Scattering factors for the hydrogen atom were taken from Stewart et.[26]

The final full-matrix least-squares refinement converged to $R = \sum||F_o| - F_c|| / \sum|F_o| = 0.034$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(|F_o|^2]^{1/2} = 0.032$ with $w = 1/\sigma^2(F_o)$. The error in an observation of unit weight was $S = [\sum w(|F_o| - |F_c|)^2/(n - m)]^{1/2} = 1.9$ with $n = 3250$ observations and $m = 437$ variables. An analysis of variance showed no unusual trends. In the last cycle of refinement the shifts for all parameters were less than 0.76 (mean value 0.2σ).

A final difference Fourier map showed a residual electron density of 0.7 e/Å^3 near metal atoms. The final fractional atomic coordinates are listed in Table III.

Acknowledgment. We thank Dr. Astiê, Université des Sciences et Techniques du Languedoc, Montpellier, for recording the X-ray data.

Registry No. $Co_3(CO)_9[CC(O)OCHC]Co_2Fe(CO)_9]$, 113892-47-0; $[Co_3(CO)_9CCO][PF_6]$, 36834-91-0; $(PPh_4)[HFe(CO)_4]$, 103616-27-9; Fe, 7439-89-6; Co, 7440-48-4.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and bond lengths and angles (4 pages); a listing of structure factors (16 pages). Ordering information is given on any current masthead page.

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Tetrahedral Complexes of Nickel(0) and Platinum(0) Containing a Chelating Olefinic Tertiary Phosphine. Synthesis, Reactivity, and X-ray Crystal Structures of $M(o\text{-}CH_2{=}CHC_6H_4PPh_2)_2$ (M = Ni, Pt)

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Zerovalent metal complexes of general formula $M(SP)_2$ [M = Ni (1), Pt (2)] containing (2-vinylphenyl)diphenylphosphine (*o*-styryldiphenylphosphine, $o\text{-}CH_2{=}CHC_6H_4PPh_2$, abbreviated SP) have been prepared by reaction of SP with the bis(1,5-cyclooctadiene)metal complexes, $M(1,5\text{-}COD)_2$. The nickel complex **1** has also been made by reduction of anhydrous bis(2,4-pentanedionato)nickel(II) with triethylaluminum in the presence of SP. Spectroscopic studies [NMR (^{1}H, ^{13}C, ^{31}P) and IR] suggest that the phosphorus atoms and both vinyl groups are coordinated, both in solution and in the solid state. Crystals of **1** are monoclinic, space group $P2_1/n$, with $a = 13.432$ (2) Å, $b = 11.486$ (2) Å, $c = 21.630$ (3) Å, $\beta = 104.34$ (1)°, and $Z = 4$; those of $\mathbf{2}\cdot 0.5C_6H_5CH_3$ are triclinic, space group $P\bar{1}$, with $a = 11.245$ (7) Å, $b = 14.127$ (4) Å, $c = 14.417$ (2) Å, $\alpha = 119.05$ (2)°, $\beta = 110.62$ (1)°, $\gamma = 91.05$ (1)°, and $Z = 2$. The structures were solved by direct (**1**) and heavy-atom methods (**2**) and refined by least-squares methods to $R = 0.041$ and $R_w = 0.045$ for 3299 independent reflections (**1**) and to $R = 0.026$ and $R_w = 0.030$ for 5273 independent reflections (**2**). In both molecules the metal atom is coordinated in a distorted tetrahedron by two bidentate SP ligands, the average M–P distances being 2.199 Å (**1**) and 2.284 Å (**2**). In **1** one vinyl group is coordinated symmetrically [Ni–C(19) = 2.033 (4) Å, Ni–C(20) = 2.037 (5) Å] while the other is bound asymmetrically, the Ni–C_α bond length [Ni–C(39) = 2.059 (4) Å] being significantly longer than the Ni–C_β separation [Ni–C(40) = 2.034 (5) Å]. By contrast, both vinyl groups in **2** are coordinated asymmetrically, although the difference in the Pt–C distances in each vinyl group is only just statistically significant and is such that Pt–C_α < Pt–C_β. The C=C distances show the expected lengthening on coordination [1.400 (6) Å (**1**); 1.416 (6) Å (**2**)]. The relative ordering of the metal–olefin bond strengths in **1** and **2** cannot be inferred unambiguously from the trends in various vinyl group parameters, such as ^{1}H and ^{13}C chemical shifts and coupling constants, C=C bond lengths, and bend-back angles of the vinylic hydrogen atoms. Free and coordinated SP exchange more readily in **2** than in **1**. **2** reacts with HBF_4 or HPF_6 to give five-membered ring chelate (σ-alkyl)platinum(II) salts $[Pt(o\text{-}CH_3CHC_6H_4PPh_2)(SP)]Y$ (Y = BF_4, PF_6), as a mixture of cis and trans isomers **3a** and **3b**, respectively. An unstable nickel(II) analogue is formed similarly from **1**.

Introduction

Nickel, palladium, and platinum in their zero oxidation states form a range of monomeric complexes with π-acceptor ligands such as CO, isocyanides, olefins, and tertiary phosphines and phosphites.[1-6] The metal atom in these complexes can adopt an 18e, 16e, or 14e configuration, and the stereochemical arrangement may be, respectively, tetrahedral (ML_4), trigonal planar (ML_3), or linear (ML_2). In general, small, terminally bound ligands such as CO and phosphites favor the formation of ML_4, whereas bulky tertiary phosphines and laterally bound ligands such as olefins and acetylenes favor ML_3 or ML_2. In addition,

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higher coordination numbers seem to be attained more readily by nickel(0) than by either of its congeners, as is dramatically illustrated by the existence of $Ni(CO)_4$ and by the nonexistence under normal conditions of $Pd(CO)_4$ or $Pt(CO)_4$.

