

# Palladium(0) Complexes Formed by a Chelating Olefinic Tertiary Phosphine. Synthesis, Fluxional Behavior, and X-ray Crystal Structure of Pd(*o*-CH<sub>2</sub>=CHC<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>, a Three-Coordinate Complex Containing a Weak Interaction between the Metal Atom and an $\alpha$ -Vinyllic Hydrogen Atom

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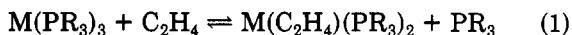
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Reaction of Pd( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) with exactly 2 mol equiv of (2-vinylphenyl)diphenylphosphine (*o*-styryldiphenylphosphine, *o*-CH<sub>2</sub>=CHC<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>, abbreviated SP) gives the zerovalent palladium complex Pd(SP)<sub>2</sub> (4). The reaction proceeds via a thermally unstable intermediate, Pd(C<sub>3</sub>H<sub>5</sub>)(C<sub>5</sub>H<sub>5</sub>)(SP) (3), which can be isolated from the reaction of Pd( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) with SP at -70 °C. Crystals of 4 are triclinic, space group *P* $\bar{1}$ , with *a* = 21.456 (3) Å, *b* = 9.483 (2) Å, *c* = 9.202 (2) Å,  $\alpha$  = 60.84 (1)°,  $\beta$  = 87.67 (1)°,  $\gamma$  = 81.12 (2)°, and *Z* = 2. The structure was solved by heavy-atom methods and refined by least-squares methods to *R* = 0.032 and *R*<sub>w</sub> = 0.036 for 5536 independent reflections. In contrast to Ni(SP)<sub>2</sub> and Pt(SP)<sub>2</sub>, which are tetrahedral, crystalline 4 adopts an approximately trigonal-planar structure, one SP ligand being bidentate and the other being bound through phosphorus only. There is also a weak "agostic" interaction between the palladium atom and the  $\alpha$ -hydrogen atom H(19) of the uncoordinated vinyl group. With the assumption of a C(19)-H(19) bond length of 1.08 Å, the Pd-H(19) distance is calculated to be 2.46 Å. The coordinated vinyl group is displaced markedly from the trigonal plane, the dihedral angle between the planes P(1)-Pd-P(2) and C(39)-Pd-C(40) being 24.7 (2)°, and is bound asymmetrically, the distances to the terminal and inner carbon atoms being 2.213 (4) Å and 2.141 (3) Å, respectively. The Pd-P bond lengths are equal [Pd-P(1) = 2.3029 (7) Å, Pd-P(2) = 2.3054 (7) Å], and the C=C distances in the free and coordinated vinyl groups are 1.293 (5) and 1.387 (5) Å, respectively. The variable-temperature <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of 4 at -80 °C shows that the trigonal complex 4a, which has inequivalent phosphorus atoms, coexists with a species 4b containing equivalent phosphorus atoms; the proportion of 4b increases at -50 °C. 4b is suggested to be a two-coordinate complex in which both vinyl groups interact weakly with the palladium atom. Above -50 °C 4a and 4b equilibrate rapidly on the NMR time scale leading to equivalence of the free and coordinated vinyl groups. 4 reacts with additional SP to give Pd(SP)<sub>3</sub> (5), in which all the vinyl groups are free, and with aqueous HBF<sub>4</sub> to give the five-membered ring chelate ( $\sigma$ -alkyl)palladium(II) salt *trans*-[Pd(*o*-CH<sub>3</sub>CHC<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)(SP)]BF<sub>4</sub> (6). Comparison of the properties of the M(SP)<sub>2</sub> complexes (M = Ni, Pd, Pt) confirms that olefin binding is weakest in the palladium compound.

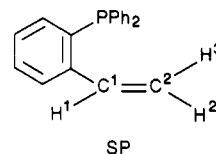
## Introduction

Olefin complexes of zerovalent palladium, especially those of the type Pd(olefin)L<sub>2</sub> containing tertiary phosphines, have not been studied as extensively as their nickel or platinum counterparts, probably on account of their generally lower thermal stability.<sup>1-4</sup> For example, bis-(1,5-cyclooctadiene)palladium(0) is stable only below room temperature, whereas the corresponding nickel(0) and platinum(0) compounds are stable at room temperature.<sup>5</sup> The complex Pd(C<sub>2</sub>H<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub> readily loses ethylene and deposits metallic palladium in benzene solution,<sup>6</sup> whereas Ni(C<sub>2</sub>H<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub> and Pt(C<sub>2</sub>H<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub> do not decompose in this way. These qualitative observations are confirmed by the order of equilibrium constants for eq 1, measured in benzene at 25 °C, viz., M = Ni  $\gg$  Pt > Pd.<sup>7,8</sup>



R = Ph, Et

In the preceding paper<sup>9</sup> we reported the preparation and structural characterization of the complexes M(SP)<sub>2</sub> (M = Ni, Pt) formed by the chelating olefinic tertiary phosphine (2-vinylphenyl)diphenylphosphine, *o*-CH<sub>2</sub>=CHC<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub> (sometimes called *o*-styryldiphenylphosphine and abbreviated SP). These compounds are



rare examples of stable, tetrahedral complexes of the zerovalent metals in which two olefins and two phosphorus donors are coordinated to the metal atom. It was of interest to see whether a palladium(0) analogue could be made and whether it too would adopt a tetrahedral structure.

## Experimental Section

Preparative and spectroscopic procedures are described in the preceding paper.<sup>9</sup> The complex Pd( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) was prepared by the literature method.<sup>10</sup>

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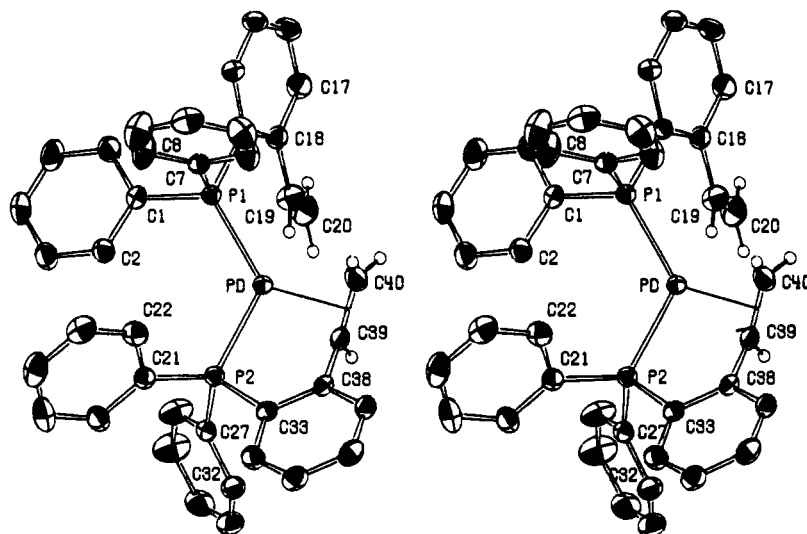
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**Figure 1.** Molecular structure of  $\text{Pd}(\text{SP})_2$  (4): 30% ellipsoids; H atoms omitted (phenyl groups) or as 0.1 Å radius spheres (vinyl groups).

