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Vanadacyclopropene Phosphane $Cp_2V(\eta^2\text{-}PhC{=}C)P(C{\equiv}CPh)Ar$

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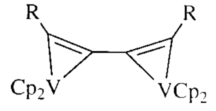
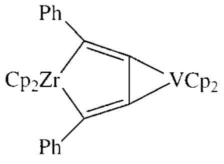
*Summary: Treatment of the bis(alkynyl)phosphane Ar−P(C≡CPh)$_2$ (**3**) (Ar = 2,4,6-t-Bu$_3$C$_6$H$_2$) with Cp$_2$V gives the vanadacyclopropene phosphane **5**, which was characterized by X-ray diffraction. The reactivity of **5** toward HCl in THF or toluene gives **3** or the alkenyl alkynyl phosphane (E/Z isomers) isolated as its sulfur analogue (PhCH=CH)(PhC≡C)PAr(=S).*

The successful use of the zirconocene "Cp$_2$Zr" applied as a synthon in a large variety of chemical reactions is well-documented.[1] In particular, investigations into the reactivity of different classes of bis(alkynyl) derivatives have enabled the preparation of various metallacycles to be carried out.[2] Bearing in mind that vanadocene Cp$_2$V can react with alkynes to give metallacyclopropene vanadium complexes,[3] we were interested to ascertain whether the use of Cp$_2$V, in place of "Cp$_2$Zr", could offer possible ways to trap certain intermediate complexes observed or suggested in reactions involving group 4 elements. Recently, one of us has demonstrated that homobimetallic $V^{IV}-V^{IV}$ species **1** with vanadacyclopropene moieties are formed when Cp$_2$V is treated with diynes RC≡CC≡CR (R = SiMe$_3$, PPh$_2$),[4] whereas in the presence of bis(alkynyl)zirconium Cp$_2$Zr(C≡CPh)$_2$, a more complicated situation occurs and the compound **2** (Cp$_2$V(μ-η^2-η^4-butadiyne)ZrCp′$_2$, Cp′ = C$_5$H$_4$SiMe$_3$) with a vanadacyclopropane moiety and a tetracoordinated planar carbon on the butadiyne ligand can be isolated.[5]



1 R= Ph, SiMe$_3$



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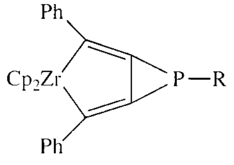
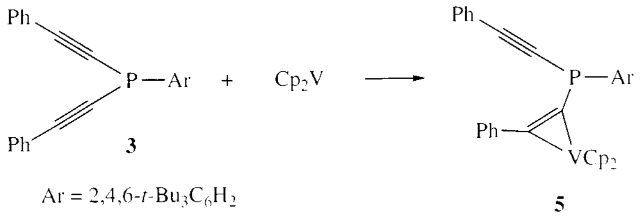


4 R= *t*-Bu, N-*i*-Pr$_2$, 2,4,6-*t*-Bu$_3$C$_6$H$_2$

Scheme 1



We report here the reactivity of the bis(alkynyl)phosphane ArP(C≡CPh)$_2$ (**3**) (Ar = 2,4,6-*t*-Bu$_3$C$_6$H$_2$) with Cp$_2$V. Phosphanes RP(C≡CPh)$_2$ (R = *t*-Bu, N-*i*-Pr$_2$, Ar (2,4,6-*t*-Bu$_3$C$_6$H$_2$)) were recently found to react with zirconocene to give zirconacyclopentadiene phosphirane complexes **4** isolated as powder.[6] Attempts to obtain suitable crystals for X-ray crystallography studies failed, and NMR techniques and chemical derivatizations were used in its identification.[7]

