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Notes

Trapping Intermediates in Phosphavinyl Coupling Reactions: Synthesis and Structural Characterization of a Novel Bis(phosphinoalkylidene)−Tantalum Complex, [{Cp*TaCl$_2$[=C(Bu^t)−P(Cy)−]}$_2$]

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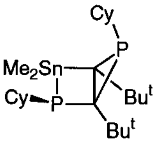
*Summary: The reactions of the stable phosphavinyl Grignard reagent (Z)-[MgCl(OEt$_2$){C(Bu^t)=PCy}] with [Cp*TaCl$_4$] or [Cp*NbCl$_4$] have been investigated. In both cases phosphavinyl coupling reactions are the ultimate outcome to give the known 2,4-diphosphabicyclo-[1.1.0]butane, Cy$_2$P$_2$C$_2$Bu$^t_2$, in the former and a mixture of this compound and its 1,2-dihydro-1,2-diphosphete valence isomer in the latter. A novel bis(phosphinoalkylidene)−tantalum complex, [{Cp*TaCl$_2$[=C(Bu^t)−P(Cy)−]}$_2$], has been isolated and structurally characterized as an intermediate in the tantalum reaction.*

Introduction

Vinyl Grignard reagents have been widely utilized in organic and organometallic synthesis.[1] We have recently developed a high-yielding synthetic route to a range of stable phosphavinyl Grignard reagents, e.g., (*Z*)-[MgCl(OEt$_2$){C(Bu^t)=PCy}], **1**, Cy = cyclohexyl,[2] which we saw as having a potentially similar synthetic utility to their hydrocarbon counterparts given the well-documented analogy between P and the valence isoelectronic CR fragment.[3] To date we have investigated this analogy by looking at the use of **1** in methathesis reactions with main group halide complexes. These reactions sometimes lead to the expected phosphavinyl complexes, e.g., [Me$_2$Sn{−C(Bu^t)=PCy}$_2$][4] or [CyIn{−C(Bu^t)=PCy}],[5] but more often than not the high reactivity of the phosphavinyl fragment leads to facile coupling reactions and the formation of strained metallocage and heterocyclic compounds, e.g., **2**[4] and **3**.[5] In addition, elimination of the main group metal can occur, as in the oxidative coupling reaction of **1** with PbCl$_2$, which gives the unusual diphosphabicyclo[1.1.0]butane compound **4**.[6]



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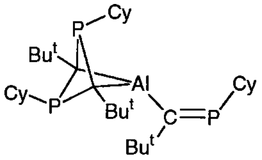

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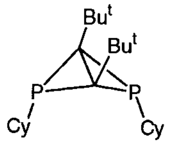

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Given our success with main group metals, we have extended this work to explore the possibility of forming transition metal phosphavinyl complexes and investigating their reactivity. Organo-group 5 metal complexes are of particular interest as precursors in these reactions because of their well-known ability to oligomerize and polymerize unsaturated hydrocarbons, either stoichiometrically or catalytically.[7] In addition, the metal centers in organo-group 5 complexes can exist in a number of oxidation states, which lends them to the coupling of phosphavinyl fragments via red-ox processes. Herein we discuss two such coupling reactions and in one case describe the trapping of a novel intermediate.

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(1) *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 11.

(2) Hibbs, D. E.; Jones, C.; Richards, A. F. *J. Chem. Soc., Dalton Trans.* **1999**, 3531.

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(5) Jones, C.; Richards, A. F. *J. Organomet. Chem.*, in press.

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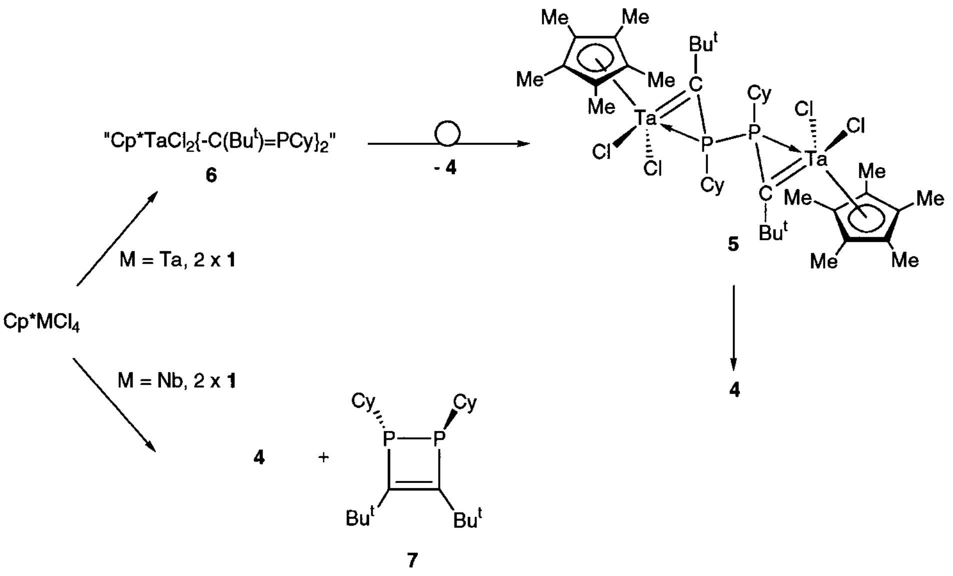
Scheme 1