**Reaction of  $\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\eta^5\text{-C}_5\text{H}_5)$  with 1 Mol Equiv of SP.** To a solution of  $\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\eta^5\text{-C}_5\text{H}_5)$  (0.64 g, 3.01 mmol) in toluene (30 mL) at  $-70^\circ\text{C}$  was added SP (5.0 g, excess), and the mixture was stirred for 1 h. Addition of hexane (40 mL) at  $-70^\circ\text{C}$  gave a bright yellow solid, which was filtered off at  $-70^\circ\text{C}$ . The yield of  $\text{Pd}(\text{C}_3\text{H}_5)(\text{C}_6\text{H}_5)(\text{SP})$  (3) was 1.3 g (85%).

Anal. Calcd for  $\text{C}_{28}\text{H}_{27}\text{PPd}$ : C, 67.1; H, 5.4; P, 6.2; Pd, 21.2. Found: C, 67.2; H, 5.4; P, 5.9; Pd, 21.1.

The compound is air-sensitive and thermally unstable. It is slightly soluble in toluene to give a red solution that decomposes within 1 h at room temperature. The  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra are described in the text.

**Preparation of Bis[(2-vinylphenyl)diphenylphosphine]palladium(0),  $\text{Pd}(\text{SP})_2$  (4).** (1) Addition of toluene (2 mL) to a solid mixture of 3 (0.215 g, 0.43 mmol) and SP (0.124 g, 0.43 mmol) gave initially a clear, dark red solution, but after 1 h a yellow solid had precipitated. This was filtered off, washed with hexane ( $3 \times 10$  mL), and dried in vacuo to give 4 (0.19 g, 65%).

(2) A clear, dark red solution containing  $\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\eta^5\text{-C}_5\text{H}_5)$  (2.85 g, 13.8 mmol) and SP (7.73 g, 26.8 mmol) in toluene (5 mL) was stirred vigorously for 15 min whereupon a thick suspension formed. The mixture was stirred for 3 h, and the pale yellow precipitate was isolated by filtration, washed with pentane, and dried in vacuo to give 4 (5.95 g, 65%), mp  $118\text{--}120^\circ\text{C}$ . The  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR spectra of 4 are described in the text.

Anal. Calcd for  $\text{C}_{40}\text{H}_{34}\text{P}_2\text{Pd}$ : C, 70.3; H, 5.0; P, 9.1; Pd, 15.6; mol wt, 683. Found: C, 70.6; H, 5.1; P, 9.4; Pd, 15.4; mol wt (by osmometry in toluene at  $37^\circ\text{C}$ ), 572.

The compound is only slightly soluble in alkanes and ether but is more soluble in toluene, THF, and ethanol. It is very soluble in dichloromethane to give solutions that are stable, in the absence of air, for ca. 10 h at room temperature and for longer periods at lower temperatures. The solid is somewhat air-sensitive and solutions are much more so.

**Preparation of Tris[(2-vinylphenyl)diphenylphosphine]palladium(0),  $\text{Pd}(\text{SP})_3$  (5).** A clear red solution of  $\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\eta^5\text{-C}_5\text{H}_5)$  (0.22 g, 0.44 mmol) in toluene (5 mL) was added to a solution of SP (0.51 g, 1.77 mmol) in toluene (5 mL). The color changed immediately to yellow, but the mixture was stirred overnight to ensure complete reaction. The volume was reduced to about half under reduced pressure, and pentane (20 mL) was added to give a yellow precipitate. This was filtered off, washed with pentane ( $3 \times 10$  mL), and dried in vacuo to give 5 (0.35 g, 81%), mp  $130\text{--}135^\circ\text{C}$ . The compound can be recrystallized from toluene/pentane. Its NMR spectra are described in the text.

Anal. Calcd for  $\text{C}_{60}\text{H}_{51}\text{P}_3\text{Pd}$ : C, 74.2; H, 5.3; P, 9.6; mol wt, 971. Found: C, 74.4; H, 5.3; P, 9.3; mol wt (by osmometry in toluene at  $37^\circ\text{C}$ ), 471.

**Protonation of  $\text{Pd}(\text{SP})_2$ .** A solution of 4 (0.050 g, 0.073 mmol) in ether (20 mL) was cooled to  $-30^\circ\text{C}$  and treated with 43% aqueous  $\text{HBF}_4$  (0.02 mL). The mixture was allowed to warm to room temperature. The white solid that had separated was removed by filtration, washed with ether ( $3 \times 5$  mL), and dried in vacuo to give *trans*- $[\text{Pd}\{\text{o-CH}(\text{CH}_3)\text{C}_6\text{H}_4\text{PPh}_2\}(\text{SP})]\text{BF}_4$  (6) (0.45 g, 80%):  $^1\text{H}\{^{31}\text{P}\}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 5.50 (d,  $\text{H}^2$ ), 4.70 (d,  $\text{H}^3$ ,  $J_{12} = 8.0$  Hz,  $J_{13} = 15.0$  Hz), 4.20 (q,  $\text{CHCH}_3$ ), 1.10 (d,  $\text{CHCH}_3$ ,  $J_{\text{HH}} = 7.5$  Hz,  $J_{\text{PH}} = 7.5$  Hz), signal due to  $\text{H}^1$  probably beneath aromatic resonances;  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\delta$ ,  $\text{CHCl}_3/\text{CDCl}_3$ ) 48.4, 31.2 (AB,  $J_{\text{AB}} = 326$  Hz).

**Crystallography.** Crystals of 4 suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into a toluene solution of the complex under a nitrogen atmosphere. Crystals are air-sensitive and were coated with Araldite prior to data collection.

**Crystal data:**  $\text{C}_{40}\text{H}_{34}\text{P}_2\text{Pd}$  (mol wt 683.1); triclinic, space group  $P\bar{1}$ ;  $a = 21.456$  (3) Å,  $b = 9.483$  (2) Å,  $c = 9.202$  (2) Å,  $\alpha = 60.84$  (1)°,  $\beta = 87.67$  (1)°,  $\gamma = 81.12$  (2)°,  $V = 1614$  Å<sup>3</sup>,  $D_{\text{meas}} = 1.40$  (1),  $D_{\text{calcd}} = 1.41$  g cm<sup>-3</sup>;  $Z = 2$ ;  $F(000) = 700$ ;  $\mu(\text{Mo K}\alpha) = 6.95$  cm<sup>-1</sup>; specimen crystal dimensions  $0.08 \times 0.22 \times 0.12$  mm, developed forms {100} {010} {001} {101}; Picker diffractometer;  $t = 294$  K; graphite monochromated Mo K $\alpha$  radiation;  $\theta$ - $2\theta$  scan mode;  $2 < 2\theta < 55^\circ$ ;  $\pm h, -k, \pm l$ ; 8939 reflections including standards; crystal degradation<sup>11</sup> 4%; analytical absorption correction;<sup>12</sup> maximum transmission 0.96; minimum transmission 0.92; unique reflections accepted ( $I \geq 3\sigma(I)$ ) 5536.