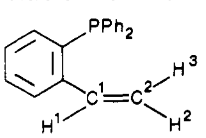
An especially well-studied set of compounds is that containing both tertiary phosphines and olefins or acetylenes, i.e. $M(olefin)(PR_3)_2$ and $M(olefin)_2(PR_3)$ (M = Ni, Pd, Pt), which are useful synthetic and catalytic precursors.[2-7] These compounds are trigonal-planar, the olefin usually lying almost in the coordination plane. Tolman et al.[8,9] have studied equilibria of the type shown in eq 1

$$M(PR_3)_3 + C_2H_4 \rightleftharpoons M(C_2H_4)(PR_3)_2 + PR_3 \qquad (1)$$
$$R = Ph, Et$$

and have shown that, in benzene at 25 °C, the equilibrium constant varies in the order M = Ni ≫ Pt > Pd. The nickel and platinum compounds $M(C_2H_4)(PPh_3)_2$ undergo intermolecular exchange with ethylene.[8,10] In the case of the platinum complex, the exchange occurs at an intermediate rate on the NMR time scale at room temperature via an associative mechanism (eq 2). For the nickel compound, exchange is rapid on the NMR time scale and the mechanism is again likely to be associative. The implied intermediate is a tetrahedrally coordinated bis(ethylene)bis(tertiary phosphine) metal complex, which has not been isolated or detected. However, there is spectroscopic evidence for η^2-C═C-bonded acrylonitrile complexes $Ni(CH_2{=}CHCN)_2(PR_3)_2$ (R = Me, *n*-Bu, OMe).[11] Recently, thermally labile tris(tertiary phosphine)(ethylene)nickel(0) complexes $Ni(C_2H_4)(Me_2PCH_2CH_2PMe_2)(PR_3)$ (R = Me, Cy, Ph) have been isolated, and the PPh_3 derivative has been shown by X-ray crystallography to contain tetrahedrally coordinated nickel.[12] Tetrafluoroethylene complexes of nickel(0) and platinum(0) of the type $M(C_2F_4)\{(PPh_2CH_2)_3CMe\}$ are also known to have a distorted tetrahedral geometry,[13,14] although these compounds may be better regarded as metallacyclopropanes.

$$Pt(C_2H_4)L_2 + C_2H_4{}^* \rightleftharpoons Pt(C_2H_4)(C_2H_4)^*L_2 \rightleftharpoons Pt(C_2H_4)^*L_2 + C_2H_4 \qquad (2)$$

In earlier papers[15] we have shown that the ligand (2-vinylphenyl)diphenylphosphine, *o*-$CH_2{=}CHC_6H_4PPh_2$ (sometimes called *o*-styryldiphenylphosphine and abbreviated SP), forms stable olefin complexes with many transition elements, olefin coordination being assisted by the chelate effect. All such compounds have had additional ligands such as halide, alkyl, or CO, and no complexes containing SP as the only ligand are known. This paper reports the preparation and structural characterization of tetrahedrally coordinated, chelate bis(olefin) complexes of nickel(0) and platinum(0), $M(SP)_2$ (M = Ni, Pt), while the following paper[16] discusses the palladium(0) compound $Pd(SP)_2$ and compares the binding of the olefinic ligand with these zerovalent elements.



SP

Experimental Section

All reactions and isolation of products were carried out in an atmosphere of dry nitrogen or argon with use of standard Schlenk techniques. Benzene, toluene, ether, and THF were distilled from sodium benzophenone ketyl under nitrogen, dichloromethane was distilled from calcium hydride under nitrogen, and *n*-pentane and *n*-hexane were dried over sodium wire and degassed before use. Deuteriated solvents for NMR studies were degassed by several freeze–thaw cycles.

Microanalyses and osmometric molecular weight determinations (Knauer vapor pressure osmometer) were carried out in the microanalytical laboratory of this School. Melting points were obtained on a Gallenkamp melting point apparatus in capillaries sealed under argon and are uncorrected.

The following instruments were used: Perkin-Elmer 225, 457, and 683, calibrated with polystyrene (IR); Varian HA100 (^1H NMR), JEOL FX200 (^1H NMR; ^{13}C NMR at 50.10 MHz with internal $(CH_3)_4Si$), Bruker B-KR322S (^{31}P NMR at 24.28 MHz with 85% H_3PO_4 as external reference), and Bruker CXP200 (^1H NMR; ^{13}C NMR at 50.29 MHz with internal $(CH_3)_4Si$; ^{31}P NMR at 80.98 MHz with 85% H_3PO_4 as external reference); VG-Micromass 7070F (medium resolution mass spectra).

Anhydrous bis(2,4-pentanedionato)nickel(II) was obtained by heating the dihydrate with toluene for 12 h and removing the water by azeotropic distillation.[17] The compounds (2-vinylphenyl)diphenylphosphine (SP),[18] $PtCl_2(SP)$,[19] $Ni(1,5\text{-}COD)_2$,[20] and $Pt(1,5\text{-}COD)_2$[21] were prepared by literature methods. The vinyl ^{13}C chemical shifts of SP, which have not been reported previously, are as follows: δ (CD_2Cl_2) 125.7 (C^1, J_{PC} = 4.3 Hz, J_{CH} = 156 Hz), 115.9 (C^2, J_{PC} = 1.7 Hz, J_{CH} = 156 Hz).

Preparations. (1) Bis{(2-vinylphenyl)diphenylphosphine}nickel(0), Ni(SP)$_2$ (1). **(a)** A solution of $Ni(1,5\text{-}COD)_2$ (4.7 g, 17.0 mmol) in ether (50 mL) was added slowly with stirring to a solution of SP (9.8 g, 34.1 mmol) in ether (250 (mL) at −50 °C. The mixture was allowed to warm to room temperature and was stirred overnight. The solution was evaporated under reduced pressure to ca. half volume and was set aside at −70 °C. The bright yellow, crystalline solid that formed was filtered off, washed with pentane (3 × 40 mL), and dried in vacuo to give **1** (9.5 g, 89%).

