, whereas **8** is fluxional. Several mechanisms can equivalence the methylene groups in a structure analogous to **13**. A mechanism (Scheme I) involving the symmetrical intermediate **15** could account for a faster equivalencing of the methylene groups in **8** compared with those in **7** because chloride is a better leaving group than hydride. However, this ionic pathway is unlikely in the nonpolar reaction solvent, benzene. Dissociation of a methylene group from Zr(IV) to give **16**, followed by rotation and recombination, is the probable means of equivalencing the methylene groups of **8** (Scheme I). An important difference between **7** and **8** is that

Scheme I



(Zr) = $Cp_2Zr$

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(14) Harnisch, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 468.

(15) The Cp ligands are the only other source of proton. No net attack on these ligands occurs in the reaction.

(16) Insertion into sp$^2$ (and some sp$^3$) C–H bonds is a general property of 16-electron, low-valent metallocene intermediates: Parshall, G. W. *Catalysis* **1977**, *1*, 335 and references therein.

(17) A zirconium(II) methylenephosphine complex has been prepared by using methylenetriphenylphosphorane: Gell, K. I.; Schwartz, J. *J. Organomet. Chem.* **1980**, *184*, C1.

(18) The cryoscopic molecular weight of **7** has not been determined. However, $^1H$ NMR evidence establishes conclusively that the hydride ligand is terminal rather than bridging. A dimeric structure containing bridging units (such as in **4**) is discounted because the hydride ligand is coupled to only *one* phosphorus.

(19) The three available ligand binding orbitals lie in the plane bisecting the angle between the normals to the Cp rings. For a discussion of bonding in $Cp_2MX_3$ complexes and leading references to earlier work see: Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

(20) The analogy between the bonding of $BH_4^-$ and $\pi$-allyl has been developed: Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263, and ref 19. In a Ni(II) dimer the tilted bridging arrangement of **2** has been interpreted as a pseudophosphaallyl structure, with some electron donation into a nonbonding molecular orbital: Brauer, D. J.; Krüger, C.; Roberts, P. J.; Tsay, Y.-H. *Chem. Ber.* **1974**, *107*, 3706.

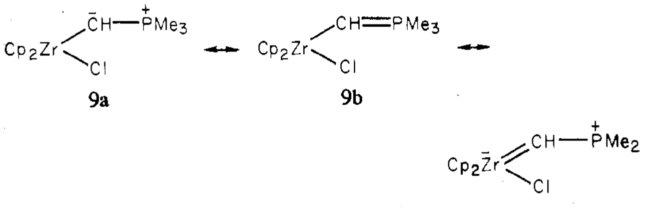
(21) $^1J_{PC}$ has been successfully related to the percentage of s character in the carbon hybrid orbital comprising the P–C bond in a variety of tervalent phosphorus compounds. It depends also on the hybridization, stereochemistry, and substitution at phosphorus and at carbon: (a) Mavel, G. *Annu. Rep. NMR Spectrosc.* **1973**, *5B*. (b) Albright, T. A.; Gordon, M. D.; Freeman, W. J.; Schweizer, E. E. *J. Am. Chem. Soc.* **1976**, *98*, 6249. (c) Llinas, J.-R.; Vincent, É.-J.; Pfeiffer, G. *Bull. Soc. Chim. Fr.* **1973**, 3209.

(22) The downfield methylene group, $CH_2(\alpha)$, is coupled to the hydride on Zr ($^2J_{HH} \simeq 2$ Hz), but the upfield methylene, $CH_2(\beta)$, shows no detectable coupling to the hydride. However, this does not imply that $CH_2(\beta)$ is a free methylene group as in structure **14**.[23] In a formally analogous structure the outer (downfield) protons ($H_a$) of the $\eta^2$-ethylene ligand are coupled ($^3J_{PH} \simeq 2$ Hz) to the hydride ligand, but no coupling of the inner protons ($H_b$) to the hydride is observed.[24]

the chloride ligand in **8** has an electron pair which can be donated (in a formal d$\pi$–p$\pi$ sense) to the Zr(IV) center and may promote dissociation of the methylene ligand.