**Structure Solution and Refinement.** The structure was solved by conventional heavy-atom methods and refined by full-matrix least-squares analysis<sup>13</sup> based on  $F$ , with reflection weights  $w = [\sigma^2(F) + 0.0005F^2]^{-1}$ . Scattering factors, with anomalous dispersion corrections, were taken from ref 14. Anisotropic thermal parameters were specified for non-hydrogen atoms. Hydrogen atoms of the coordinated vinyl group were located by difference synthesis and refined ( $x, y, z, B$ ); other hydrogen atoms were located by calculation ( $\text{C-H} = 0.95$  Å;  $B_{\text{H}} = 1.1B_{\text{C}}$ ). At convergence  $R = 0.032$ ,  $R_w = 0.036$ ,  $S = 1.07$ , shift/error  $< 0.2$ , and  $\Delta\rho < \pm 0.32$  e Å<sup>-3</sup> for 5536 reflections and 400 variable parameters. Final atom coordinates are listed in Table I and selected bond lengths and bond angles in Table II. A comprehensive bond length and angle listing, including comparative values for  $\text{Ni}(\text{SP})_2$  and  $\text{Pt}(\text{SP})_2$ ,<sup>9</sup> has been deposited, along with listings of hydrogen atom coordinates, anisotropic thermal

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Table I. Atomic Coordinates for Pd(*o*-CH<sub>2</sub>=CHC<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>

atom	x/a	y/b	z/c
Pd	0.23135 (1)	0.47325 (3)	0.36053 (3)
P(1)	0.33259 (3)	0.43121 (9)	0.28080 (9)
P(2)	0.15326 (3)	0.66032 (9)	0.17024 (9)
C(1)	0.3621 (1)	0.6033 (4)	0.1018 (3)
C(2)	0.3190 (1)	0.7247 (4)	-0.0175 (4)
C(3)	0.3377 (2)	0.8578 (4)	-0.1543 (4)
C(4)	0.4004 (2)	0.8746 (5)	-0.1735 (4)
C(5)	0.4438 (2)	0.7559 (6)	-0.0565 (5)
C(6)	0.4257 (2)	0.6205 (5)	0.0799 (4)
C(7)	0.3373 (1)	0.2762 (4)	0.2150 (3)
C(8)	0.3545 (2)	0.2997 (5)	0.0609 (5)
C(9)	0.3532 (2)	0.1781 (6)	0.0199 (6)
C(10)	0.3376 (2)	0.0315 (5)	0.1318 (6)
C(11)	0.3200 (2)	0.0064 (5)	0.2849 (5)
C(12)	0.3194 (2)	0.1278 (4)	0.3265 (4)
C(13)	0.4002 (1)	0.3508 (4)	0.4317 (3)
C(14)	0.4509 (1)	0.2422 (4)	0.4243 (4)
C(15)	0.5032 (1)	0.1857 (4)	0.5312 (4)
C(16)	0.5057 (1)	0.2346 (5)	0.6478 (4)
C(17)	0.4565 (2)	0.3390 (5)	0.6584 (4)
C(18)	0.4032 (1)	0.4016 (4)	0.5500 (4)
C(19)	0.3526 (2)	0.5147 (5)	0.5686 (5)
C(20)	0.3573 (2)	0.6060 (5)	0.6345 (5)
C(21)	0.1543 (1)	0.7016 (4)	-0.0457 (3)
C(22)	0.1827 (2)	0.5748 (4)	-0.0728 (4)
C(23)	0.1890 (2)	0.5968 (5)	-0.2316 (5)
C(24)	0.1680 (2)	0.7454 (6)	-0.3669 (5)
C(25)	0.1398 (2)	0.8726 (5)	-0.3427 (4)
C(26)	0.1332 (2)	0.8508 (4)	-0.1829 (4)
C(27)	0.1269 (1)	0.8591 (4)	0.1556 (3)
C(28)	0.1714 (2)	0.9615 (5)	0.1199 (6)
C(29)	0.1571 (2)	1.1081 (5)	0.1197 (7)
C(30)	0.0984 (2)	1.1524 (5)	0.1630 (5)
C(31)	0.0540 (2)	1.0527 (5)	0.2003 (5)
C(32)	0.0679 (2)	0.9073 (4)	0.1955 (4)
C(33)	0.0874 (1)	0.5446 (4)	0.2529 (4)
C(34)	0.0325 (1)	0.5679 (4)	0.1627 (4)
C(35)	-0.0128 (1)	0.4677 (5)	0.2349 (4)
C(36)	-0.0033 (1)	0.3429 (5)	0.3977 (4)
C(37)	0.0505 (1)	0.3208 (4)	0.4886 (4)
C(38)	0.0966 (1)	0.4196 (4)	0.4184 (3)
C(39)	0.1533 (1)	0.4031 (4)	0.5194 (4)
C(40)	0.2010 (2)	0.2696 (5)	0.5892 (5)

Table II. Selected Bond Distances (Å) and Bond Angles (deg) in Pd(*o*-CH<sub>2</sub>=CHC<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub> (4)

Bond Distances			
Pd-P(1)	2.303 (1)	P(2)-C(27)	1.823 (3)
Pd-P(2)	2.305 (1)	P(2)-C(33)	1.831 (3)
Pd-C(39)	2.141 (3)	C(18)-C(19)	1.470 (5)
Pd-C(40)	2.213 (4)	C(19)-C(20)	1.293 (5)
P(1)-C(1)	1.842 (3)	C(33)-C(38)	1.399 (4)
P(1)-C(7)	1.831 (3)	C(38)-C(39)	1.503 (4)
P(1)-C(13)	1.846 (3)	C(39)-C(40)	1.387 (5)
P(2)-C(21)	1.828 (3)	C-H(olefin) <sup>a</sup>	0.98 (4)
Bond Angles			
P(1)-Pd-P(2)	121.36 (3)	C(38)-C(39)-C(40)	126.0 (3)
P(1)-Pd-MPV <sup>b</sup>	135.2 (1)	C(38)-C(39)-H(39)	113 (2)
P(2)-Pd-MPV <sup>b</sup>	100.3 (1)	C-C-H(olefin) <sup>a</sup>	118 (2)
Pd-P(2)-C(33)	98.5 (1)	H-C-H(olefin) <sup>a</sup>	121 (3)
P(2)-C(33)-C(38)	114.7 (2)		
C(18)-C(19)-C(20)	127.5 (3)	C(38)-C(39)-H(39) $\wedge$	
C(33)-C(38)-C(39)	119.7 (3)	H(401)-C(40)-H(402)	32 (3)

<sup>a</sup>Coordinated olefin group only. <sup>b</sup>MPV is the midpoint of the C-(39)-C(40) bond.

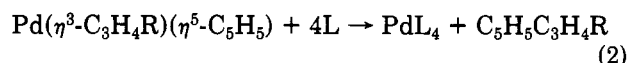
parameters, hydrogen atom parameters, and structure factor amplitudes. The atomic nomenclature is defined in the ORTEP<sup>15</sup> diagram (Figure 1).