Results and Discussion

Treatment of a toluene suspension of [Cp*$TaCl_4$] with 2 equiv of **1** at −78 °C gave a deep blue-green solution which changed to a brown color on warming to room temperature and stirring overnight (Scheme 1). When the reaction was followed by ^{31}P NMR, two major peaks of almost equal intensity were initially seen at 12 and −6 ppm, the latter of which diminished as the solution became brown, while the former grew in intensity. Workup of this brown solution led to a moderate yield of the known diphosphabicyclobutane **4**, which accounts for the peak at 12 ppm. Interestingly, when [Cp*$TaCl_4$] was treated with 4 equiv of **1**, the reaction followed the same course, but a significant amount of unreacted **1** remained in the reaction mixture. It seemed that in the 2:1 reaction the peak at −6 ppm probably arose from an intermediate, and thus efforts were made to isolate this from the solution before it converted to **4**. Accordingly, placing the reaction solution at −30 °C without allowing it to warm to room temperature effected crystallization of the dimeric phosphinoalkylidene−tantalum complex, **5**, in moderate yield.

This blue-green compound is thermally stable in the solid state. Surprisingly, it proved difficult to redissolve in most solvents, although some success was had with THF-d_8. In this solvent it rapidly decomposed at room temperature and more slowly so at −50 °C to yield a product mixture, the main component of which was **4**. With regards to a mechanism of formation for **5**, it seems likely that the bis(phosphavinyl)tantalum compound **6** is the initial product. This then rapidly undergoes an intermolecular oxidative coupling reaction to give **4**, significant amounts of which were observed in the low-temperature reaction mixture. A series of electronic rearrangements of the expected initial tantalum(IV) product, [Cp*$Ta^{\bullet}Cl_2${−C(Bu^t)=PCy}], then occur to give the tantalum(V)alkylidene radical, [Cp*$TaCl_2${=C(Bu^t)−$P^{\bullet}$Cy], which couples to give **5**. If this is so, the reaction of [Cp*$TaCl_4$] with **1** yields **4** via two different processes. In the second process, i.e., the decomposition of **5**, the $P_2Cy_2C_2Bu^t_2$ fragment is presumably eliminated and rearranges to give **4**. It is possible that the tantalum byproduct in this reductive elimination reaction is the known dimer [{Cp*Ta(III)(μ-Cl)$_2$}$_2$],[8] although this could not be identified or recovered from the product mixture.

The molecular structure of **5** is depicted in Figure 1 (see also Table 1). This shows it to be dimeric and to sit on a crystallographic inversion center. The P−P distance is in the normal region for single bonded interactions

