

Preparation and Properties of Substituted (η^5 -Divinylborane)(η^5 -cyclopentadienyl)cobalt Complexes

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(η^5 -Chlorodivinylborane)(η^5 -cyclopentadienyl)cobalt (1) readily undergoes the nucleophilic substitution at boron. Treatment of 1 with 2 equiv of an amine or an alcohol in the presence of base produces (η^5 -aminodivinylborane)(η^5 -cyclopentadienyl)cobalt and (η^5 -alkoxydivinylborane)(η^5 -cyclopentadienyl)cobalt complexes, respectively. Treatment of 1 with Grignard reagents gives alkyl- and aryl(η^5 -divinylborane)(η^5 -cyclopentadienyl)cobalt complexes. LiBH_4 reacts with 1 to produce (η^5 -divinylborane)(η^5 -cyclopentadienyl)cobalt in high yield.

Introduction

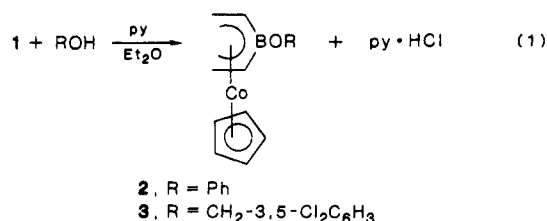
Boron-containing heterocycles have been extensively used as ligands in organotransition-metal chemistry;¹⁻³ however, acyclic divinylboranes have received relatively little attention.⁴⁻⁶ Organodivinylboranes would be expected to serve as η^5 ligands in transition-metal complexes analogous to the isoelectronic pentadienyl cation. The ^1H NMR spectra of the four reported organodivinylborane transition-metal complexes indicate that the divinylborane serves as a η^5 ligand in these complexes, implying a direct boron to transition-metal bond.^{4,6} There have been several reports of cyclic divinylborane derivatives, including two X-ray crystallographic studies which have confirmed the η^5 nature of divinylborane ligands.⁷⁻¹³

Although several complexes of cyclic divinylborane have now been reported, they all contain either an alkyl or an aryl substituent at boron.⁷⁻¹³ Having recently developed a convenient high-yield route to (η^5 -chlorodivinylborane)(η^5 -cyclopentadienyl)cobalt (1),⁵ it was of interest to examine its potential as a starting material to prepare a wide range of substituted divinylborane complexes.

We report here the preparation and properties of a wide range of substituted divinylborane complexes.

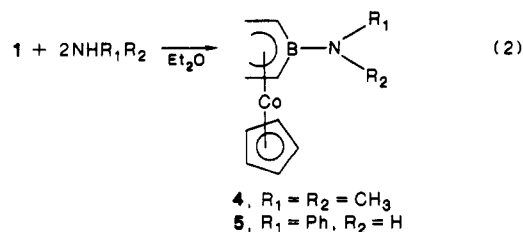
Results and Discussion

Nucleophilic Substitution at Boron. Treatment of (η^5 -chlorodivinylborane)(η^5 -cyclopentadienyl)cobalt with alcohols or phenols leads to immediate decomposition of the organometallic complex. However, 1 readily undergoes nucleophilic substitution at boron when treated with alcohols or phenols in the presence of a stoichiometric amount of base. (η^5 -Phenoxydivinylborane)(η^5 -cyclopentadienyl)cobalt (2) and (η^5 -((3,5-dichlorobenzyl)oxy)divinylborane)(η^5 -cyclopentadienyl)cobalt (3) are formed in high yield by treatment of 1 with phenol or 3,5-dichlorobenzyl alcohol, respectively, in ether in the presence of pyridine (eq 1).

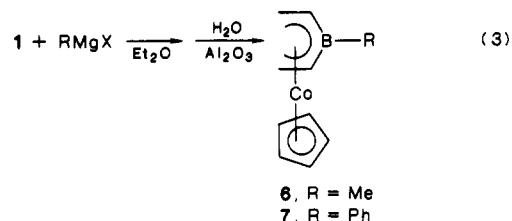


In analogous manner complex 1 undergoes nucleophilic substitution at boron upon treatment with 2 equiv of di-

methylamine or aniline to give (η^5 -(dimethylamino)divinylborane)(η^5 -cyclopentadienyl)cobalt (4), and (η^5 -anilindivinylborane)(η^5 -cyclopentadienyl)cobalt (5), respectively, in high yield (eq 2).