## Results

The palladium complex Pd(SP)<sub>2</sub> proved to be more difficult to prepare than the corresponding nickel and

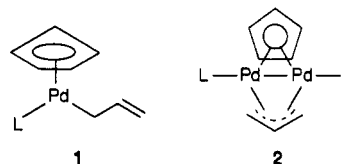
platinum compounds. Attempted reduction of PdCl<sub>2</sub>(SP) in the presence of SP with 1% sodium amalgam gave metallic palladium. No characterizable products were obtained when PdCl<sub>2</sub>(SP) and SP were treated with reducing agents such as hydrazine in Me<sub>2</sub>SO at 140 °C or zinc dust or when bis(2,4-pentanedionato)palladium(II) was reduced with diethylethoxyaluminum in the presence of SP, although these methods can be used to make Pd-(PPh<sub>3</sub>)<sub>4</sub>.<sup>16-19</sup> A mixture of products, including Pd(SP)<sub>2</sub> and Pd(SP)<sub>3</sub> (see below), was obtained on treatment of the dibenzylideneacetone complex Pd<sub>2</sub>(dba)<sub>3</sub>dba with SP; this precursor can also be used to make Pd(PPh<sub>3</sub>)<sub>4</sub>.<sup>20</sup> Success was finally achieved by starting with the  $\eta^3$ -allylic complex Pd( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>).

Werner and co-workers<sup>21,22</sup> have shown that  $\eta^3$ -allylic complexes of general formula Pd( $\eta^3$ -C<sub>3</sub>H<sub>4</sub>R)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) react with tertiary phosphines or phosphites (L) in excess to give PdL<sub>4</sub> (eq 2). If the ligand to metal ratio is 1:1, interme-



R = H, various alkyl groups, Cl

mediate  $\eta^1$ -allyl complexes 1 can be detected by <sup>1</sup>H NMR



spectroscopy,<sup>22</sup> but these decompose to give binuclear palladium(I) complexes 2.<sup>23</sup> We find that Pd( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) reacts with an excess of SP in toluene at -70 °C to give, after addition of pentane, an air-sensitive and thermally unstable solid of empirical formula Pd-(C<sub>3</sub>H<sub>5</sub>)(C<sub>5</sub>H<sub>5</sub>)(SP) (3). The IR spectrum, measured in a KBr disk at 0 °C, shows a band at 1620 cm<sup>-1</sup> indicative of a free double bond, but the <sup>1</sup>H NMR spectrum is very complicated, temperature-dependent, and not completely reproducible. In toluene-*d*<sub>3</sub> at -80 °C the main features are a pair of C<sub>5</sub>H<sub>5</sub> singlets in the region of  $\delta$  6.1-6.2 whose relative intensity varies with different preparations, a pair of doublets due to the  $\beta$ -vinyl protons of monodentate SP at  $\delta$  5.6 and 4.9 ( $J$  = 16 and 11 Hz, respectively), a doublet at  $\delta$  3.5 overlapping a broad multiplet, a broad multiplet at ca.  $\delta$  2.5, and several broad multiplets at  $\delta$  1.0-1.4. The relative intensities are difficult to measure accurately but are approximately in the ratio 17:10:5:5:27. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum in toluene at -80 °C shows two sharp singlets at  $\delta$  17.9 and 24.0 in ca. 4:1 intensity ratio; the latter peak decreases in intensity as the solution is allowed to warm to -30 °C. The <sup>1</sup>H NMR spectrum broadens as the solution is allowed to warm to room temperature and the sample then decomposes. Although structures 3a-c

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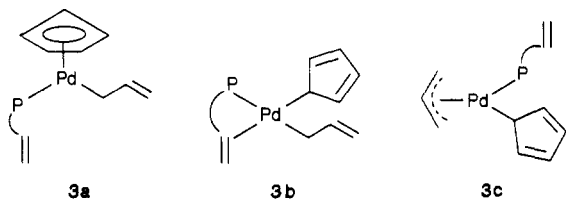
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are obvious suggestions for the species that might be present in solution, they do not readily account for all the features observed in the  $^1\text{H}$  NMR spectrum, so the nature of **3** is unresolved. However, **3** reacts with exactly 1 mol equiv of SP at room temperature to give the required compound Pd(SP)<sub>2</sub> (**4**) as a yellow, air-sensitive solid. The same compound can also be made directly from Pd( $\eta^3\text{-C}_3\text{H}_5$ )( $\eta^5\text{-C}_5\text{H}_5$ ) and exactly 2 mol equiv of SP at room temperature. In both cases, the molar ratio of reactants is crucial because Pd(SP)<sub>3</sub> is formed in the presence of even a slight excess of SP (see below). In our experience, the second method is satisfactory only for fairly large scale preparations using 1 g or more of Pd( $\eta^3\text{-C}_3\text{H}_5$ )( $\eta^5\text{-C}_5\text{H}_5$ ); on a smaller scale, errors introduced in weighing this volatile material can cause problems.

**4** is less soluble than Ni(SP)<sub>2</sub> or Pt(SP)<sub>2</sub> in benzene, toluene, and ether. It is monomeric in toluene by osmometry and in the solid state by X-ray crystallography (see below). Over a period of months the solid compound decomposes, even under argon, to give a pale yellow solid of unknown constitution that is insoluble in toluene and THF. This material shows no free vinyl absorption in the IR spectrum, and, unlike **4**, it does not react with SP to give Pd(SP)<sub>3</sub>. The 70-eV mass spectrum of **4** shows no parent ion, only fragments arising from SP. The IR spectrum in a KBr disk contains a weak band at 1620 cm<sup>-1</sup>, suggesting that at least one of the vinyl groups in **4** is uncoordinated, and this is confirmed by the single-crystal X-ray analysis.

**Structure of Pd(SP)<sub>2</sub> (4).** The molecular structure is illustrated in Figure 1. The complex contains one bidentate SP ligand and one monodentate P-bonded ligand; if the coordination centers are taken to be the two phosphorus atoms and the midpoint of the coordinated vinyl group (MPV), the geometry about the palladium atom is approximately trigonal [P(1)-Pd-P(2) = 121.36 (3)°, P-Pd-MPV = 100.3 (1) (chelate), 135.2 (1)°]. However, the palladium atom is displaced 0.22 Å from the P1, P2, MPV coordination plane toward the  $\alpha$ -hydrogen atom [H(19)] of the uncoordinated vinyl group. H(19) thus completes a distorted tetrahedral array of "ligands" about the metal atom. With the assumption that the C(19)-H(19) distance is 1.08 Å, the calculated Pd...H distance is 2.46 Å, intermediate between those to the proximal hydrogen atoms in *trans*-PdBr[C<sub>4</sub>(CO<sub>2</sub>Me)<sub>4</sub>H](PPh<sub>3</sub>)<sub>2</sub> (2.3 Å; hydrogen atom at apex of square pyramid)<sup>24</sup> and in Pd(P-*t*-Bu<sub>2</sub>Ph)<sub>2</sub> (2.70, 2.83 Å).<sup>25</sup> The interaction undoubtedly is attractive because rotation about any of the three connecting single bonds would remove or modify it.<sup>26</sup> The dihedral angles P-Pd-P  $\wedge$  MPV-Pd-H(19) and P(1)-Pd-H(19)  $\wedge$  P(2)-Pd-MPV (53.3 and 66.9°, respectively) are fairly similar to those characterizing the distorted tetrahedron in Pt(SP)<sub>2</sub> [P-Pt-P  $\wedge$  MPV(1)-Pt-MPV(2) (61.8°) and P(1)-Pt-MPV(1)  $\wedge$  P(2)-Pt-MPV(2) (73.6°)].<sup>27</sup> There are no

unusual intermolecular contacts.