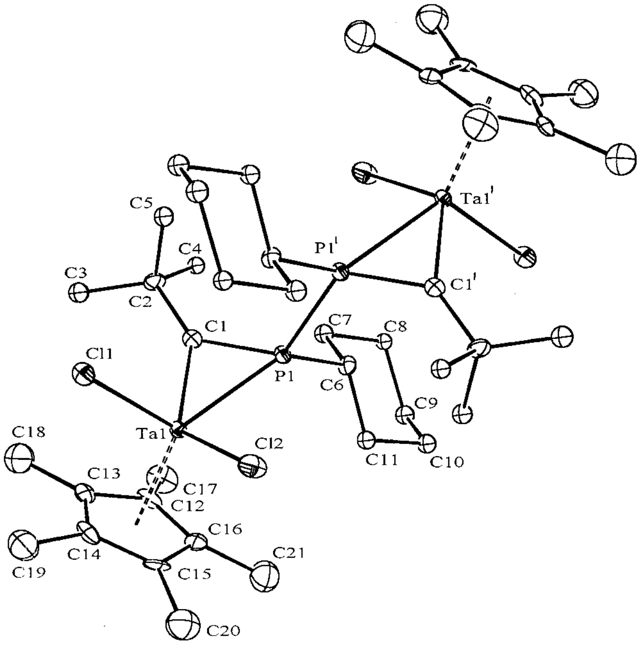


Figure 1. Molecular structure of **5**·C_7H_8 (25% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Ta(1)−C(1) 2.036(12), Ta(1)−Cl(1) 2.351(3), Ta(1)−Cl(2) 2.385(3), Ta(1)−P(1) 2.480(3), P(1)−C(1) 1.748(12), P(1)−P(1)′ 2.298(6), C(1)−Ta(1)−Cl(1) 91.2(3), C(1)−Ta(1)−Cl(2) 124.8(3), Cl(1)−Ta(1)−Cl(2) 93.60(13), C(1)−Ta(1)−P(1) 44.2(3), Cl(1)−Ta(1)−P(1) 117.18(10), Cl(2)−Ta(1)−P(1) 86.32(12), C(1)−P(1)−P(1)′ 116.2(4), C(6)−P(1)−P(1)′ 102.6(4), C(1)−P(1)−Ta(1) 54.3(4), P(1)′−P(1)−Ta(1) 122.74(17), C(2)−C(1)−P(1) 133.6(9), C(2)−C(1)−Ta(1) 144.6(8), P(1)−C(1)−Ta(1) 81.5(5).

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[8] Poli, R. *Chem. Rev.* **1991**, *91*, 509.

Table 1. Summary of Crystallographic Data for Complexes $5\cdot C_7H_8$ and 7

	5	7
formula	$C_{49}H_{78}Cl_4P_2Ta_2$	$C_{22}H_{40}P_2$
M_r	615.37	366.48
a, Å	11.300(2)	9.158(8)
b, Å	13.985(2)	10.539(7)
c, Å	16.372(3)	12.241(8)
α, deg	90	88.33(6)
β, deg	103.35(2)	88.66(6)
γ, deg	90	70.88(5)
V, Å^3	2517.5(7)	1115.7(14)
cryst syst	monoclinic	triclinic
space group	$P2(1)/n$	$P\bar{1}$
λ, Å	0.71073	0.71073
T, K	150(2)	150(2)
Z	2	2
size, mm	0.20 × 0.15 × 0.15	0.40 × 0.20 × 0.20
color	green-blue	colorless
μ, cm^{-1}	46.51	1.97
$F(000)$	1228	404
no. of reflns collected	9334	3911
no. of unique reflns	4557	3634
no. of params varied	243	223
$R\ \{I > 2\sigma(I)\}$	0.0535	0.0514
R_w {all data}	0.1687	0.1934

but significantly longer than the mean (2.211 Å) for all crystallographically determined P−P bond lengths.[9] The Ta(1)−C(1) distance [2.036(12) Å] is short and strongly suggestive of a double bond (cf. the mean Ta═C distance, 1.968 Å).[9] The Ta(1)−P(1) distance is shorter than observed for phosphine complexes of $[Cp^rTaCl_4]$ ($Cp^r = C_5Me_5$, C_5H_4Me), e.g., 2.710(2) Å in $[(C_5H_4Me)TaCl_4\{PH_2(C_6H_2Pr^i_3\text{-}2,4,6\}]$.[10] Interestingly, the P(1)−C(1) distance [1.748(12) Å] lies between the normal values for double and single bonds and suggests a degree of delocalization. In this context it is noteworthy that **5** is related to a series of previously reported phosphinoalkylidene complexes, e.g., $[Cp^*TaH_2\{{=}C(H){-}PMe_2\}(PMe_3)]$,[11] which also display short P−C bonds. As in these cases, the short P−C bond in **5** can be explained by the compound existing as a resonance hybrid of a four-electron λ^3-phosphinocarbene complex and a four-electron λ^5-phosphaalkyne complex.

The analogous reaction of 2 equiv of **1** with $[Cp^*NbCl_4]$ was also carried out, though in this case no compound related to **5** was observed in the reaction mixture. Instead the two major products were **4** and its 1,2-dihydro-1,2-diphosphete valence isomer, **7**, which was identified by a singlet at −52 ppm in the ^{31}P NMR spectrum of the reaction solution. These two compounds were formed in an approximately 35:65 ratio and could not be separated by chromatography and crystallized together from hexane.[12] It is not known why a mixture of isomers is seen in this reaction but not in the tantalum case, but it is noteworthy that 1,2-dihydro-1,2-diphosphetes are theoretically more stable than their 2,4-diphosphabicyclobutane valence isomers.[13]