Reaction of 1 with Grignard reagents allows the formation of a boron-carbon bond. For example, treatment of 1 with methylmagnesium iodide or phenylmagnesium bromide gives (η^5 -methyldivinylborane)(η^5 -cyclopentadienyl)cobalt (6) and (η^5 -phenyldivinylborane)(η^5 -cyclopentadienyl)cobalt (7), respectively, in high yield (eq 3).



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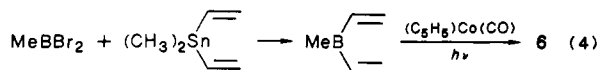
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Table I. Proton NMR Spectra of Complexes 2-8^{a-c}

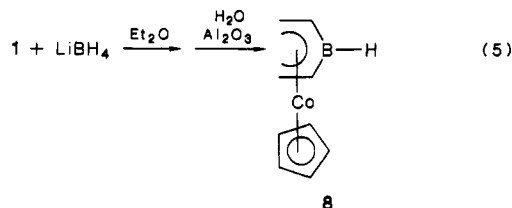
compd	H ₁ ^d	H _a ^d	H _s ^d	C ₅ H ₅	other	aromatic
2	3.56 (2 H) t (12.4)	2.80 (2 H) d (11.3)	0.92 (2 H) d (13.5)	4.30 (5 H) s		7.0-7.4 (5 H) m
3	3.57 (2 H) t (10.5)	2.82 (2 H) d (12.0)	0.90 (2 H) d (13.5)	4.37 (5 H) s	5.47 (2 H) s (CH ₂)	6.52 (1 H) t (12.5) 7.03 (2 H) d (12.5)
4	3.96 (2 H) t (12.7)	2.90 (2 H) d (10.5)	0.90 (2 H) d (12.7)	4.45 (5 H) s	2.87 (6 H) s (CH ₃)	
5	3.30 (2 H) t (12.8)	2.85 (2 H) d (11.3)	1.04 (2 H) d (14.0)	4.18 (5 H) s		7.2-7.4 (5 H) m
6	3.80 (2 H) t (12.8)	3.05 (2 H) d (11.6)	1.08 (2 H) d (12.0)	4.30 (5 H) s	1.19 (3 H) s (CH ₃)	
7	4.25 (2 H) t (12.0)	3.16 (2 H) d (12.0)	1.22 (2 H) d (14.3)	4.18 (5 H) s		7.45 (3 H) m 8.23 (2 H) m
8	4.13 (2 H) d (135.6)	3.10 (2 H) d (11.3)	1.18 (2 H) d (14.1)			

^a Determined in C₆D₆ solution. ^b δ, relative to internal TMS. ^c Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet. ^d J values (Hz) in parentheses.

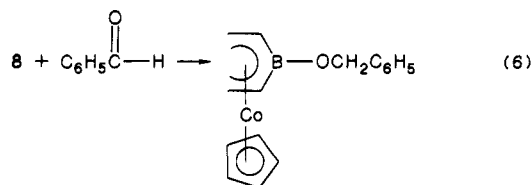
Complex 6 could also be prepared by photolysis of cyclopentadienyldicarbonylcobalt in the presence of methyldivinylborane which was prepared in situ from methylboron dibromide and dimethyldivinyltin in a manner analogous to that used to prepare 1 (eq 4).⁵



Treatment of 1 with an excess of LiBH₄ in ether gives, upon hydrolysis, (η⁵-divinylborane)(η⁵-cyclopentadienyl)cobalt (8) in high yield (eq 5). Although hydride 8 was



found to be unreactive toward water or alcohols, it adds rapidly and cleanly to benzaldehyde to give (η⁵-benzyl-oxo-divinylborane)(η⁵-cyclopentadienyl)cobalt⁵ in high yield (eq 6) in a manner similar to anionic borohydrides.