Rendering the methylene groups of **8** equivalent and the facile isomerization of this complex to give **9** could be competitive processes proceeding from a common intermediate **16**. An intra- (or inter-) molecular transylidation,[1,25] in which the free methylene group in **16** deprotonates the Zr(IV)-bound methylene group, isomerizes **8** to **9**.

The bonding of the $CHPMe_3$ group in the rearrangement product **9** can be represented by two basic resonance structures: a metalated phosphorane (**9a** or **9b**) or a phosphorus-substituted carbene ligand **9c**. The predominance of a metalated phosphorane structure is suggested by the chemical shift of the methine carbon ($\delta$ 122.6) which is far upfield of the normal range for carbene ligands[26] and by the $^{31}P$ resonance at $\delta$ 0.25 which is typical of an ylide rather than a phosphonium phosphorus.[27]



**9c**

Our preliminary work does not fully define the role of **7** and **8** as methylene-transfer reagents. Both **7** and **8** react with ketones to give the expected olefin, but salt-free $Me_3PCH_2$ also performs this reaction.[28] The rate of methylene transfer from $Me_3PCH_2$, **8**, and **9** to ketones has not been determined. A comparison of these data should indicate whether the Zr(IV) center in **8** and **9** participates in the transfer reaction, perhaps by polarization of the carbonyl group of the ketone substrate.

## Experimental Section

**General Procedures and Techniques.** Reactions were performed under purified argon, by using standard Schlenk techniques,[29] on a high-vacuum line or in a nitrogen-filled Vacuum Atmospheres Corp. drybox.

Solvents were distilled from sodium benzophenone ketyl under nitrogen. Nuclear magnetic resonance (NMR) solvents (benzene-$d_6$, toluene-$d_8$) were vacuum distilled from lithium aluminum hydride. *tert*-Butyl alcohol was distilled from sodium *tert*-butoxide. Methyl chloride was obtained from Matheson Gas Co. (Cyclohexylmethyl)bis($\eta^5$-cyclopentadienyl)hydridozirconium(IV) and the corresponding deuteride were prepared as previously described[8] and were used without purification. The preparation of $Cp_2Zr(dmpe)$ [dmpe = bis(1,2-dimethylphosphino)ethane] has also been described.[7c] Trimethylmethylenephosphorane ($Me_3PCH_2$) was prepared from tetramethylphosphonium bromide and sodium amide by a literature method.[30]

Proton, $^{13}C$, and $^{31}P$ NMR spectra were recorded on a Varian XL-100 spectrometer. Temperatures were measured with a calibrated thermocouple situated at the coil. Proton NMR (90 MHz) spectra were recorded on a Perkin-Elmer R32 spectrometer; 60-MHz $^1H$ NMR spectra were recorded by using a Varian A-60 or A-60A instrument. Chemical shifts ($^1H$, $^{13}C$ NMR) are referenced to tetramethylsilane, are calculated from the position of solvent absorption, and are reported in ppm. Phosphorus chemical shifts ($\delta$) are referenced to external $H_3PO_4$ (85%) and are positive to low field.

Infrared (IR) spectra were obtained on a Perkin-Elmer PE-283 spectrometer; pellets were prepared in the drybox by using KBr which had been dried at 120 °C for 24 h under high vacuum. Gas chromatographic/mass spectral (GC/MS) analysis was performed by using a Du Pont 21-490 GC mass spectrometer. Gas chromatographic (GC) analysis for hydrogen was performed on a Perkin-Elmer PE-3920 thermal conductivity instrument using argon as a carrier gas. Other GC analyses were carried out on a Hewlett-Packard 402 instrument equipped with flame ionization detector.

Elemental analyses were performed by Alfred Bernhardt, Müllheim, West Germany, using drybox sampling techniques.