A single crystal of **7** was manually separated from the crystallized mixture of **4** and **7** and its structure confirmed by its X-ray crystal structure (Figure 2, Table 1), which shows it to contain a four-membered PPCC ring with *trans*-cyclohexyl substituents. The overall geometry of the ring system is unremarkable and similar to that seen in other 1,2-dihydro-1,2-diphosphetes, e.g., $Ph_2P_2C_2Bu^t_2$.[14]

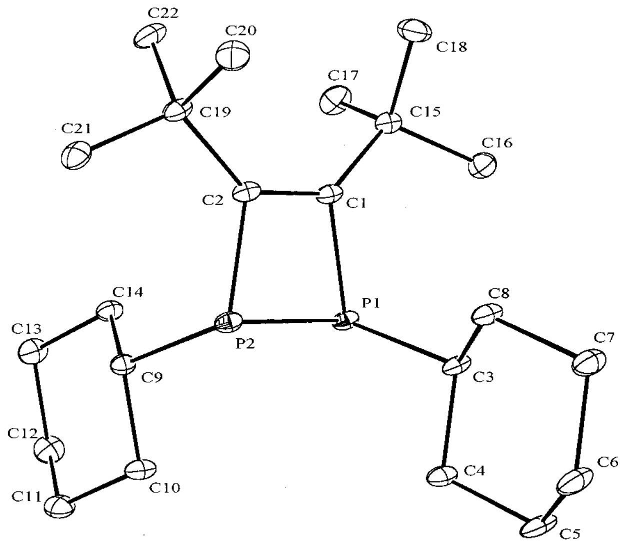

Figure 2. Molecular structure of **7** (25% probability ellipsoids). Selected bond lengths (Å) and angles (deg): P(1)−C(1) 1.849(4), P(1)−C(3) 1.876(4), P(1)−P(2) 2.216(2), P(2)−C(2) 1.853(4), P(2)−C(9) 1.870(4), C(1)−C(2) 1.376(6), C(1)−C(15) 1.514(6), C(2)−C(19) 1.546(5), C(1)−P(1)−C(3) 107.50(17), C(1)−P(1)−P(2) 77.17(15), C(3)−P(1)−P(2) 101.55, C(2)−P(2)−C(9) 107.94(17), C(2)−P(2)−P(1) 76.03(15), C(9)−P(2)−P(1) 102.20(15), C(2)−C(1)−C(15) 136.0(3), C(2)−C(1)−P(1) 101.9(3), C(15)−C(1)−P(1) 121.4(3), C(1)−C(2)−C(19) 135.7(4), C(1)−C(2)−P(2) 103.4(2), C(19)−C(2)−P(2) 120.4(3)

In conclusion, the reactions of the phosphavinyl Grignard reagent, **1**, with $[Cp^*MCl_4]$, M = Ta or Nb, leads to coupling reactions in both cases. In the tantalum reaction a novel intermediate has been isolated and has helped explain the reaction mechanism operating in that case. We are currently systematically investigating the interaction of phosphavinyl Grignard reagents with other transition metal halide complexes. The results of these studies will form the basis of future publications.

Experimental Section

General Procedures. All manipulations were carried out using standard Schlenk and glovebox techniques under an atmosphere of high-purity argon or dinitrogen. Toluene and hexane were distilled over potassium then freeze/thaw degassed prior to use. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on either a Bruker DPX400 or JEOL Eclipse 300 spectrometer in C_6D_6 or THF-d_8 and were referenced to the residual resonances of the solvent used (^1H and ^{13}C NMR) or to external 85% H_3PO_4, 0.0 ppm (^{31}P NMR). Mass spectra were recorded using a VG Fisons Platform II instrument under APCI conditions. Melting points were determined in sealed glass capillaries under argon and are uncorrected. Reproduc-

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(9) Values determined from a survey of the Cambridge Structural Database.

(10) (a) Hadi, G. A. A.; Fromm, K.; Blaurock, S.; Jelonek, S.; Hey-Hawkins, E. *Polyhedron* **1997**, *16*, 721. (b) Blaurock, S. Ph.D. Thesis, Universität Leipzig, 2000, and references therein.

(11) Gibson, V. C.; Kee, T. P.; Carter, S. T.; Sanner, R. D.; Clegg, W. *J. Organomet. Chem.* **1991**, *418*, 197.

(12) Compound **7** has also been obtained in high yield from the reaction of 2 equiv of **1** with $[NiCl_2(PBu^n_3)_2]$: Jones, C.; Richards, A. F. Unpublished results.

(13) (a) Niecke, E.; Fuchs, A.; Nieger, M. *Angew. Chem., Int. Ed.* **1999**, *38*, 3028, (b) Schmidt, O.; Fuchs, A.; Gudat, D.; Nieger, M.; Hoffbauer, W.; Niecke, E.; Schoeller, W. W. *Angew. Chem., Int. Ed.* **1998**, *37*, 949.