Spectra of Substituted Derivatives of 1. The proton NMR spectra of substituted (η⁵-divinylborane)cyclopentadienylcobalt complexes are summarized in Table I. The chemical shift of the cyclopentadienyl resonance in complexes 1-8 was observed as a sharp singlet in the range δ 4.2-4.4 and was found to be relatively insensitive to the substituent at boron. The protons of the divinylborane unit give rise to a distinctive pattern indicative of a cross conjugated η⁵-divinylborane system that is somewhat analogous to what is observed for pentadienyl and butadiene transition-metal complexes.¹⁴⁻¹⁶ The proton syn (H_s) to boron is observed at high field δ 0.80-1.22 as a doublet, due to coupling to the proton on the carbon adjacent to boron (H₁). The proton anti (H_a) to boron is observed as a doublet at δ 2.8-3.2, coupled only to proton H₁. The resonance of H₁ is observed at lower field than either H_a or H_s and is observed as an apparent triplet, due to coupling with both H_a and H_s. Although the resonances of the divinylborane protons vary markedly with varying substitution at boron, no clear relationship emerges be-

Table II. Carbon and Boron NMR Spectra of Selected (η⁵-Divinylborane)cyclopentadienylcobalt Complexes^{a-c}

compd	C ₅ H ₅	β-carbon	¹¹ B
1	82.0	56.9	29.5
2	82.2	55.0	29.5
4	81.7	51.9	30.0
5	82.2	53.7	30.0
6	82.0	58.8	30.6
7	82.4	59.6	25.3
8	81.9	60.4	21.2 d (116) ^d

^a Determined in C₆D₆ solution. ^b ppm relative to internal TMS. ^c ppm downfield from BF₃·OEt₂. ^d See footnotes c and d in Table I.

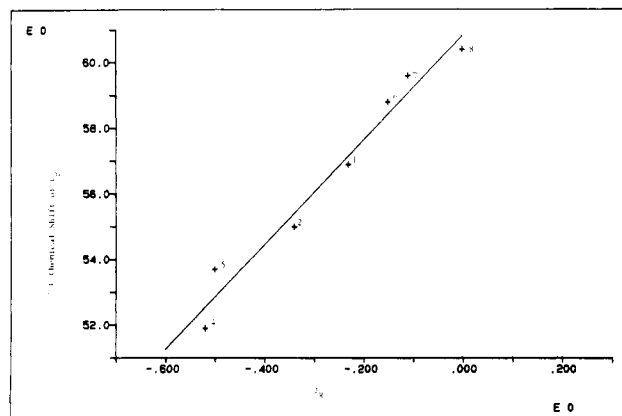


Figure 1. Plot of the ¹³C chemical shift of C_β of substituted (η⁵-divinylborane)(η⁵-cyclopentadienyl)cobalt complexes vs σ_R.

tween the resonances of H₁, H_a, and H_s and the substituent at boron.

Although the ¹³C resonances of C_α in the complexed divinylborane ligands were not observed, due to quadrupolar broadening by both boron (¹¹B, I = 3/2, 80%; ¹⁰B, I = 3, 20%) and cobalt (I = 7/2, 100%), the resonances of C_β in these ligands were readily observed. The carbon chemical shifts of C_β of a series of η⁵-divinylborane complexes are given in Table II. The importance of the interaction of a lone pair on an atom bonded to boron is well-known and for boron-nitrogen compounds is especially important.¹⁷⁻¹⁹ It appears from the data in Table II that there is a correlation between the ¹³C chemical shift of C_β in these complexes and the π-electron-donating ability of the substituent at boron; that this is the case is confirmed by Figure 1 which is a plot of the ¹³C chemical shift of C_β in the divinylborane unit in these complexes vs σ_R, the resonance parameter of the substituent.²⁰

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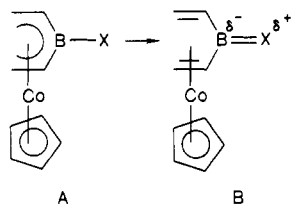
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Carbon NMR shifts have been found to be a good indication of the π -electron density on carbon atoms of similar hybridization and substitution.²¹ Although the ¹³C resonances of C _{β} vary over a relatively narrow range, these data suggest that resonance hybrid B is at least a minor con-



tributor to the bonding description of divinylborane complexes, as increasing the π -electron-donating ability of the substituent at boron leads to the expected increase in π -electron density at C _{β} as reflected in the ¹³C NMR shifts. The ¹¹B NMR data are more complicated due to a combination of σ and π effects, and no simple correlation was found.