In trigonal-planar d<sup>10</sup> metal-olefin complexes the double bond is expected, on electronic grounds, to lie in the plane.<sup>28,29</sup> In **4** the dihedral angle between the planes P(1)-Pd-P(2) and C(39)-Pd-C(40) is 24.7 (2)°, but the deviation from planarity cannot be described simply by a twist of these two planes since carbon atoms C(39) and C(40) are each displaced to the same side of the P(1)-Pd-P(2) plane (by 0.39 and 0.82 Å, respectively). Similar distortions have been observed in other trigonal olefin complexes containing tertiary phosphines, e.g. Ni(C<sub>2</sub>H<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub>,<sup>30</sup> Ni(C<sub>2</sub>H<sub>4</sub>)[P(O-*o*-tol)<sub>3</sub>]<sub>2</sub>,<sup>31</sup> Ni(CH<sub>2</sub>=CHCN)[P(O-*o*-tol)<sub>3</sub>]<sub>2</sub>,<sup>31</sup> Ni(PhCOCH=CHCO<sub>2</sub>Me)(PPh<sub>3</sub>)<sub>2</sub>,<sup>32</sup> and Pt(*p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>-*p*)(PPh<sub>3</sub>)<sub>2</sub>,<sup>33</sup> and have been ascribed to nonbonded interactions. In the case of **4**, the deformation presumably arises from the bonding character of the Pd...H19 interaction and the concomitant tendency to tetrahedral coordination of the metal atom.

The Pd-P distances are equal within experimental error [Pd-P(1) = 2.3029 (7) Å, Pd-P(2) = 2.3054 (7) Å] and are shorter than those observed in Pd(CH<sub>2</sub>=C=CH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub> [2.314 (2), 2.324 (2) Å]<sup>34</sup> and in Pd(MeO<sub>2</sub>CC<sub>2</sub>CO<sub>2</sub>Me)(PPh<sub>3</sub>)<sub>2</sub> [2.321 (2), 2.330 (2) Å].<sup>35</sup> The equality of the Pd-P distances in **4** is unexpected, since in Fe(CO)<sub>2</sub>(SP)<sub>2</sub> the Fe-P distance in the chelate SP ligand is about 0.034 Å shorter than that in the monodentate SP ligand.<sup>36</sup>

The distance from the palladium atom to the terminal carbon atom of the vinyl group [Pd-C(40) = 2.213 (4) Å] is significantly longer ( $\Delta/\sigma \approx 14$ ) than the corresponding distance to the inner carbon atom [Pd-C(39) = 2.141 (3) Å]. This type of asymmetry is evident, though to a lesser extent, in the coordinated vinyl groups of Pt(SP)<sub>2</sub>.<sup>9</sup> Surprisingly, the opposite asymmetry is observed in the planar platinum(II) complexes PtMe<sub>2</sub>(SP),<sup>37</sup> Pt(CF<sub>3</sub>)<sub>2</sub>(SP),<sup>37</sup> and PtCl<sub>2</sub>(PhCH=CH<sub>2</sub>)(*p*-tolyl)MeSO,<sup>38</sup> and for one of the vinyl groups in Ni(SP)<sub>2</sub>.<sup>9</sup>

The Pd-C bond lengths to the coordinated vinyl group in **4** [Pd-C(39) = 2.141 (3) Å; Pd-C(40) = 2.213 (4) Å] are similar to the corresponding distance of 2.23 (2) Å (av) observed in Pd(DBA)<sub>3</sub><sup>39</sup> but are greater than the value of 2.090 (8) Å (av) found in Pd(CH<sub>2</sub>=C=CH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>.<sup>34</sup> Distances to the other vinyl group [Pd...C(19) = 3.470 (3) Å; Pd...C(20) = 4.466 (4) Å] show that there is no metal-olefin bonding in this case. The C=C bond of the coordinated vinyl group [1.387 (5) Å] is, as expected, lengthened on coordination, cf. 1.38 (2) Å in Pd(DBA)<sub>3</sub><sup>39</sup> and 1.401 (11) Å in Pd(CH<sub>2</sub>=C=CH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>.<sup>34</sup> Although the difference from the values of 1.400 (6) and 1.417 (11) Å in Ni(SP)<sub>2</sub> and Pt(SP)<sub>2</sub>, respectively, is not statistically significant, the trend is consistent with a weaker metal-olefin interaction in the palladium compound. A similar com-

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(26) C(20) is already 0.41 Å out of the C(13)-C(18) ring plane.

(27) Values for Ni(SP)<sub>2</sub> are P-Ni-P  $\wedge$  MPV(1)-Ni-MPV(2) = 69.0° and P(1)-Ni-MPV(1)  $\wedge$  P(2)-Ni-MPV(2) = 79.3°.

ment applies to the coordinated olefin bend-back angles  $\alpha^{40}$  [ $\text{Pd}(\text{SP})_2$ , 31 (4)°;  $\text{Ni}(\text{SP})_2$ , 36 (4)°;  $\text{Pt}(\text{SP})_2$ , 47 (6)°].

Surprisingly, and for no obvious reason, the C=C distance of the uncoordinated vinyl group in **4** [1.293 (5) Å] is considerably less than the standard value for a free vinyl group [1.335 (5) Å] and less than the corresponding value for the monodentate SP ligand in  $\text{Fe}(\text{CO})_2(\text{SP})_2$  [1.339 (10) Å].<sup>36</sup> Vibration amplitudes for the relevant carbon atoms in **4** are unexceptional, and the estimated C=C shortening due to riding motion [C(20) on C(19)] is only ca. 0.006 Å. The C-C distances adjacent to the free and coordinated vinyl groups of **4** also differ significantly [1.470 (5) and 1.503 (4) Å, respectively]. Similar distances [1.496 (9) and 1.515 (8) Å, respectively] are found for the free and coordinated vinyl groups of  $\text{Fe}(\text{CO})_2(\text{SP})_2$ ;<sup>36</sup> they presumably reflect the expected increased conjugation to the free vinyl groups.