The reaction of phosphane ArP(C≡CPh)$_2$ (**3**) with 1 equiv of Cp$_2$V in pentane at room temperature leads to the formation of Cp$_2$V(η^2-PhC=C)P(C≡CPh)Ar (**5**) as a crystalline product in 70% yield (Scheme 1). The complex **5** has a magnetic moment as would be expected for a V^{IV} d^1 electronic configuration ($\mu_{eff} = 1.83\ \mu B$). The IR and Raman spectroscopies carried out in the solid state demonstrate the presence of a triple C≡C and a double C=C bond (2176 and 1590 cm^{-1}, respectively), which precludes the molecular arrangement of **5**. Addition of 2 equiv of Cp$_2$V to the phosphane or the addition of a second equivalent of Cp$_2$V to **5** at room temperature, or in refluxing conditions (THF, toluene), leaves the second alkynyl bond of phosphane untouched.

The solid-state structure of **5** determined by X-ray analysis is shown in Figure 1. The geometry around the metal center is tetrahedral. One alkynyl group of the phosphane is coordinated to the vanadium to form a cyclopropene type complex, whereas the second is intact.

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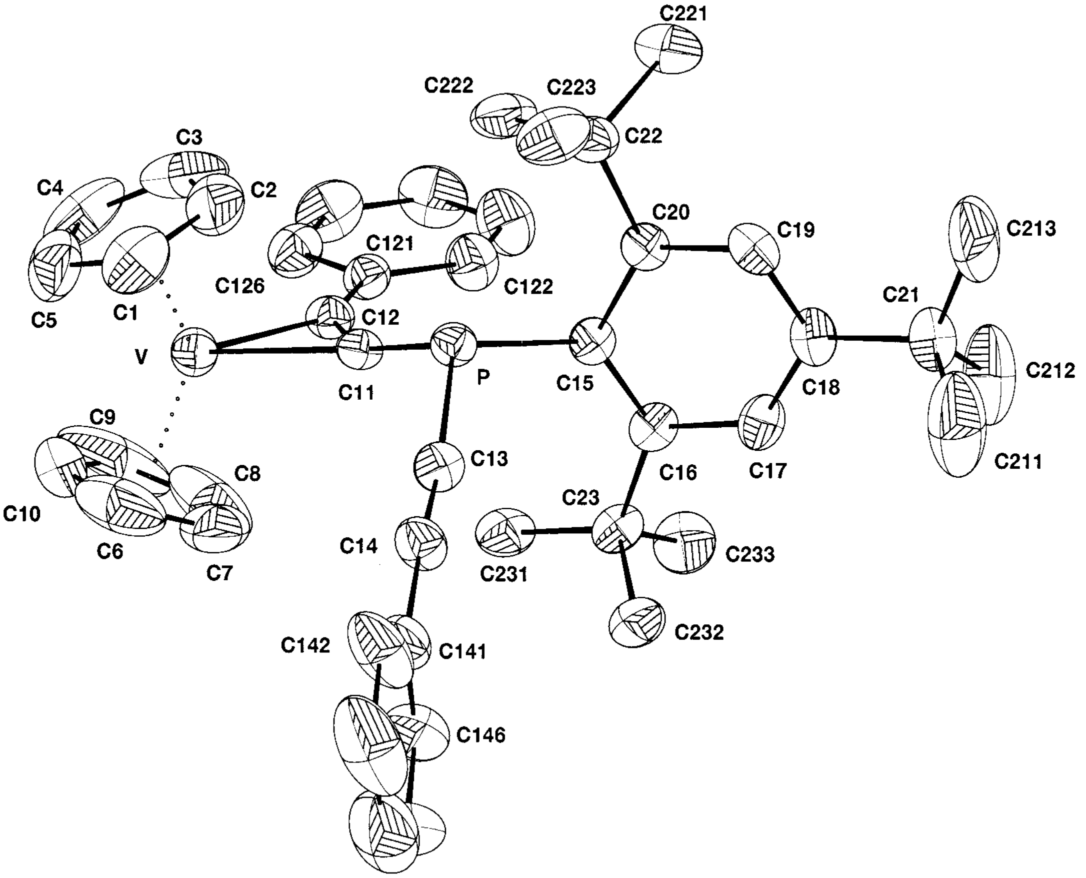
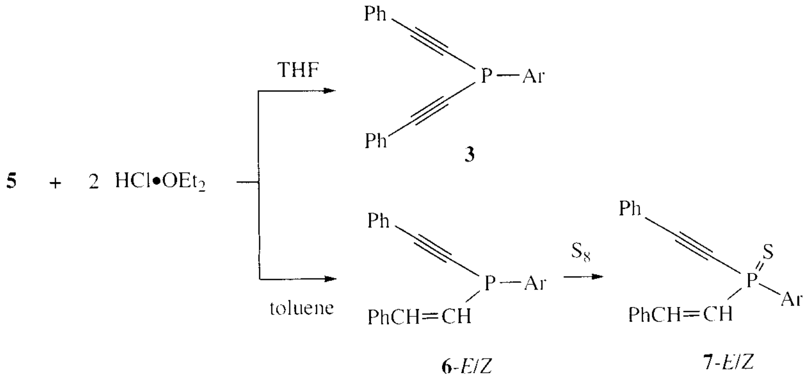