(b) Anhydrous $Ni(acac)_2$ (2.08 g, 8.1 mmol) and SP (4.69 g, 16.3 mmol) were dissolved in toluene (10 mL), and the solution was cooled to −50 °C. Butadiene (ca. 3 mL) that had been dried by passing through a U-tube containing molecular sieves (Type 3A) was condensed in the solution. A solution of triethylaluminum (3 mL, 21.9 mmol) in toluene (3 mL) was added slowly from a syringe to the rapidly stirred mixture which was maintained at below −20 °C. Stirring was continued, and the mixture was allowed to warm to room temperature overnight. The resulting yellow solution was cooled to −70 °C, and hexane (60 mL) was added to give an immediate bright yellow precipitate. This was filtered off, washed with hexane (3 × 20 mL) and cold ether (10 mL), and dried in vacuo to give **1**: mp 175–180 °C (4.7 g, 91%); $^1H\{^{31}P\}$ NMR (δ, toluene-d_8) 4.45 (dd, H^1), 3.38 (d, H^2), 2.72 (d,

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H^3, J_{12} = 8.7 Hz, J_{13} = 11.8 Hz); ^{13}C NMR (δ, THF) 82.7 (C^1, J_{PC} = 23.6 Hz, J_{CH} = 156 Hz), 54.7 (C^2, J_{PC} = 0, J_{CH} = 156 Hz); $^{31}P\{^1H\}$ NMR (δ, toluene/toluene-d_8) 42.5 (s). Anal. Calcd for $C_{40}H_{34}NiP_2$: C, 75.6; H, 5.4; P, 9.7; mol wt, 635. Found: C, 75.4; H, 5.4; P, 9.6; mol wt (by mass spectrometry), 634.

(2) Bis{(2-vinylphenyl)diphenylphosphine}platinum(0), Pt(SP)$_2$ (2). **(a)** A solution of Pt(1,5-COD)$_2$ (0.09 g, 0.22 mmol) in toluene (5 mL) was added to a solution of SP (0.13 g, 0.44 mmol) in toluene (5 mL). The color immediately turned yellow. The mixture was stirred for 3 h, evaporated to dryness, and dried in vacuo to give Pt(SP)$_2$ as a bright yellow, crystalline solid, mp 150–155 °C (0.15 g, 88%).

(b) A mixture of $PtCl_2$(SP) (1.3 g, 2.3 mmol) and SP (0.7 g, 2.3 mmol) was suspended in THF (50 mL), and the suspension was added to 1% sodium amalgam (64.6 g, 27.8 mmol of Na). The mixture was cooled to –30 °C and stirred vigorously for 3 h. After the mixture was allowed to warm to room temperature, the excess of sodium amalgam was removed by centrifugation. The clear yellow solution was evaporated to dryness, and the residue was treated with ether (40 mL), which left some insoluble solid. The solution was passed through a column of alumina (Grade 2, 2 × 5 cm) and evaporated to dryness. Recrystallization of the solid, either from ether or toluene/hexane, gave **2** as a bright yellow, crystalline solid in variable yield (10–50%): $^1H\{^{31}P\}$ NMR (δ, toluene-d_8) 4.05 (dd, H^1), 3.33 (d, H^2), 2.47 (d, H^3, J_{12} = 8.3 Hz, J_{13} = 9.4 Hz), each with ^{195}Pt satellites (J_{PtH^1} = 43.3 Hz, J_{PtH^2} = 60.6 Hz, J_{PtH^3} = 57.2 Hz); ^{13}C NMR (δ, CD_2Cl_2) 64.8 (C^1, J_{PC} = 37.0 Hz, J_{CH} = 154 Hz, J_{PtC} = 168 Hz), 32.1 (C^2, J_{PC} = 0, J_{PtC} = 196 Hz); $^{31}P\{^1H\}$ NMR (δ, toluene/toluene-d_8) 17.6 (1:4:1 t, J_{PtP} = 3130 Hz). Anal. Calcd for $C_{40}H_{34}P_2Pt$: C, 61.3; H, 4.4; P, 8.1; mol wt, 772. Found: C, 62.0; H, 4.7; P, 8.2; mol wt (osmometry in toluene at 37 °C), 769.

Protonation of Pt(SP)$_2$. Addition of aqueous HBF_4 (43% w/w, 0.03 mL) to a solution of **2** (0.15 g, 0.19 mmol) in ether (10 mL) gave an immediate white precipitate. This was removed by filtration, washed with ether (3 × 5 mL), and dried in vacuo to give [Pt{*o*-CH(CH_3)$C_6H_4PPh_2$}(SP)]BF_4 (**3**) (0.12 g, 72%) as a colorless, air-stable solid, mp 197–205 °C, which was soluble in $CHCl_3$, CH_2Cl_2, and acetone but insoluble in most other common organic solvents. NMR spectroscopy showed the product to be a mixture of cis and trans isomers **3a** and **3b**, respectively, in differing proportions. These isomers could not be separated by fractional crystallization. Heating in CH_2Cl_2 for 12 h caused complete conversion into **3b**.

3a: $^1H\{^{31}P\}$ NMR (δ, $CDCl_3$) 5.85 (d with ^{195}Pt satellites, H^2), 4.80 (d with ^{195}Pt satellites, H^3, J_{12} = 8.0 Hz, J_{13} = 15.0 Hz, J_{PtH^2} = 63 Hz, J_{PtH^3} = 59 Hz), 3.50 (q with ^{195}Pt satellites, C*H*CH_3, J_{PtH} = 68 Hz), 1.65 (d with ^{195}Pt satellites, CHCH_3, J_{HH} = 7.5 Hz, J_{PH} = 7.5 Hz, J_{PtH} = 30 Hz), signal due to H^1 probably beneath aromatic resonances; $^{31}P\{^1H\}$ NMR (δ, $CHCl_3$/$CDCl_3$) 44.1, 33.0 (dd with ^{195}Pt satellites, J_{AB} = 16 Hz, J_{PtP^A} = 4200 Hz, J_{PtP^B} = 1633 Hz); minor conformer (see text) (ca. 10%) also present having δ_P 43.5, 32.4 (dd, similar coupling constants to those of major conformer).