(14) Charrier, C.; Maigrot, N.; Mathey, F.; Robert, F.; Jeannin, Y. *Organometallics* **1986**, *5*, 623.

ible elemental analyses of **5** could not be obtained due to its air sensitivity and the fact that it slowly loses toluene of crystallization over time. An elemental analysis of **9** could not be obtained as it crystallizes as an inseparable mixture with **4**. Meaningful ^{13}C data for **5** could not be obtained due to its very low solubility in noncoordinating solvents and the fact that it decomposes in THF-d_8 over 30 min, even at −50 °C. Compound **1**,[2] [Cp*TaCl$_4$],[15] and [Cp*NbCl$_4$][15] were prepared by literature procedures. All other reagents were used as received.

X-ray Crystallography. Crystals of **5** and **7** suitable for X-ray structure determination were mounted in silicone oil. Crystallographic measurements were made using an Enraf-Nonius CAD4 diffractometer for both compounds. The structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX97)[16] using all unique data. All non-hydrogen atoms are anisotropic with H atoms included in calculated positions. A disordered molecule of toluene is included in the crystal lattice of **5**. Both the tertiary butyl and cyclohexyl groups in **5** proved to be disordered. This disorder was successfully modeled, although only one set of the disordered atoms is shown in Figure 1. Crystal data, details of data collections, and refinements are given in Table 1. The molecular structures of the complexes are depicted in Figures 1 and 2.

Synthesis of [{Cp*TaCl$_2$[=C(Bu^t)−P(Cy)−]}$_2$], 5. To a suspension of [Cp*TaCl$_4$] (0.28 g, 0.62 mmol) in toluene (20 mL) at −78 °C was added **1** (0.38 g, 1.24 mmol) in toluene (15 mL) over 15 min. The resulting green solution was warmed to −30 °C, filtered, and placed at −30 °C overnight to yield blue-green crystals of **5** (0.17 g, 48%), mp 168−170 °C dec; ^{1}H NMR (400 MHz, THF-d_8, 223 K) δ 1.86 (s, 18H, Bu^t), 1.94 (s, 30H, C$_5$Me$_5$), 1.0−2.3 (m, 22H, Cy); ^{31}P{^{1}H} NMR (121.7 MHz, THF-d_8, 223 K) δ −6.0 (Ta=CP); IR ν cm^{-1} (Nujol) 1604(w), 1360(s), 942(m), 694(m); MS APCI m/z 570 ([Cp*TaCl$_2${C(Bu^t)−PCy}]$^+$, 100%), 387 ([Cp*TaCl$_2$]$^+$, 10%).

Synthesis of Cy$_2$P$_2$C$_2$Bu$^t_2$, 7. To a suspension of [Cp*NbCl$_4$] (0.09 g, 0.24 mmol) in toluene (20 mL) at −78 °C was added **1** (0.15 g, 0.49 mmol) in toluene (15 mL) over 15 min. The resulting brown solution was warmed to room temperature, stirred overnight, and filtered. Volatiles were removed in vacuo, and the residue was extracted with hexane (10 mL). The extract was concentrated to ca. 3 mL and placed at −30 °C overnight to yield colorless crystals containing an approximately 65:35 mixture of **7** and **4** (0.04 g). Data for **7**: mp 128−130 °C; ^{1}H NMR (400 MHz, C$_6$D$_6$, 298 K) δ 1.34 (s, 18H, Bu^t), 0.9−2.3 (m, 22H, Cy); ^{13}C NMR (101.6 MHz, C$_6$D$_6$, 298 K) δ 26.4 (CH$_2$), 27.4 (CH$_2$), 28.5 (CH$_2$, $^2J_{PC}$ 4 Hz), 29.8 (CH$_3$, $^3J_{PC}$ 3 Hz), 34.8 (CH, $^1J_{PC}$ 14 Hz), 36.6 (*C*Me$_3$, $^2J_{PC}$ 8 Hz), 156.8 (PPC, $^1J_{PC}$ 15 Hz); ^{31}P{^{1}H} NMR (121.7 MHz, C$_6$D$_6$, 298 K) δ −52.0 (CyP); IR ν cm^{-1} (Nujol) 1664(w), 1377(m), 1260(m), 968(m), 722(m); MS APCI m/z 367 ([MH]$^+$, 100%), 283 ([M − Cy]$^+$, 32%).

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Supporting Information Available: Full crystallographic data for **5** and **7** and the ^{31}P{^{1}H} NMR spectrum of **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Sheldrick, G. M. *SHELX-97*; University of Göttingen, 1997.