**Nature of  $\text{Pd}(\text{SP})_2$  in Solution.** In addition to sharp aromatic resonances in the region  $\delta$  6.3–7.5, the  $^1\text{H}$  NMR spectrum of **4** at room temperature contains a broad, unsymmetrical multiplet at  $\delta$  4.0 and a triplet at  $\delta$  6.2 in a ratio of about 2:1, attributable to  $\beta$ - and  $\alpha$ -vinyl protons ( $\text{H}^2$ ,  $\text{H}^3$ , and  $\text{H}^1$ ), respectively. The whole spectrum broadens at  $-50$  °C, and at  $-80$  °C it resolves into overlapping multiplets in the region  $\delta$  7.0–3.5. These resonances are still broad, and a limiting spectrum could not be obtained. However, in the  $^1\text{H}\{^{31}\text{P}\}$  NMR spectrum it is possible to distinguish a pair of doublets at  $\delta$  5.60 ( $J = 17$  Hz) and 5.15 ( $J = 12$  Hz) arising from  $\text{H}^2$  and  $\text{H}^3$  of a free vinyl group and a pair of doublets at  $\delta$  4.05 ( $J = 12$  Hz) and 3.85 ( $J = 14$  Hz). The last two doublets are not coupled to each other and probably belong to  $\text{H}^2$  or  $\text{H}^3$  of different coordinated vinyl groups. In general, despite the complexity of the spectrum, it is clear that the coordinated vinyl proton resonances are deshielded relative to the corresponding resonances of  $\text{Ni}(\text{SP})_2$  and  $\text{Pt}(\text{SP})_2$ , suggestive of weaker olefin binding in  $\text{Pd}(\text{SP})_2$ .

The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4** in  $\text{THF}-d_8$  at room temperature shows two broad singlets at  $\delta$  109.8 and 81.5 due to the vinyl carbon atoms  $\text{C}^1$  and  $\text{C}^2$ , respectively, the chemical shifts being intermediate between those for free SP ( $\delta$  125.7, 115.9) and for the nickel and platinum compounds [ $\delta$  82.7, 54.7 (Ni);  $\delta$  64.8, 32.1 (Pt)]. At  $-80$  °C the spectrum shows four broad singlets, a pair at  $\delta$  106.2 and 78.3 assigned to coordinated vinyl carbon atoms, and a pair at  $\delta$  122.5 and 115.5 due to uncoordinated vinyl carbon atoms; the intensity ratio of these two pairs of resonances is about 1.5:1. Thus, both  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **4** at  $-80$  °C indicate the presence of free and coordinated vinyl groups, in agreement with the crystal structure, and show that these groups exchange rapidly on the NMR time scale at room temperature.

The variable-temperature  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **4** shows unexpected behavior (Figure 2). At room temperature in  $\text{CD}_2\text{Cl}_2$  there is a singlet at  $\delta$  25.2 (width at half-height 14 Hz) which broadens on cooling to  $-30$  °C. At  $-50$  °C an AB pattern appears on the low-frequency side of the singlet, and at  $-80$  °C both resonances have sharpened considerably, the AB pattern [ $\delta(\text{P}_\text{A})$  21.2,  $\delta(\text{P}_\text{B})$  20.2,  $J_{\text{AB}} = \text{ca. } 37$  Hz] being about twice as intense as the singlet at this temperature. The broadness and slight asymmetry of the AB pattern show that the limiting spectrum has not been reached at  $-80$  °C. The magnitude of  $^2J_{\text{PP}}$  is similar to those observed in tetrahedral platinum(0) complexes containing inequivalent phosphorus atoms, e.g.  $\text{Pt}(\text{PPh}_3)_2(\text{SP})$  (50 Hz),<sup>41</sup> so the species responsible for the

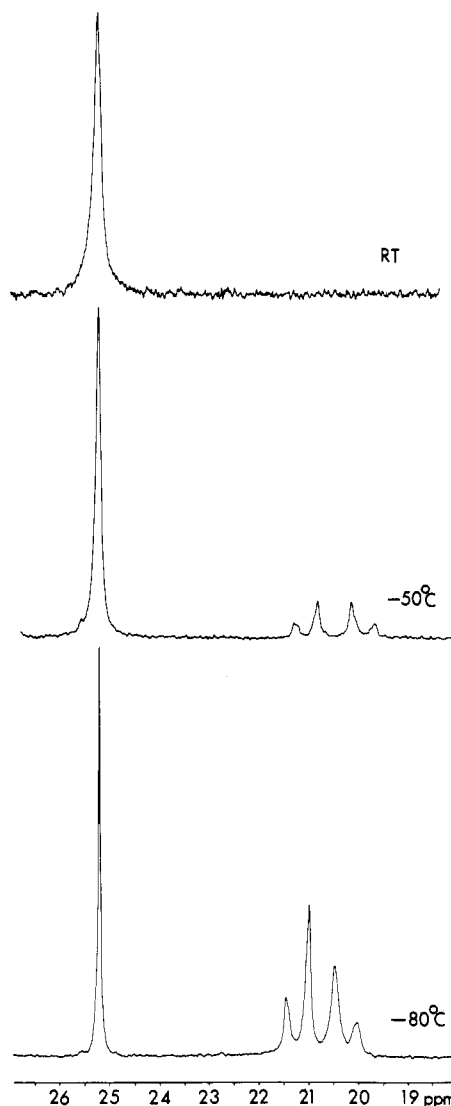


Figure 2. Variable-temperature  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $\text{Pd}(\text{SP})_2$  (**4**).

AB pattern presumably is the trigonal complex **4a** present in the solid.

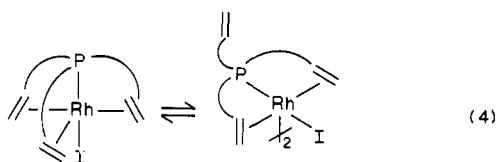
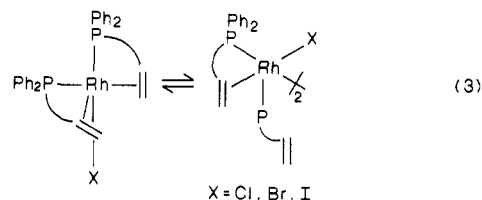
In toluene- $d_8$  and THF the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum behaves similarly as the temperature is changed, although there are small changes in chemical shift and the AB quartet at  $-80$  °C in both solvents is less well-resolved than in  $\text{CD}_2\text{Cl}_2$ .