3b: $^1H\{^{31}P\}$ NMR (δ, $CDCl_3$) 5.45 (dd, H^1), 5.15 (d, H^2), 4.15 (d, H^3, J_{12} = 8.0 Hz, J_{13} = 15.0 Hz, ^{195}Pt satellites not observed), 3.65 (q with ^{195}Pt satellites, C*H*CH_3, J_{PtH} = 75 Hz), 1.40 (d with ^{195}Pt satellites, CHCH_3, J_{HH} = 7.5 Hz, J_{PH} = 7.5 Hz, J_{PtH} = 60 Hz); $^{31}P\{^1H\}$ NMR (δ, $CHCl_3$/$CDCl_3$) 47.2, 33.9 (AB with ^{195}Pt satellites, J_{AB} = 367 Hz, J_{PtP^A} = J_{PtP^B} = 2883 Hz); minor conformer (ca. 10%) also present having δ_P 48.2, 35.6 (AB), similar coupling constants to those of major conformer. Anal. Calcd for $C_{40}H_{35}BF_4P_2Pt$: C, 52.3; H, 3.8. Found: C, 52.1; H, 3.9.

The corresponding PF_6 salt was prepared similarly in 75% yield by use of 60% aqueous HPF_6 and was recrystallized from CH_2Cl_2/ether as a dichloromethane solvate; mp 197–200 °C. Anal. Calcd for $C_{40}H_{35}F_6P_3Pt\cdot0.25CH_2Cl_2$: C, 54.9; H, 4.1; P, 7.0. Found: C, 55.0; H, 4.2; P, 7.4. The presence of CH_2Cl_2 was confirmed by the presence of a peak at δ 5.3 in the ^1H NMR spectrum in $CDCl_3$.

Table I. Crystal Data for M(*o*-CH_2═$CHC_6H_4PPh_2$)$_2$ [M = Ni (1), Pt (2)]

	1	2
cryst system	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a, Å	13.432 (2)	11.245 (7)
b, Å	11.486 (2)	14.127 (4)
c, Å	21.630 (3)	14.417 (2)
α, deg	90.00	119.05 (2)
β, deg	104.34 (2)	110.62 (1)
γ, deg	90.00	91.05 (1)
V, Å^3	3233	1823
D_{measd}, g·cm^{-3}	1.32 (1)	1.49 (1)
D_{calcd} g·cm^{-3}	1.31	1.49
empirical formula	$C_{40}H_{34}NiP_2$	$C_{40}H_{34}P_2Pt\cdot0.5C_6H_5CH_3$
fw	635.38	817.83
Z	4	2
F(000), electrons	1328	814
absptn coeff, cm^{-1}	19.5	39.7
dimens, mm	0.18 × 0.16 × 0.06	0.20 × 0.19 × 0.13
developed forms	{101}, {111}	{100}, {110}, {101}, {011}
absptn corrn	analytical[a]	num integratn[b]
transmissn (min, max)	0.72, 0.91	0.57, 0.71
cryst degradatn[c]	14%	10–14%
temp, K	294	296
diffractometer	Picker FACS-1	Philips PW1100/20
radiatn	Cu Kα	Mo Kα
monochromator	graphite	graphite
scan mode	θ–2θ	θ–2θ
2θ range, deg	3–125	4–50
forms/no of measd reflctns	±*h*,+*k*,+*l*/5930	±*h*,±*k*,+*l*/6482
reflctns used ($I \geq 3\sigma(I)$)	3299	5273
reflctn weights	$[\sigma(F) + 0.0005F^2]^{-1}$	$[\sigma^2(F) + 0.0004F^2]^{-1}$
functn minimized	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
scattering factor source (dispersn corrected)	*d*	*d* (Pt) and SHELX[b]
no. of variables	412	407
R	0.041	0.026
R_w	0.045	0.030
S	1.32	1.11
shift/esd	<0.04	<0.05
max excursions in final diff map, e Å^3	±0.25	±0.6

[a] De Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014. [b] Reference 24. [c] Corrected for by the method of: Churchill, M. R.; Kalra, K. I. *Inorg. Chem.* **1974**, *13*, 1427. [d] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, 1974; Vol. IV.

Protonation of Ni(SP)$_2$. A solution of **1** (1.00 g, 1.57 mmol) in ether (50 mL) was cooled to –30 °C and treated dropwise with aqueous HBF_4 (43% w/w, 0.15 mL). When the solution was warmed to room temperature, an orange solid precipitated. On some occasions, colorless or pale green paramagnetic solids also formed, presumably as a result of decomposition; the exact recipe for a successful preparation could not be defined. The orange solid was removed by filtration, washed with ether, and dried in vacuo to give [Ni{*o*-CH(CH_3)$C_6H_4PPh_2$}(SP)]BF_4 (**4**) (0.79 g, 70%), which had a similar IR spectrum to that of **3**. The compound is very air-sensitive and is soluble only in acetone, chlorobenzene, CH_2Cl_2, and $CHCl_3$ to give solutions that blacken rapidly. The ^1H NMR spectrum of a solution in acetone-d_6 at –20 °C showed only broad resonances attributable to **1**. Anal. Calcd for $C_{40}H_{35}BF_4NiP_2$: C, 66.4; H, 4.9; Ni, 8.1; P, 8.6. Found: C, 67.9; H, 5.3; Ni, 7.2; P, 7.4.

Crystallography. Crystals of both **1** and **2** suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into the appropriate toluene solution under a nitrogen atmosphere. Crystals of **1** are air-sensitive and were coated with Araldite prior to data collection. Crystals of **2** are air-stable but contain 0.5 molecule of lattice toluene per molecule of complex. Data collection details are summarized in Table I.