**Preparation of $Cp_2Zr[(CH_2)_2PMe_2]H$ (7).** (a) Trimethylmethylenephosphorane (0.14 mL, 1.6 mmol) was added dropwise to a stirred solution of **6a** (0.5 g, 1.5 mmol) in toluene (25 mL) at −20 °C. The yellow solution was warmed to room temperature and stirred for 20 min. It slowly darkened to brown-yellow. The solvent volume was reduced to approximately 5 mL, and green crystals of **7** (0.33 g, 75%) formed, which were filtered off, washed with hexane, dried, and stored at −30 °C under nitrogen. This compound is thermally unstable in solution and does not react with $Me_3PCH_2$. An analysis sample was obtained by recrystallization from toluene (−30 °C).

Anal. Calcd for $C_{14}H_{21}PZr$: C, 53.98; H, 6.80. Found: C, 53.67; H, 6.63.

IR (KBr): 3120, 3060 (m), 2980, 2965, 2920, 1465 (m, br), 1440, 1345, 1295, 1285 (m), 1020 (s), 995 (sm), 940 (sm), 800 (vs, br), 740, 670 cm$^{-1}$.

NMR ($^1H$, $^{13}C$, $^{31}P$) details are recorded in Table I.

(b) An analogous reaction was performed by using **6b** in benzene-$d_6$. The methylcyclohexane (80%) produced in the reaction was analyzed by GC/MS (Carbowax 20 M, 20 ft × 0.125 in., 50 °C) and its composition was 2% for $d_0$, 9% for $d_1$, and 89% for $d_2$, where the $d_1$ compound is a mixture of methylcyclohexane-*1-d* and methylcyclohexane-$\alpha$-*d* and $d_2$ is methylcyclohexane-*1*,$\alpha$-$d_2$.

No deuterium from **6b** or from the solvent was incorporated into the inorganic product **7** ($^1H$ NMR determination).

(c) A mixture of $Cp_2Zr(dmpe)$ (10 mg) and $Me_3PCH_2$ (1 equiv) in benzene-$d_6$ (0.3 mL) was sealed under vacuum in an NMR tube (5 mm). No reaction occurred over 4 h at room temperature. The tube was then heated at 55 °C. Free dmpe formed slowly and the inorganic product was identified as **7** (10% on the basis of Zr in 36 h).

**Preparation of $Cp_2Zr[(CH_2)_2PMe_2]Cl$ (8).** (a) Methyl chloride (0.47 mmol) was distilled through a −30 °C trap and condensed into a degassed (three freeze–thaw cycles) solution of **7** (0.14 g, 0.45 mmol) in toluene (8 mL). The vessel was sealed, and the mixture was warmed to 0 °C when gas evolution was observed. The solution was stirred at 0 °C for 1 h and 15 min and then at room temperature for 20 min. A white crystalline compound precipitated from the yellow solution.

The noncondensable gases formed in the reaction were collected via a Toepler pump and consisted solely of methane (GC identification, Porapak QS, 8 ft × 0.25 in., 135 °C) in 80% yield (on the basis of **7**). Only a trace of methyl chloride was detected in the condensable gases.

The solvent was reduced in volume to 3 mL, and the mixture was cooled (−30 °C). The white solid, **8** (0.12 g, 76%), was filtered off, washed with hexane, dried, and stored at −30 °C under nitrogen. An analysis sample was obtained by recrystallization from toluene (−30 °C). The compound **8** is thermally unstable in solution (20% decomposed in 4 h at room temperature).

(b) Reaction of **7** with excess methylene chloride (10 equiv) produced **8** and methyl chloride (1 equiv on the basis of **7**). However, the first method usually gave a purer product.

Anal. Calcd for $C_{14}H_{20}ClPZr$: C, 48.60; H, 5.83; Cl, 10.25. Found: C, 48.46; H, 5.81; Cl, 10.30.