The ¹¹B NMR spectra of selected (η^5 -divinylborane)-cyclopentadienylcobalt complexes are listed in Table II along with the ¹¹B resonance of the free ligand in the cases in which the free ligand is known. The boron chemical shifts of these complexes fall into a very narrow range and are indicative of η^5 -divinylborane transition-metal complexes.^{3,9,22}

Conclusion

(η^5 -Chlorodivinylborane)(η^5 -cyclopentadienyl)cobalt readily undergoes nucleophilic substitution at boron and serves as a convenient starting material for the preparation of boron-substituted divinylborane cyclopentadienylcobalt complexes. Although the divinylborane ligand serves as an η^5 -four-electron donor in transition-metal complexes, nucleophilic substitution at boron is an important reactivity pattern analogous to what is found in tricoordinate borane. Resonance structure B is at least a minor contributor to the bonding description of divinylborane complexes, and π -electron donation by substituents at boron is reflected by the ¹³C NMR shifts of C _{β} .

Experimental Section

All operations were carried out under a nitrogen atmosphere by means of Schlenk techniques. The nitrogen was dried with H₂SO₄ and P₂O₅, and trace oxygen was removed with BASF catalyst. Hexane and pentane were dried over Na/K alloy and freshly distilled under nitrogen. Diethyl ether was dried with activated alumina and distilled under nitrogen from sodium-benzophenone.

(η^5 -Chlorodivinylborane)cyclopentadienylcobalt (1) was prepared as previously described.⁵

Silica gel and alumina were prepared for use by heating overnight at 300 °C followed by cooling under high vacuum. The alumina was then deactivated with 7% (by weight) nitrogen-saturated water. The silica gel and alumina were stored under nitrogen until use.

Proton NMR spectra were recorded on a JEOL-C60 HL spectrometer. Carbon and boron NMR spectra were recorded

on a JEOL-JNM PS 100 spectrometer. Melting points were determined in sealed tubes under nitrogen and are uncorrected. Microanalyses were performed by Alfred Bernhardt Analytical Laboratory.

(η^5 -Phenoxydivinylborane)cyclopentadienylcobalt (2). Pyridine (0.71 mL, 0.88 mmol) was added rapidly to a stirred solution of (η^5 -chlorodivinylborane)cyclopentadienylcobalt (0.1977 g, 0.88 mmol) in 10 mL of ether. To the resulting mixture was immediately added phenol (0.0830 g, 0.88 mmol) in 5 mL of ether dropwise, with the precipitation of pyridine-hydrochloride. The reaction mixture was stirred at room temperature for 1 h and then diluted with 10 mL of hexane. The resulting reaction mixture was filtered. The filtrate was concentrated under vacuum to 10 mL. The resulting solution was cooled to -78 °C to produce, upon filtration and drying under high vacuum, (η^5 -phenoxydivinylborane)cyclopentadienylcobalt: 0.1802 g (76%); mp 68.5–69.5 °C.

Anal. Calcd for C₁₅H₁₆BCoO: C, 64.11; H, 5.38. Found: C, 63.99; H, 5.38.

(η^5 -((3,5-Dichlorobenzyl)oxy)divinylborane)cyclopentadienylcobalt (3). A solution of 3,5-dichlorobenzyl alcohol (0.4987 g, 2.82 mmol) and pyridine (0.227 mL, 2.82 mmol) in 6 mL of ether was added dropwise to a stirred solution of (η^5 -chlorodivinylborane)cyclopentadienylcobalt (0.630 g, 2.82 mmol) in 30 mL of ether at room temperature. Immediate precipitation of pyridine-hydrochloride occurred. After it had been stirred for 5 min, the mixture was filtered through a 5 × 1 cm plug of alumina (7% H₂O) and the resulting clear solution was concentrated under vacuum to a volume of 5 mL. Hexane (2 mL) was added and the resulting solution cooled slowly to -78 °C. Filtration gave 0.8249 g (80%) of (η^5 -((3,5-dichlorobenzyl)oxy)divinylborane)cyclopentadienylcobalt, mp 132 °C.

Anal. Calcd for C₁₆H₁₆BCl₂CoO: C, 52.66; H, 4.42. Found: C, 52.70; H, 4.51.