The structure of **1** was solved with MULTAN[22] was refined by full-matrix least-squares analysis.[23] All non-hydrogen atoms

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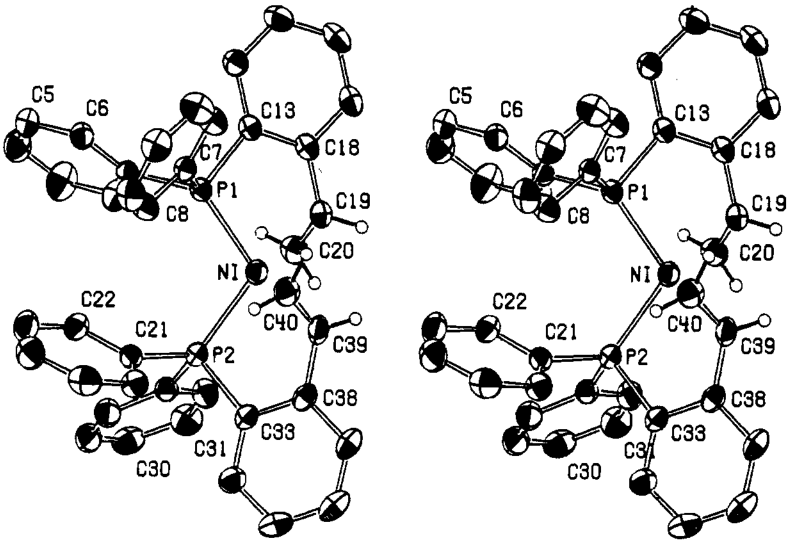

Figure 1. Molecular structure of $Ni(SP)_2$ (1): 30% ellipsoids; H atoms omitted (phenyl groups) or as 0.1 Å radius spheres (vinyl groups).

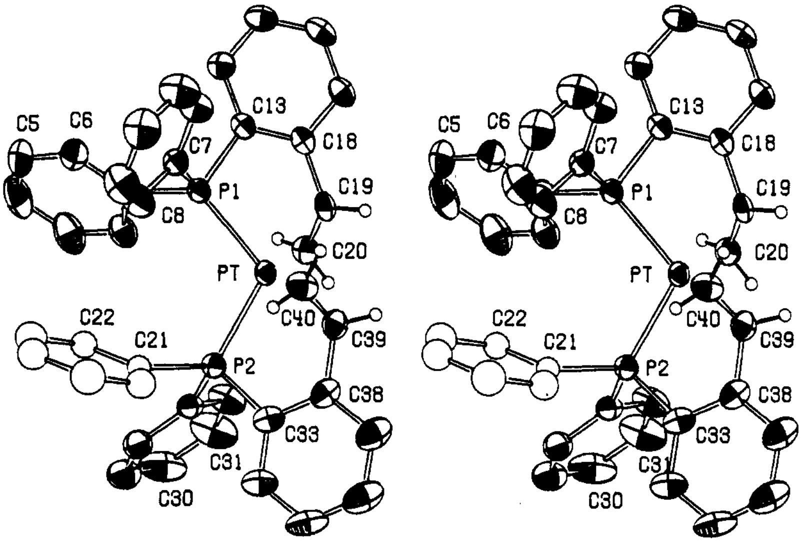

Figure 2. Molecular structure of $Pt(SP)_2$ (2): drawing parameters as for Figure 1.

were assigned anisotropic thermal parameters. Vinyl hydrogen atoms were allowed to refine, but phenyl hydrogen atoms (located by calculation, C–H = 0.95 Å; $B_H = 1.1B_c$) were not. At convergence $R = 0.041$ and $R_w = 0.045$ (3299 reflections).

The structure of 2 was solved by conventional heavy-atom methods and was refined (in space group $P\bar{1}$) by large-block least-squares analysis with SHELX.[24] The toluene solvent molecule is disordered about an inversion center in $P\bar{1}$, and one phenyl ring of the complex is also disordered between two sites, the refined occupancy parameters being 0.58 and 0.42, respectively. There is no other evidence of a noncentrosymmetric packing array, and refinement was concluded successfully in $P\bar{1}$. Bond lengths in the toluene molecule were constrained [$C(sp^2)–C(sp^2) = 1.395$ Å, $C(sp^2)–C(sp^3) = 1.53$ Å, C–H = 0.95 Å], and the disordered phenyl group components of 2 were modeled as rigid groups. Methyl hydrogen atoms from the toluene molecule were not located and were not included in the scattering model. Vinyl hydrogen atoms were refined (after location in difference syntheses), and all other hydrogen atoms were located by calculation. Isotropic thermal parameters were specified for the carbon atoms of the disordered phenyl ring. A single group isotropic thermal parameter was specified for the toluene carbon atoms, and anisotropic thermal parameters were specified for all remaining non-hydrogen atoms. At convergence $R = 0.026$, $R_w = 0.030$ (5273 reflections), and $\Delta\rho < \pm 0.6$ e Å^{-3}.

Additional refinement details for both structures are included in Table I. Terminal atom coordinates are listed in Tables II and III and selected bond lengths and interbond angles are compared in Table IV. A comprehensive bond length/bond angle listing, including comparative values for $Pd(SP)_2$,[16] has been deposited, together with listings of hydrogen atom coordinates, anisotropic thermal parameters, and observed and calculated structure factor amplitudes. The atomic nomenclature is defined in Figures 1 and 2. The figures were drawn with ORTEP.[25]

Results

Synthesis and Spectroscopic Properties. The complexes $M(SP)_2$ [M = Ni(1), Pt(2)] are prepared in high yield by treatment of the appropriate bis(1,5-cyclooctadiene)metal complex in toluene with 2 equiv of SP. The nickel compound 1 can also be made in excellent yield by direct reduction of a mixture of bis(2,4-pentanedionato)nickel and SP in a mole ratio of 1:2 with triethylaluminum. The platinum compound 2 is also formed by reduction of a mixture of $PtCl_2(SP)$ and SP with 1% sodium amalgam in THF at −30 °C, but yields are erratic (10–50%) and much polymeric material is formed; at room

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[23] McLaughlin, G. M.; Taylor, D.; Whimp, P. O. The ANUCRYS Structure Determination Package; Australian National University: Canberra, Australia, 1977.

[24] Sheldrick, G. M. SHELX 76, Program for Crystal Structure Determination; University of Cambridge: Cambridge, 1976.