IR (KBr): 3080, 2975 (m), 2905, 1440 (m), 1420 (m), 1370, 1340,

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(23) $^2J_{PH}$ is very different for each of the methylene groups $CH_2(\alpha)$ and $CH_2(\beta)$. The coupling of phosphorus to the downfield methylene group $CH_2(\alpha)$ ($^2J_{PH}$ = 5.6 Hz) is much smaller than its coupling to the upfield group, $CH_2(\beta)$ ($^2J_{PH}$ = 13 Hz). In phosphines, $^2J_{PH}$ is dependent not only on hybridization at carbon but also on the dihedral angle between the C–H bond and the lone pair on phosphorus.[21a] Similarly, in compounds containing the P═X unit, the relative orientation of the C–H bond and the P═X bond is important.[21a] It is not obvious how to apply these concepts to the tetravalent phosphorus in **7**, except to note that electronic factors, perhaps arising from the inequivalence of the metal orbitals at which the methylenes are bound, or perhaps from the orientation of the methylene groups, may affect the magnitude of $^2J_{PH}$ differently for $CH_2(\alpha)$ and $CH_2(\beta)$.

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1305 (s), 1285, 1265, 1015 (m), 990 (vs), 950 (s), 815 (vs, br), 740 (m), 680 cm$^{-1}$.

NMR ($^1$H, $^{13}$C) details are recorded in Table I.

**Preparation of $Cp_2Zr(CHPMe_3)Cl$ (9).** A solution of **8** (0.2 g, 0.58 mmol) in toluene (35 mL) was heated (65–70 °C) in a sealed tube under nitrogen. The initially colorless solution rapidly turned dark yellow and remained homogeneous. After 14 h, the rearrangement to **9**, the sole product, was complete (by $^1$H NMR). The mixture was cooled to room temperature, filtered, reduced to a small volume, and refrigerated (−30 °C). Small yellow plates of **9** were filtered off, washed with hexane, and stored under nitrogen. An analysis sample was obtained by recrystallization from toluene.

Anal. Calcd for $C_{14}H_{20}ClPZr$: C, 48.60; H, 5.83; Cl, 10.25. Found: C, 48.46; H, 5.86; Cl, 10.39.

IR (KBr): 3080, 2975 (m), 2905, 1440 (m), 1420 (m), 1370, 1340, 1305 (s), 1285, 1265, 1015 (m), 990 (vs), 950 (s), 815 (vs, br), 740 (m), 680 cm$^{-1}$.

NMR ($^1$H, $^{13}$C, $^{31}$P) details are recorded in Table I.

**Reaction of $Cp_2Zr(CHPMe_3)Cl$ (9) with *tert*-Butyl Alcohol.** A solution of **9** (60 mg, 0.19 mmol) in toluene (12 mL) was sealed under nitrogen in a small tube (total volume 25 mL), fitted with a stopcock, side arm, and serum cap. *tert*-Butyl alcohol (29.6 mg, 0.4 mmol, 2.1 equiv) was added via a syringe. A white compound precipitated immediately from the yellow solution, which was stirred for 1 h at room temperature. The atmosphere in the reaction vessel was sampled by using an argon-flushed 0.25-mL gastight syringe. No hydrogen was detected by GC (Porapak QS, 20 ft × 0.125 in., 30 °C, nitrogen internal standard). The reaction mixture was filtered, and the white precipitate was washed with hexane. It was identified [$^1$H NMR ($D_2O$) $\delta$ 1.85 (d, PMe, $^2J_{PH}$ = 14.8 Hz); mp >300 °C] as tetramethylphosphonium chloride.[28] The filtrate was pumped down to give a cream solid, which was identified [$^1$H NMR comparison with an authentic sample prepared by reaction of $Cp_2ZrCl_2$ with sodium *tert*-butoxide (2 equiv) in diethyl ether: $^1$H NMR (benzene-$d_6$) $\delta$ 6.01 (s, 10, Cp), 1.13 (s, 18, Me)] as $Cp_2Zr(O(t\text{-}Bu))_2$ (98% yield by $^1$H NMR). A minor reaction product [$^1$H NMR (benzene-$d_6$) $\delta$ 1.23 (s), 1.04 (s)] was not identified.

**Reaction of 7 with Ketones.** The concentration of a solution of **7** in benzene-$d_6$ was determined ($^1$H NMR, DME internal standard) as 38 mM.