Figure 1. Molecular structure of **5**, with crystallographic numbering scheme (drawn with 30% thermal ellipsoids). Selected bond lengths (Å) and bond angles (deg) are as follows: V–C(11) 2.109(4), V–C(12) 2.081(4), C(11)–C(12) 1.280(5), P–C(11) 1.772(4), P–C(15) 1.863(4), P–C(13) 1.770(4), C(13)–C(14) 1.190(5), V–Cp 1.969, V–Cp′ 1.972, V–C(12)–C(11) 73.4(2), V–C(11)–C(12) 71.0(2), Cp–V–Cp′ 137.14 [Cp, Cp′ are the centroids of the C_5H_5 rings C(1)–C(5), C(6)–C(10)].

Scheme 2



V–C bonds (VC(11) = 2.109(4) Å; VC(12) = 2.081(4) Å), and C(11)VC(12) having an angle of (35.6(1)°) fall in the range observed for vanadacyclopropene compounds.[4] The C(11)–C(12) distance corresponds to a double C=C bond (1.280(5) Å), and the sum of the angles around C(11) and C(12) (354° and 360° respectively) confirms the sp^2 hybridization of both carbons. The V–C(11)–C(12) plane is nearly coplanar with the C(121)–C(126) phenyl group (2.11°) and perpendicular to both the other phenyl groups (C(15)–C(20) and C(141)–C(146)) of the phosphane (91.65° and 87.32°, respectively), minimizing steric effects in the molecule.

The reactivity of **5** toward HCl was examined. Reaction of **5** in THF with HCl gives selectively the starting phosphane **3** as the main product (evolution of D_2 with DCl was characterized by MS) along with the green precipitate of Cp_2VCl_2. The same reaction performed in toluene leads to the alkenyl–alkynyl phosphane **6** (1:1 ratio, *E*/*Z* isomers), isolated as its sulfur analogue **7**, and Cp_2VCl_2 (Scheme 2).[8] We are able to initially propose that the difference in the reactivity of **5** could be connected to the THF or toluene solvent used for the reaction. However the IR (registered in deuterated THF and toluene solvents) and EPR (registered in THF and toluene) spectra of **5** do not show any detectable difference, and similar data are observed for both solvents ($\nu_{(C=C)}$ = 1592 cm^{-1}; g_{av} = 2.001; $a(^{51}V)$ = 44.2 G). The high g_{av} value implies a significant electron delocaliza-

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tion onto the alkenyl ligand. This observation supports the view that the facile protonation of **5** could occur indifferently in toluene or in THF, in contrast to the release of **3** observed in THF.

Extension of this work to include the reactivity of vanadocene Cp_2V with various unsaturated main group element species is under way.