[25] Johnson, C. K. ORTEP-II, Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Table II. Atomic Coordinates for $Ni(o\text{-}CH_2{=}CHC_6H_4PPh_2)_2$

atom	x/a	y/b	z/c
Ni	0.56127 (4)	0.81052 (5)	0.86917 (3)
P(1)	0.71202 (7)	0.77263 (8)	0.93308 (4)
P(2)	0.52719 (7)	0.68081 (9)	0.79168 (5)
C(1)	0.8252 (3)	0.7296 (3)	0.9057 (2)
C(2)	0.8328 (3)	0.7651 (4)	0.8462 (2)
C(3)	0.9185 (4)	0.7386 (5)	0.8243 (2)
C(4)	0.9963 (3)	0.6749 (5)	0.8613 (2)
C(5)	0.9907 (3)	0.6385 (4)	0.9202 (2)
C(6)	0.9055 (3)	0.6655 (3)	0.9424 (2)
C(7)	0.7203 (3)	0.6749 (3)	1.0008 (2)
C(8)	0.7029 (3)	0.5573 (4)	0.9877 (2)
C(9)	0.7067 (4)	0.4782 (4)	1.0364 (3)
C(10)	0.7278 (4)	0.5144 (4)	1.0984 (2)
C(11)	0.7424 (4)	0.6294 (4)	1.1119 (2)
C(12)	0.7385 (3)	0.7097 (4)	1.0636 (2)
C(13)	0.7486 (3)	0.9139 (3)	0.9688 (2)
C(14)	0.8404 (3)	0.9389 (3)	1.0133 (2)
C(15)	0.8563 (3)	1.0467 (4)	1.0420 (2)
C(16)	0.7800 (4)	1.1288 (4)	1.0277 (2)
C(17)	0.6903 (3)	1.1076 (3)	0.9823 (2)
C(18)	0.6744 (3)	0.9995 (3)	0.9510 (2)
C(19)	0.5800 (3)	0.9789 (3)	0.8987 (2)
C(20)	0.5839 (5)	0.9710 (4)	0.8349 (2)
C(21)	0.5708 (3)	0.5328 (3)	0.8131 (2)
C(22)	0.6704 (3)	0.5003 (4)	0.8136 (2)
C(23)	0.7063 (4)	0.3895 (4)	0.8316 (2)
C(24)	0.6460 (4)	0.3118 (4)	0.8524 (2)
C(25)	0.5483 (4)	0.3426 (4)	0.8552 (2)
C(26)	0.5100 (3)	0.4524 (4)	0.8343 (2)
C(27)	0.5457 (3)	0.6965 (3)	0.7109 (2)
C(28)	0.5812 (3)	0.6102 (4)	0.6774 (2)
C(29)	0.5938 (3)	0.6313 (5)	0.6163 (2)
C(30)	0.5695 (3)	0.7371 (5)	0.5886 (2)
C(31)	0.5313 (4)	0.8213 (4)	0.6200 (2)
C(32)	0.5214 (3)	0.8022 (4)	0.6813 (2)
C(33)	0.3880 (3)	0.6714 (3)	0.7750 (2)
C(34)	0.3259 (3)	0.6080 (4)	0.7260 (2)
C(35)	0.2204 (3)	0.6164 (4)	0.7133 (2)
C(36)	0.1768 (3)	0.6913 (5)	0.7488 (2)
C(37)	0.2368 (3)	0.7536 (4)	0.7982 (2)
C(38)	0.3440 (3)	0.7427 (3)	0.8137 (2)
C(39)	0.4087 (3)	0.8004 (4)	0.8703 (2)
C(40)	0.4703 (3)	0.7376 (5)	0.9212 (2)

Table III. Atomic Coordinates for $Pt(o\text{-}CH_2{=}CHC_6H_4PPh_2)_2$[a]

atom	x/a	y/b	z/c
Pt	0.37456 (2)	0.20750 (1)	0.01077 (1)
P(1)	0.40295 (10)	0.34001 (9)	0.19454 (9)
P(2)	0.18280 (10)	0.20050 (9)	−0.12260 (10)
C(1)	0.3637 (4)	0.4747 (3)	0.2279 (4)
C(2)	0.3615 (5)	0.5099 (4)	0.1530 (5)
C(3)	0.3344 (6)	0.6115 (5)	0.1742 (7)
C(4)	0.3083 (6)	0.6776 (5)	0.2688 (7)
C(5)	0.3096 (6)	0.6440 (5)	0.3423 (6)
C(6)	0.3372 (5)	0.5426 (4)	0.3232 (5)
C(7)	0.3320 (4)	0.2974 (4)	0.2680 (4)
C(8)	0.1972 (5)	0.2712 (5)	0.2265 (5)
C(9)	0.1367 (6)	0.2316 (5)	0.2733 (6)
C(10)	0.2083 (7)	0.2181 (5)	0.3619 (6)
C(11)	0.3400 (7)	0.2415 (5)	0.4026 (5)
C(12)	0.4033 (5)	0.2818 (4)	0.3570 (4)
C(13)	0.5798 (4)	0.3740 (4)	0.2781 (4)
C(14)	0.6445 (4)	0.4519 (4)	0.3961 (4)
C(15)	0.7770 (5)	0.4613 (4)	0.4535 (4)
C(16)	0.8425 (4)	0.3942 (4)	0.3918 (5)
C(17)	0.7796 (4)	0.3211 (4)	0.2743 (4)
C(18)	0.6474 (4)	0.3103 (3)	0.2143 (4)
C(19)	0.5827 (4)	0.2352 (4)	0.0861 (4)
C(20)	0.5488 (4)	0.2801 (5)	0.0147 (5)
C(21)	0.048 (1)	0.236 (1)	−0.076 (1)
C(22)	0.043(1)	0.345 (1)	−0.008 (1)
C(23)	−0.048 (1)	0.368 (1)	0.039 (1)
C(24)	−0.134 (1)	0.281 (1)	0.018 (1)
C(25)	−0.129 (1)	0.173 (1)	−0.050 (1)
C(26)	−0.038 (1)	0.150 (1)	−0.097 (1)
C(21′)	0.042 (1)	0.195 (1)	−0.093 (1)
C(22′)	0.022 (1)	0.297 (1)	−0.025 (1)
C(23′)	−0.076 (1)	0.304 (1)	0.013 (1)
C(24′)	−0.154 (1)	0.209 (1)	−0.017 (1)
C(25′)	−0.134 (1)	0.106 (1)	−0.085 (1)
C(26′)	−0.036 (1)	0.099 (1)	−0.123 (1)
C(27)	0.1760 (4)	0.2818 (3)	−0.1908 (3)
C(28)	0.0693 (5)	0.3221 (4)	−0.2275 (4)
C(29)	0.0727 (7)	0.3818 (5)	−0.2798 (5)
C(30)	0.1818 (8)	0.4012 (5)	−0.2963 (6)
C(31)	0.2848 (7)	0.3613 (6)	−0.2613 (6)
C(32)	0.2835 (5)	0.3035 (5)	−0.2072 (5)
C(33)	0.1400 (5)	0.0576 (4)	−0.2440 (4)
C(34)	0.0340 (5)	0.0149 (4)	−0.3507 (4)
C(35)	0.0166 (7)	−0.0925 (5)	−0.4435 (4)
C(36)	0.1075 (8)	−0.1519 (5)	−0.4283 (5)
C(37)	0.2120 (7)	−0.1121 (4)	−0.3236 (5)
C(38)	0.2284 (5)	−0.0075 (4)	−0.2286 (4)
C(39)	0.3346 (5)	0.0320 (4)	−0.1130 (4)
C(40)	0.3017 (6)	0.0460 (4)	−0.0206 (5)
C(41)	0.477 (2)	−0.034 (2)	0.313 (1)
C(42)	0.480 (1)	−0.010 (2)	0.431 (1)
C(43)	0.594 (2)	−0.009 (2)	0.511 (1)
C(44)	0.579 (2)	0.012 (2)	0.612 (2)
C(45)	0.465 (2)	0.031 (2)	0.627 (2)
C(46)	0.347 (2)	0.027 (2)	0.547 (1)
C(47)	0.365 (2)	0.001 (2)	0.447 (2)