(η^5 -((Dimethylamino)divinylborane)cyclopentadienylcobalt (4). Dimethylamine was bubbled slowly through a stirred solution of (η^5 -chlorodivinylborane)cyclopentadienylcobalt (0.4881 g, 2.17 mmol) in 30 mL of ether. Dimethylamine-hydrochloride immediately started to precipitate. The addition of dimethylamine was continued for 15 min. The resulting mixture was filtered and the solvent reduced under high vacuum. The resulting residue was extracted with a minimum amount of pentane and the resulting clear red solution cooled slowly to -78 °C to produce, upon filtration and drying under high vacuum, (η^5 -((dimethylamino)divinylborane)cyclopentadienylcobalt: 0.2717 g (54%); mp 82.5–83.5 °C.

Anal. Calcd for C₁₁H₁₇BCoN: C, 56.70; H, 7.36. Found: C, 56.46; H, 7.49.

(η^5 -Anilindivinylborane)cyclopentadienylcobalt (5). Aniline (0.52 mL, 5.7 mmol) was added to a stirred solution of (η^5 -chlorodivinylborane)cyclopentadienylcobalt (0.6421 g, 2.87 mmol) in 40 mL of ether. The resulting mixture was allowed to stir at room temperature for 2 h. The resulting solution was then filtered and the solvent removed from the resulting filtrate under high vacuum. The residue was recrystallized from hexane to give 0.6939 g of red crystalline (η^5 -anilindivinylborane)cyclopentadienylcobalt (86%), mp 65.5–67 °C.

Anal. Calcd for C₁₅H₁₇BCoN: C, 64.10; H, 6.10. Found: C, 63.82; H, 6.05.

(η^5 -Methyldivinylborane)cyclopentadienylcobalt (6). Methylmagnesium iodide (3.6 mol) in 3.6 mL of ether was added slowly to a stirred solution of (η^5 -chlorodivinylborane)cyclopentadienylcobalt (0.5517 g, 2.46 mmol) in 30 mL of ether at room temperature and then stirred at room temperature for 1 h. The resulting reaction mixture was cooled to 0 °C and then hydrolyzed by the slow addition of 1 g of alumina (7% H₂O). After being allowed to warm to room temperature, the reaction mixture was filtered over alumina (7% H₂O) (2 × 10 cm plug). The solvent was removed under high vacuum and the resulting residue extracted with a minimum amount of pentane. The resulting pentane solution was cooled slowly to -78 °C to give, upon filtration and drying under high vacuum, 0.3144 g (63%) of (η^5 -methyldivinylborane)cyclopentadienylcobalt.

Anal. Calcd for C₁₀H₁₄BCo: C, 58.89; H, 6.92. Found: C, 58.64; H, 6.72.

(η^5 -Phenyldivinylborane)cyclopentadienylcobalt (7). Phenylmagnesium bromide (2.6 mmol) in 1.5 mL of ether was

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added slowly to a stirred solution of (η^5 -chlorodivinylborane)cyclopentadienylcobalt (0.4135 g, 1.84 mmol) in 20 mL of ether. The resulting mixture was stirred at room temperature for 1 h. The resulting solution was filtered over a short plug of alumina (7% H₂O) (2 × 3 cm). The solvent was removed from the filtrate under high vacuum. The residual oil was extracted with a minimum amount of pentane and the resulting solution slowly cooled to -78 °C to give a red crystalline solid. The solvent was decanted, and the crystals melted as the sample was allowed to warm to room temperature under high vacuum to give (η^5 -phenyldivinylborane)cyclopentadienylcobalt, 0.4541 g (93%), as a red oil.

Anal. Calcd for C₁₅H₁₆BCo: C, 67.72; H, 6.06. Found: C, 67.21; H, 5.86.