Experimental Section

All manipulations were conducted under an argon atmosphere using either standard Schlenk tube or glovebox techniques. Nuclear magnetic resonance (NMR) spectra were recorded on Bruker MSL 400, AM-250, AC-200, and AC-80 Fourier transform spectrometers. Positive chemical shifts are downfield relative to Me_4Si (^1H, ^{13}C) or H_3PO_4 (^{31}P) references, respectively. Mass spectrum analyses were performed by the analytical service of the Laboratoire de Chimie de Coordination (LCC) of the CNRS. Magnetic susceptibility measurements were carried out using Faraday's method. EPR spectra were recorded on a Bruker ER 200T spectrometer. Infrared spectra were recorded in solution (5 mg of **5** in 0.150 mL of THF-d_8 or toluene-d_8) or in Nujol on a Perkin-Elmer FT-IR spectrophotometer. The reference spectrum of the solvents was subtracted. Solvents were freshly distilled from sodium/benzophenone ketyl (THF, toluene) or lithium aluminum hydride (pentane). C_6D_6 was treated with CaH_2, distilled, and stored under argon. HCl−OEt$_2$ was purchased from Aldrich. Cp_2V[9a] and Ar−P(C≡CPh)$_2$[9b] (Ar = 2,4,6-*t*-Bu$_3$(C_6H_2)) were prepared according to the literature.

Synthesis of $Cp_2V(\eta^2\text{-PhC=C})P(C{\equiv}CPh)Ar$, 5. A solution of **3** (0.530 g, 1.10 mmol) in 10 mL of pentane was added slowly to a pentane solution (20 mL) of Cp_2V (0.200 g, 1.10 mmol). After 1 h stirring, the solution was left overnight to give black crystals of **5**, which were collected by filtration and dried in vacuo (0.510 g, 70% yield). Anal. Calcd for $C_{44}H_{49}PV$: C, 80.02; H, 7.42; V, 7.73. Found: C, 79.82; H, 7.32; V, 7.80.

Crystal Structure Data for 5. Crystallographic data: $C_{44}H_{49}PV$; M_w = 659.79; triclinic; space group $P\bar{1}$; unit cell a = 11.083(5) Å, b = 11.788(2) Å, c 15.414(2) Å, α = 76.34(2)°, β = 79.31(3)°, γ = 74.87(3)°; V = 1872.6(9) Å^3; ρ_{calcd} = 1.17 cm^{-3}; μ = 3.25 cm^{-1}; crystal dimensions 0.4 × 0.3 × 0.2 mm^3. The X-ray diffraction data were collected at 293 K on an Enraf Nonius CAD4 diffractometer using graphite-monochromatized Mo Kα radiation. A total of 7520 reflections were measured (7228 independent) with $R_{average}$ = 0.03. The structure was solved using direct methods (SIR92) and refined by least-squares procedures on F_{obs}. H atoms were located on difference Fourier maps, but they were introduced into the calculation in idealized positions (d(C−H) = 0.96 Å), and their atomic coordinates were recalculated after each cycle of refinement. They were given isotropic thermal parameters 20% higher than those of the carbon to which they were attached. All non-hydrogen atoms were refined anisotropically. The final R (R_w) values were 0.0387 (0.0389) for 2872 reflections used with the criterion $I > \sigma(I)$, and 416 variables were refined. The calculation were carried out with the aid of CRYSTALS. The drawing of the molecule was realized with CAMERON with thermal ellipsoids at the 50% probability level.

Preparation of 6-*E*/*Z* and 7-*E*/*Z*. To a solution of **1** (0.182 g, 0.270 mmol) in toluene (3 mL), at −78 °C, was added HCl·OEt$_2$ (552 μL; 1 M). The mixture was then stirred for 2 h at room temperature. In the course of the reaction, a green precipitate, identified after filtration by EPR and chemical analysis as Cp_2VCl_2, appeared with the formation of **6**-*E*/*Z* in 1:1 ratio as monitored by $^{31}P\{^1H\}$ NMR spectroscopy. After addition of sulfur (10 equiv) to **6**-*E*/*Z*, the resulting solution was refluxed for 16 h and then evaporated to dryness. The corresponding products **7**-*E*/*Z* were separated by chromatography (silica gel eluted with pentane/THF 95/5) in 60% total isolated yield.