[a] Atoms C(21)–C(26) have occupancy factors of 0.58; atoms C(21′)–C(26′) have occupancy factors of 0.42.

temperature extensive decomposition to metallic platinum occurs. Both compounds are bright yellow solids, the nickel compound being air-sensitive and the platinum compound less so. They are soluble in aromatic solvents and THF and insoluble in alkanes and alcohols; **2** is more soluble in ether than is **1**. Both compounds are readily decomposed by chlorinated solvents. Their mass spectra exhibit parent ions, and $Pt(SP)_2$ was shown to be monomeric in toluene by osmometry.

The solid-state IR spectra of **1** and **2** are very similar; in neither case is there a ν(C=C) band in the 1620 cm^{-1} region, which suggests that both vinyl groups are coordinated. The ^{1}H NMR spectra show three multiplets in the region δ 4.1–2.5 due to the vinyl protons H^1, H^2, and H^3, the splittings arising from H–H and P–H couplings. On ^{31}P decoupling, the multiplets simplify to a doublet of doublets due to H^1 and a pair of doublets due to H^2 and H^3. The chemical shifts are significantly less than those of free SP, which confirms that the vinyl groups are coordinated. The resonance due to H^3 in **1** and **2** is more shielded than that due to H^2, as is true also for $Fe(CO)_3$(SP) and $W(CO)_4$(SP),[14] whereas in free SP the reverse order holds. The magnitudes of the trans- and, to a lesser extent, of the cis-interproton coupling constants are reduced in both **1** and **2** relative to their value in free SP [17.5 (trans) and 11.0 Hz (cis)], a feature which is also diagnostic of vinyl group coordination. In the case of **2**, the three vinyl proton multiplets have ^{195}Pt satellites, the values of the ^{195}Pt–^{1}H coupling constants being 43.3 (H^1), 60.6 (H^2), and 57.2 Hz (H^3). These are comparable with those observed in other platinum(0)–olefin complexes, e.g. Pt(1,5-COD)$_2$ (55 Hz),[21] $Pt(C_2H_4)_3$ (57 Hz),[21] and $Pt(C_2H_4)(PEt_3)_2$ (55 Hz).[26]

The ^{13}C NMR spectra of **1** and **2** show two olefinic carbon resonances which are strongly shielded with respect to those of free SP. The shielding is somewhat less for Ni than for Pt, a feature that is evident also for the proton chemical shifts. In both compounds, the resonance due to carbon atom C^1 adjacent to the phenyl ring is a doublet

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[26] Nuzzo, R. G.; McCarthy, T. J.; Whitesides, G. M. *Inorg. Chem.* 1981, *20*, 1312.

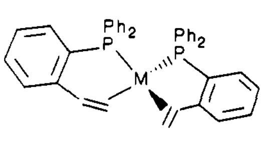
Table IV. Selected Bond Distances (Å) and Bond Angles (deg) in $M(o\text{-}CH_2{=}CHC_6H_4PPh_2)_2$ [M = Ni (1), Pt (2)]

	1	2
Bond Distances		
M–P(1)	2.194 (1)	2.278 (1)
M–P(2)	2.204 (1)	2.290 (1)
M–C(19)	2.033 (4)	2.139 (4)
M–C(20)	2.037 (5)	2.165 (4)
M–C(39)	2.059 (4)	2.152 (4)
M–C(40)	2.034 (5)	2.179 (7)
P(1)–C(1)	1.830 (4)	1.827 (5)
P(1)–C(7)	1.827 (4)	1.820 (7)
P(1)–C(13)	1.812 (4)	1.831 (4)
P(2)–C(21)	1.821 (4)	1.847 (7)
P(2)–C(21′)		1.788 (9)
P(2)–C(27)	1.833 (4)	1.828 (6)
P(2)–C(33)	1.817 (4)	1.819 (4)
C(13)–C(18)	1.385 (5)	1.395 (7)
C(18)–C(19)	1.494 (5)	1.480 (6)
C(19)–C(20)	1.397 (6)	1.404 (11)
C(33)–C(38)	1.402 (5)	1.399 (8)
C(38)–C(39)	1.472 (6)	1.478 (7)
C(39)–C(40)	1.401 (6)	1.429 (11)
C–H(olefin)	0.95 ± 0.06	0.92 ± 0.06
Bond Angles		
P(1)–M–P(2)	109.30 (4)	110.08 (4)
P(1)–M–MPV(1)[a]	95.5 (1)	90.6 (1)
P(2)–M–MPV(2)[a]	91.6 (1)	88.7 (1)
MPV(1)–M–MPV(2)[a]	113.2 (2)	112.1 (2)
M–P(1)–C(13)	101.6 (1)	103.2 (2)
P(1)–C(13)–C(18)	114.7 (3)	114.5 (3)
C(13)–C(18)–C(19)	121.0 (3)	121.6 (4)
C(18)–C(19)–C(20)	121.8 (4)	119.9 (5)
M–P(2)–C(33)	101.6 (1)	102.4 (2)
P(2)–C(33)–C(38)	114.4 (3)	115.7 (3)
C(33)–C(38)–C(39)	120.6 (3)	120.8 (4)
C(38)–C(39)–C(40)	122.3 (4)	119.0 (5)
C(phenyl)–C–H(olefin)	114 ± 1	113 ± 2
C(olefin)–C–H(olefin)	120 ± 1	120 ± 5
H(olefin)–C–H(olefin)	118 ± 1	115 ± 2
C(phenyl)–C–H(olefin) ∧ H(olefin)–C–H(olefin)	37 ± 1	49 ± 2