(η^5 -Divinylborane)cyclopentadienylcobalt (8). To a stirred solution of (η^5 -chlorodivinylborane)cyclopentadienylcobalt (0.8084 g, 3.60 mmol) in 50 mL of ether at 0 °C was added slowly solid LiBH₄ (0.2010 g, 9.26 mmol). The resulting mixture was allowed to warm to room temperature, followed by continued stirring for

2 h. The reaction mixture was diluted with 50 mL of hexane and filtered over a column of silica gel (2 × 5 cm). The silica gel column was washed with 20 mL of hexane and the combined ether-hexane solution concentrated under vacuum to ≈20 mL. The resulting solution was cooled slowly to -78 °C to give, upon filtration and drying under high vacuum, 0.4361 g of (η^5 -divinylborane)cyclopentadienylcobalt. The mother liquor was further concentrated to 5 mL to produce a second crop of product, 0.1318 g, to give a combined yield of 0.5679 g (70%); mp 83 °C.

Anal. Calcd for C₉H₁₂BCo: C, 56.71; H, 6.37. Found: C, 56.84; H, 6.48.

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Registry No. 1, 73939-32-9; 2, 114860-71-8; 3, 114860-72-9; 4, 11486-73-0; 5, 114860-74-1; 6, 114860-75-2; 7, 114860-76-3; 8, 114860-77-4; 3,5-dichlorobenzyl alcohol, 60211-57-6.

Synthesis of the Phosphorus–Carbon Double Bond by Reaction between Pentacarbonylchromium or -tungsten Complexes of Phosphinidenes and Carbenes. Application to the Synthesis of the 1,2-Dihydrophosphete Ring

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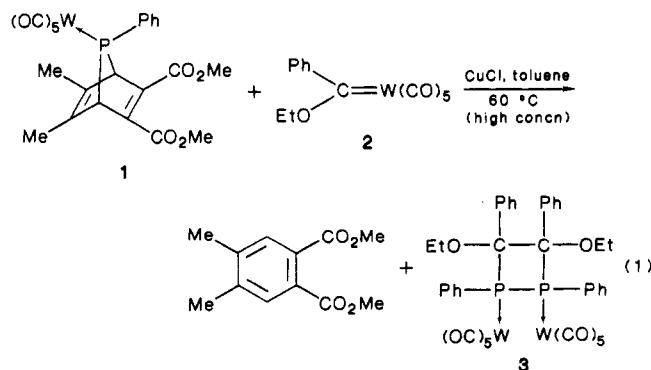
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The condensation of a carbene complex R¹R²C=M(CO)₅ with a transient terminal phosphinidene complex [RP=M(CO)₅] (M = Cr, W) primarily yields a phosphalkene complex, R¹R²C=P(R)→M(CO)₅, which, in some cases, dimerizes. This method has been applied to the synthesis of Ph₂C=P(Ph)→W(CO)₅ which is stable as a monomer. When a vinylcarbene complex such as PhCH=CH-C(OEt)=Cr(CO)₅ is reacted with (phenylphosphinidene)pentacarbonyltungsten, the transient phosphabutadiene complex thus obtained instantly undergoes a [2 + 2] cyclization to give a (1,2-dihydrophosphete(P-W))pentacarbonyltungsten complex. The X-ray crystal structure analysis of this complex [C₂₂H₁₇O₆PW, fw 592.20; space group *P* $\bar{1}$ (No. 2) with *a* = 10.519 (1) Å, *b* = 10.887 (1) Å, *c* = 11.134 (1) Å, α = 112.78 (2)°, β = 98.15 (2)°, γ = 97.13 (2)°; *V* = 1141.18 (68) Å³; *Z* = 2; *d*(calcd) = 1.723 g cm⁻³] confirms the presence of the four-membered ring with a very long P–C sp³-intracyclic bond [1.902 (5) Å]. It proved possible to convert this complex into the corresponding *P*-oxide without breaking the ring.

Recently we have shown on a preliminary example¹ that it is possible to couple a phosphinidene and a carbene to get a P=C double bond via the reaction of a transient terminal phosphinidene complex with a carbene complex. In view of the synthetic potential of this new approach to phosphalkenes, we decided to explore a little bit further this reaction in order to check some points of its postulated mechanism, to extend its scope, and to show on a precise example what kind of applications can be built around it.

Results and Discussion

In our preliminary experiment,¹ we allowed the 7-phosphanorbornadiene complex 1 to react with the carbene complex 2 (eq 1). The final product was the 1,2-diphos-



phetane complex 3. The postulated mechanism is depicted in eq 2. In this mechanism, the copper(I) chloride only plays the role of a catalyst which promotes the decomposition of the phosphinidene precursor 1² but does not in-

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