**(a) Cyclohexanone.** Cyclohexanone (12 $\mu$L, 0.11 mmol) was added to 1 mL of this solution (0.038 mmol of **7**) with stirring. The color rapidly changed from dark brown-green to yellow, and an oily solid precipitated. After 30 min, the reaction was complete (by $^1$H NMR). Methylenecyclohexane (GC identification, Carbowax 20 M, 20 ft × 0.25 in., 50 °C) was formed in 85% yield together wiith trimethylphosphine oxide (50%). Traces of cyclohexanone and some cyclohexanol were present in the hydrolysate of the reaction mixture (GC analysis, DEGS, 8 ft × 0.25 in., 110 °C).

**(b) Acetone.** In a similar manner reaction of **9** with excess acetone gave trimethylphosphine oxide (70%) and 2-methylpropene (75% by $^1$H NMR), which was identified by GC/MS (Porapak Q, 6 ft × 0.125 in., 140 °C). A white precipitate was not identified.

**Reaction of 8 with Cyclohexanone.** Cyclohexanone (10 $\mu$L, 0.1 mmol) was added to a colorless solution of **8** (0.034 mmol) in toluene-$d_8$ (1 mL). The mixture darkened to yellow (5 min), then lightened, and precipitated a solid (not identified). After 3 h, methylenecyclohexane (GC identification, Carbowax 20 M, 20 ft × 0.25 in., 50 °C) was present in 76% yield ($^1$H NMR).

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**Registry No.** **6a**, 69058-71-5; **6b**, 67660-04-2; **7**, 74592-17-9; **8**, 74592-18-0; **9**, 74592-19-1; $Cp_2Zr(dmpe)$, 71844-74-1; $Cp_2Zr(O(t\text{-}Bu))_2$, 74592-20-4; $Me_3PCH_2$, 14580-91-7; cyclohexanone, 108-94-1; acetone, 67-64-1; methylenecyclohexane, 1192-37-6; trimethylphosphine oxide, 676-96-0; 2-methylpropene, 115-11-7.

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# Reactions of the Vanadyl Group: Synthesis of $V{=}S^{2+}$ and $VBr_2^{2+}$ from $V{=}O^{2+}$ Complexes

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The vanadyl ion–Schiff base complexes V=O(salen) and V=O(acen) react with $B_2S_3$ to afford V=S(salen) and V=S(acen), the first known thiovanadyl compounds. The V=S stretching vibration appears in the 550-cm$^{-1}$ region, and its stretching force constant is substantially less than $k_{V=O}$ in the corresponding vanadyl complexes. The thiovanadyl compounds are relatively stable to air in the solid state, but their solutions are hydrolyzed to the starting vanadyl species. ESR spectra of the thiovanadyl complexes are characteristic of monomeric, axially symmetric V(IV) and show much less **g** tensor anisotropy than their vanadyl analogues; the decrease is primarily located in $g_\perp$. These data are consistent with reduced charge at the vanadium in the $V{=}S^{2+}$ species and more covalent character of the V=S bond than in V=O. V=O(salen) reacts with $Ph_3PBr_2$ to afford the deoxygenated product $VBr_2$(salen) and $Ph_3P{=}O$, while other vanadyl complexes afford $V{=}OBr_2(Ph_3P{=}O)_2$.

## Introduction

The vanadyl ion, $V{=}O^{2+}$, is ubiquitous in vanadium chemistry. The deep blue or green color of its complexes is well-known to all those who have studied the chemistry of this element, and $V{=}O^{2+}$ has been described as "perhaps the most stable diatomic cation known."[1] Numerous complexes of V(IV) have been prepared and studied, but in almost every instance the $V{=}O^{2+}$ group was present. Italian workers have shown, however, that certain vanadyl complexes $V{=}OL_n$ react with $SOCl_2$ to form $SO_2$ and $VCl_2L_n$.[2] We have discovered a synthetic route to the previously unknown thiovanadyl species, $V{=}SL_n$, which involves reaction of $V{=}OL_n$ complexes with $B_2S_3$, and report the details of the preparation and characterization here. A preliminary account of this work has already appeared.[3] We have also studied the reactions of

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