The nature of the species **4b** containing equivalent phosphorus atoms is more problematical, and two limiting possibilities can be imagined. One is a tetrahedral complex in which both vinyl groups are coordinated, as in  $\text{Ni}(\text{SP})_2$  and  $\text{Pt}(\text{SP})_2$ .<sup>1</sup> The other is a two-coordinate complex in which only the phosphorus atoms are coordinated and both vinyl groups are free. The first alternative seems unlikely because increasing temperature would not be expected to favor binding of the second vinyl group. There are several IR and variable-temperature NMR studies of "olefin-off/olefin-on" equilibria in solutions of rhodium(I) complexes containing flexible olefinic tertiary phosphines, e.g.  $\text{RhCl}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}=\text{CH}_2)_2$  (eq 3)<sup>42</sup> and  $\text{RhI}\{\text{P}(\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)_3\}$  (eq 4),<sup>43</sup> which demonstrate that olefin

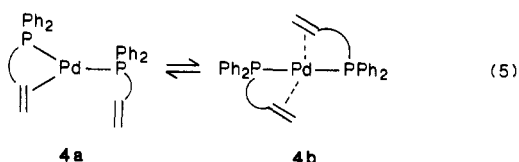
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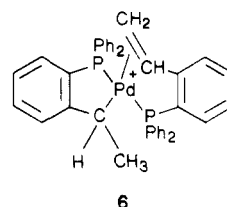
coordination is favored at lower temperatures. On the other hand, the low-temperature  $^1\text{H}$  NMR spectrum of **4** is more complex than would be expected on the basis of the second alternative. However, it should be noted that the few structures that have been determined of two-coordinate complexes of palladium(0) and platinum(0) containing bulky monodentate tertiary phosphines are not well-understood. Thus, although the palladium atom in  $\text{Pd}(\text{P}-t\text{-Bu}_2\text{Ph})_2$  is almost linearly coordinated ( $\text{P}-\text{Pd}-\text{P} = 176^\circ$ ); there are secondary interactions to adjacent phenyl and *tert*-butyl C-H bonds.<sup>25,44</sup> In  $\text{Pd}(\text{PCy}_3)_2$  and  $\text{Pt}(\text{PCy}_3)_2$ , the P-M-P bond angles ( $158^\circ$  and  $160^\circ$ , respectively) are considerably distorted from the expected value of  $180^\circ$ , for no apparent reason.<sup>25,45</sup> These results may indicate that the linear P-M-P system has a shallow potential surface for bending,<sup>46</sup> and they lead us to suggest that **4b** is essentially a two-coordinate Pd(0) complex in which the metal atom interacts weakly with both pendant vinyl groups. The equilibrium between **4a** and **4b**, which is rapid on the NMR time scale at room temperature, can be represented as shown in eq 5.



In contrast with  $\text{Ni}(\text{SP})_2$  and  $\text{Pt}(\text{SP})_2$ , **4** reacts readily with more SP to give  $\text{Pd}(\text{SP})_3$  (**5**) as a yellow, air-sensitive solid that is readily soluble in most organic solvents except alkanes. **5** can also be made by reaction of the appropriate quantity of SP with either  $\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\eta^5\text{-C}_5\text{H}_5)$  or with the unstable intermediate **3**. Its 70-eV mass spectrum shows only fragments arising from SP and its IR spectrum exhibits a band at  $1620\text{ cm}^{-1}$  due to free vinyl groups. The  $^1\text{H}$  NMR spectrum in toluene- $d_8$  shows a pattern typical of uncoordinated vinyl groups at  $\delta$  7.58 (dd,  $\text{H}^1$ ), 5.06 (d,  $\text{H}^3$ ), and 4.72 (d,  $\text{H}^2$ ) ( $J_{12} = 11.0\text{ Hz}$ ,  $J_{13} = 17.5\text{ Hz}$ ), although we have observed that different samples, even when analytically pure, give slightly different chemical shifts and line widths. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **5** at room temperature in toluene- $d_8$  consists of a broad singlet ( $\Delta\nu_{1/2} = \text{ca. } 250\text{ Hz}$ ), but this chemical shift also varies with sample in the range  $\delta$  11–18. When the solution is cooled to  $-80^\circ\text{C}$ , the signal sharpens somewhat ( $\Delta\nu_{1/2} = \text{ca. } 85\text{ Hz}$ ) and moves to higher frequency ( $\delta$  18–20); in one experiment a singlet due to free SP at  $\delta$  -15 was also ob-

served. We have not pursued this further, but we suspect that the erratic behavior of the  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra is caused by rapid exchange with small but variable amounts of free SP in samples of **5**. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra also often show a temperature-invariant singlet at  $\delta$  28, which may be due to the phosphine oxide  $o\text{-CH}_2=\text{CHC}_6\text{H}_4\text{P}(\text{O})\text{Ph}_2$  formed by Pd(0)-catalyzed air oxidation of SP, cf. the corresponding oxidation of  $\text{PPh}_3$  catalyzed by  $\text{M}(\text{PPh}_3)_3$  ( $\text{M} = \text{Ni, Pd, Pt}$ );<sup>47</sup> this may account for the apparently low molecular weight of **5** found by osmometry (see Experimental Section). The spectroscopic evidence is consistent with a trigonal-planar structure for **5** in which SP is coordinated only through phosphorus, cf. the structure of  $\text{Pt}(\text{PPh}_3)_3$ .<sup>48</sup>

Treatment of **4** in ether at  $-30^\circ\text{C}$  with 1 equiv of aqueous  $\text{HBF}_4$  immediately precipitates the  $\text{BF}_4$  salt of the chelate ( $\sigma$ -alkyl)palladium(II) cation **6** as an air-stable, off-white solid that is soluble in dichloromethane, chloroform, and acetone. The presence of a five-membered ring is confirmed by a doublet at  $\delta$  1.10 ( $J_{\text{HH}} = 7.5\text{ Hz}$ ) and a multiplet at  $\delta$  4.20 in the  $^1\text{H}$  NMR spectrum due to the methyl and methine protons respectively. The  $\beta$ -vinyl proton resonances appear in the  $^1\text{H}\{^{31}\text{P}\}$  NMR spectrum as a pair of doublets at  $\delta$  5.50 ( $\text{H}^2$ ) and 4.70 ( $\text{H}^3$ ) ( $J_{12} = 8.0\text{ Hz}$ ,  $J_{13} = 15.0\text{ Hz}$ ); the signal due to the  $\alpha$ -proton  $\text{H}^1$  is probably obscured by the aromatic resonances. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum is an AB quartet with  $^2J_{\text{pp}} = 326\text{ Hz}$  indicative of mutually trans phosphorus atoms. The spectroscopic data are similar to those of the corresponding platinum(II) complex obtained as the final, thermodynamically stable product of protonation of  $\text{Pt}(\text{SP})_2$ .<sup>1</sup> However, in the case of  $\text{Pd}(\text{SP})_2$ , there is no evidence for the formation of an intermediate isomer of **6** containing cis phosphorus atoms.



## Discussion

In contrast to  $\text{Ni}(\text{SP})_2$  and  $\text{Pt}(\text{SP})_2$ , which are tetrahedral 18e complexes,  $\text{Pd}(\text{SP})_2$  in the solid state is a trigonal 16e complex in which only one vinyl group is coordinated. The electron deficiency is partially relieved by the presence of the  $\alpha$ -hydrogen atom  $\text{H}(19)$  of the uncoordinated vinyl group in an approximately tetrahedral site at ca.  $2.46\text{ \AA}$  from the metal atom. Crabtree et al.<sup>49</sup> have recently suggested that the extent of  $\text{C}-\text{H}\cdots\text{M}$  interaction, along the  $\text{C}-\text{H} + \text{M} \rightarrow \text{C}-\text{H}-\text{M}$  reaction trajectory, is well-represented by  $d_{\text{bp}}$ , the distance from the metal atom to the centroid of the C-H bonding electron pair, or, allowing for differing metal radii, by  $r_{\text{bp}} = d_{\text{bp}} - r_{\text{covalent}}^{\text{M}}$ .  $d_{\text{bp}}$  and  $r_{\text{bp}}$  values for  $\text{Pd}(\text{SP})_2$  ( $2.74$  and  $1.46\text{ \AA}$ ) are indicative of a relatively weak interaction. Corresponding to  $r_{\text{bp}} \cong 1.46\text{ \AA}$  the  $\text{C}-\text{H}\cdots\text{M}$  angle is expected to be about  $130^\circ$ .<sup>49</sup> In  $\text{Pd}(\text{SP})_2$   $\text{C}-\text{H}\cdots\text{M}$  is substantially more linear ( $154.3^\circ$ ),

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apparently because of geometric constraints.