7-*E*: (R_f = 0.49), DCI/CH$_4$, m/e = 513 ([M + 1]$^+$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 18.6 ppm. ^1H NMR (C_6D_6): δ 8.35 (dd, ^3J(H,P) = 24.7 Hz, ^3J(H,H) = 16.4 Hz, 1H, CH$_{Ph}$); 7.67 (d, ^4J(H,P) = 4.7 Hz, 2H, CH$_{Ar}$); 7.18−7.02 (m, 7H, CH$_{Ph}$); 6.92−6.80 (m, 3H, CHPh), 6.85 (dd, ^2J(H,P) = 21.7 Hz, ^3J(H,H) = 16.4 Hz, 1H, PCH); 1.50 (s, 18H, p-^{t}Bu); 1.37 (s, 9H, o-^{t}Bu). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 152.4 (d, ^2J(C,P) = 4.6 Hz, o-C$_{Ar}$); 144.7 (d, ^2J(C,P) = 7.8 Hz, *C*HPh); 136.1 (d, ^3J(C,P) = 20.0 Hz, i-C$_{Ph}$), 132.5 (d, J(C,P) = 1.0 Hz, CHPh); 130.1, 130.0, 129.9, 129.4, 128.9, 126.3 (s, C$_{Ph}$H); 125.6 (d, ^3J(C,P) = 13.7 Hz, m-C$_{Ar}$); 102.2 (d, ^2J(C,P) = 26.1 Hz, ≡CPh); 91.3 (d, J(C,P) = 150.8 Hz, PC≡); 35.3, 31.5, 30.9 (s, C*C*H$_3$), PCH not identified. Anal. Calcd for $C_{34}H_{41}PS$: C, 79.64; H, 8.06. Found: C, 79.51; H, 7.94.

7-*Z*: (R_f = 0.24), DCI/CH$_4$, m/e = 513 ([M + 1]$^+$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 9.8 ppm. ^1H NMR (C_6D_6): δ 7.62 (d, ^4J(H,P) = 5.4 Hz, 2H, CH$_{Ar}$); 7.17−6.85 (m, 10H, CH$_{Ph}$); 6.80 (dd, ^3J(H,P) = 20.0 Hz, ^3J(H,H) = 13.6 Hz, 1H, C*H*Ph); 6.56 (dd, ^2J(H,P) = 46.5 Hz, ^3J(H,H) = 13.6 Hz, 1H, PC*H*); 1.49 (s, 18H, o-^{t}Bu); 1.31 (s, 9H, p-^{t}Bu). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 152.4 (d, J(C,P) = 4.5 Hz, o-C$_{Ar}$); 140.9 (d, ^2J(C,P) = 5.4 Hz, *C*HPh); 136.4 (d, ^2J(C,P) = 13.1 Hz, i-C$_{Ph}$); 135.7 (d, J(C,P) = 7.0 Hz, CPh); 135.3 (d, ^1J(C,P) = 92.6 Hz, i-CAr); 132.5 (d, J(C,P) = 1.2 Hz, CPh); 131.5 (d, J(C,P) = 98.6 Hz, PCH); 130.0 (d, J(C,P) = 1.0 Hz, CPh); 131.6, 129.0, 128.9, 126.3 (s, CPh); 121.9 (d, J(C,P) = 3.8 Hz, m-C$_{Ar}$); 35.3, 31.5, 30.8 (s, C*C*H$_3$). Anal. Calcd for $C_{34}H_{41}PS$: C, 79.64; H, 8.06. Found: C, 79.48; H, 7.95.

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Supporting Information Available: Listing of atomic coordinates, hydrogen positional parameters, isotropic and anisotropic displacement parameters, and complete bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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