The structural difference between the palladium complex on the one hand and the nickel and platinum complexes on the other clearly illustrate the fact that, of the three zerovalent metals of the triad, palladium has the lowest affinity for olefins. Spectroscopic and chemical evidence suggests that even the one coordinated vinyl group of Pd(SP)<sub>2</sub> is more weakly bound than the vinyl groups of Ni(SP)<sub>2</sub> and Pt(SP)<sub>2</sub>. Thus, the <sup>1</sup>H and <sup>13</sup>C nuclei of the coordinated vinyl groups of **4** are less shielded than those of Ni(SP)<sub>2</sub> and Pt(SP)<sub>2</sub>, even at -80 °C, where the exchange between free and coordinated vinyl groups has been slowed, and the C=C distance and bend-back angle of the coordinated vinyl group in **4** is somewhat less than those in Ni(SP)<sub>2</sub> and Pt(SP)<sub>2</sub>. In solution, the three-coordinate, 16e species present in the solid state is in equilibrium with an isomer which contains essentially two-coordinate, 14e palladium(0), although the "free" vinyl groups may interact weakly with the metal atom. Finally, the coordinated vinyl group of **4** is easily displaced by more SP to give Pd(SP)<sub>3</sub> (**5**), whereas the nickel(0) and platinum(0) analogues of **5** could not be made.

It has been shown<sup>50</sup> that the binding of ligands to the zerovalent d<sup>10</sup> elements can be correlated with the difference between the electron affinity (EA) and the d<sup>10</sup> → d<sup>9</sup> ionization potential of the elements. The electron affinity should parallel the tendency to form a strong σ-bond, whereas the ionization potential should correlate with the π-back-bonding ability. On this basis, the σ-bond strength is in the order Pt > Pd ≈ Ni and the π-bond strength is

in the order Ni > Pt ≈ Pd. The order of (EA - IP) is Ni > Pt > Pd, palladium(0) apparently being relatively weak at both σ- and π-bonding. The M-P distance in **4** [2.304 Å (av)] is significantly larger than that in Pt(SP)<sub>2</sub> [2.284 Å (av)], and a similar trend is evident from comparison of Pd(P-*t*-Bu<sub>2</sub>Ph)<sub>2</sub> [Pd-P = 2.285 (2) Å] with Pt(P-*t*-Bu<sub>2</sub>Ph)<sub>2</sub> [Pt-P = 2.252(1) Å]. Otsuka et al.<sup>25,46</sup> have estimated the covalent radii of Pd(0) and Pt(0) to be 1.35 and 1.38 Å, respectively, so the trend in M-P distances probably reflects the greater σ-bond strength of Pt(0)-P relative to Pd(0)-P.

As discussed in the previous paper,<sup>9</sup> the affinity of the divalent metal ions of the nickel triad for olefins is in the order Pt > Pd > Ni, so the fact that compound **6** formed by protonation of **4** is much more stable than the corresponding nickel compound is not surprising.

Finally, we note that the electron deficiency of Pd(SP)<sub>2</sub> causes it to be much more reactive than either Ni(SP)<sub>2</sub> or Pt(SP)<sub>2</sub> in oxidative addition reactions with organic halides; these reactions are described elsewhere.<sup>51</sup>

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**Supplementary Material Available:** A table of comparative bond lengths and bond angles for M(*o*-CH<sub>2</sub>=CHC<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub> (M = Ni, Pd, Pt) and tables of anisotropic thermal parameters and hydrogen atom parameters for Pd(*o*-CH<sub>2</sub>=CHC<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub> (**4**) (7 pages); a listing of structure factor amplitudes for **4** (29 pages). Ordering information is given on any current masthead page.

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## Group VI Open-Mode Dimers Based on a Binucleating Hexaphosphine Ligand System. Synthesis and Conformational Studies of *fac, fac*-M<sub>2</sub>(CO)<sub>6</sub>(eHTP) (M = Cr, Mo, W; eHTP = (Et<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>PCH<sub>2</sub>P(CH<sub>2</sub>CH<sub>2</sub>PET<sub>2</sub>)<sub>2</sub>)

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The reaction of 2 equiv of M(CO)<sub>6</sub> (M = Cr, Mo, W) with the hexatertiary phosphine (Et<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>PCH<sub>2</sub>P(CH<sub>2</sub>CH<sub>2</sub>PET<sub>2</sub>)<sub>2</sub>, eHTP, in refluxing xylene yields the binuclear complexes M<sub>2</sub>(CO)<sub>6</sub>(eHTP) (M = Cr, Mo, W). These complexes have been characterized by IR and <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy, elemental analysis, and X-ray crystallography. All three compounds are isomorphous and crystallize in the orthorhombic space group *Pcca* (*Z* = 4) with the following crystal data. Cr: *a* = 29.890 (4) Å, *b* = 8.102 (2) Å, *c* = 16.346 (2) Å, *V* = 3958 (2) Å<sup>3</sup>. Mo: *a* = 30.353 (3) Å, *b* = 8.153 (3) Å, *c* = 16.497 (2) Å, *V* = 4083 (2) Å<sup>3</sup>. W: *a* = 30.324 (3) Å, *b* = 8.137 (1) Å, *c* = 16.471 (6) Å, *V* = 4064 (2) Å<sup>3</sup>. The final discrepancy indices (*R* values) for these three structures are 0.038, 0.037, and 0.036, with quality of fit indicators of 1.15, 1.33, and 1.05 for the Cr, Mo, and W structures, respectively. The three dimer systems lie on a twofold rotation axis that passes through the central eHTP methylene bridge and have symmetric open-mode structures with M-M separations of 6.2872 (8) (Cr), 6.4687 (5) (Mo), and 6.4687 (5) Å (W). The local geometry about each metal center is a facial set of three carbonyl and three phosphine ligands with the expected angular deviations away from pure octahedral geometry caused by the tridentate phosphine donor set. Spectroscopic evidence and the results from van der Waals energy calculations are presented to show that the rotational conformation of these dimers about the eHTP methylene bridge in solution is different from that seen in the solid-state crystal structures.

Fragmentation remains a persistent problem in multimetallic complexes and continues to be a major stumbling

block to the development of these species as homogeneous catalysts. We have approached the fragmentation and