[a] MPV(1) and MPV(2) are midpoints of the C(19)–C(20) and C(39)–C(40) bonds, respectively.

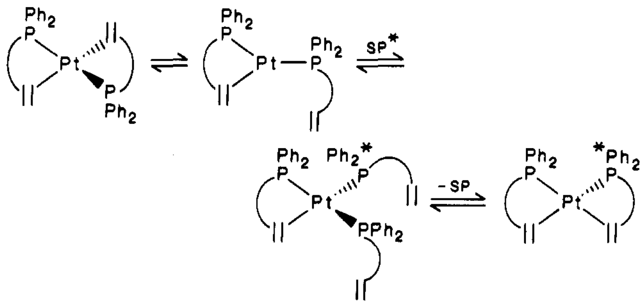
[J_{PC} = 23.6 (1), 37.0 Hz (2)], whereas the signal due to C^2 is not observably coupled to ^{31}P. The olefinic carbon signals of 2 show ^{195}Pt satellites (J_{PtC^1} = 168.0 Hz, J_{PtC^2} = 196.1 Hz), the coupling constants being of the same order of magnitude as those of other platinum(0)–olefin complexes, e.g. Pt(1,5-COD)$_2$ (143 Hz), Pt(norbornene)$_3$ (189 Hz), and Pt(cyclooctene)$_3$ (154 Hz).[21]

The $^{31}P\{^1H\}$ NMR spectrum of 1 consists of a sharp singlet at δ 42.5, and that of 2 comprises a sharp singlet with ^{195}Pt satellites at δ 17.6 (J_{PtP} = 3130 Hz). The peaks do not shift or broaden appreciably at −80 °C, which suggests that the phosphorus atoms are equivalent, consistent with tetrahedral coordination of the metal atom. We have considered the possibility that 1 and 2 have a trigonal-planar structure in solution and that the free and coordinated vinyl groups exchange rapidly on the NMR time scale even at −80 °C. If this were the case, the observed magnitudes of $^1J_{PtH}$ and $^1J_{PtC}$ in 2 would be the averages of the "free" and "coordinated" values and should be approximately half those found in typical platinum(0)–olefin complexes. The available data do not fit this interpretation, and we conclude that Ni(SP)$_2$ and Pt(SP)$_2$, in the solid state and in solution, are tetrahedral complexes containing bidentate SP ligands. This is confirmed for the solid state by the X-ray structural analyses reported below.



1: M = Ni
2: M = Pt

Scheme I



All attempts to make tris(ligand) complexes of the type M(SP)$_3$ (M = Ni, Pt) containing one or two free vinyl groups have been unsuccessful. 1 and 2 were the only products isolated when Ni(1,5-COD)$_2$ or Pt(1,5-COD)$_2$, respectively, was heated with an excess of SP in toluene, and heating of M(SP)$_2$ with an excess of SP led only to recovery of starting material. In the case of M = Pt, heating in toluene for 3 days did give another Pt-containing product, but this could not be identified. Reduction of Ni(acac)$_2$ with an excess of triethylaluminum in the presence of an excess of SP gave only 1 and reduction of PtCl$_2$(SP) with 1% sodium amalgam in the presence of an excess of SP gave a mixture of 2 and polymeric material.

The behavior of M(SP)$_2$ in the presence of an equimolar amount of SP has been monitored by ^{31}P NMR spectroscopy. For M = Ni, the spectrum at room temperature shows two sharp singlets due to 1 and SP; hence exchange is slow on the NMR time scale. In contrast, for M = Pt, there are two broad resonances at room temperature at δ 18.0 and −14.2 due to 2 and SP, respectively, but the former now has no ^{195}Pt satellites. On cooling to −75 °C the spectrum sharpens and the satellites of the peak due to Pt(SP)$_2$ reappear. After 3 h at 50 °C, the ^{31}P NMR spectroscopic behavior of the Pt(SP)$_2$/SP mixture remains unchanged, but a new singlet appears at δ 28.0. This is assigned to the phosphine oxide $o\text{-}CH_2{=}CHC_6H_4P(O)Ph_2$ on the basis of a comparison with the ^{31}P NMR spectrum of an authentic sample. Its formation in the presence of small amounts of oxygen may be catalyzed by 2 in the same way that Pt(PPh$_3$)$_3$ catalyzes the oxidation of triphenylphosphine.[27,28]

Clearly, intermolecular exchange between M(SP)$_2$ and SP occurs more readily for M = Pt than for M = Ni. The first step is probably dissociation of one of the vinyl groups to form a 16e intermediate to which the phosphorus atom of an entering SP ligand can coordinate. Replacement of the monodentate SP by the vinyl group of the new ligand completes the process (Scheme I).

Addition of about one mol equivalent of PPh$_3$ to solutions of 1 or 2 in toluene-d_8 causes broadening of their ^1H NMR spectra, indicative of partial or complete displacement of SP, but the nature of the species present has not been investigated. Both complexes also react immediately with CO, as evidenced by the color changes of yellow to pale yellow (Ni) and yellow to orange (Pt). The ^1H NMR spectra show no resonances due to the coordinated vinyl group in the region δ 5.0–2.0, but there are many overlapping resonances in the region δ 6.0–5.0 arising from free

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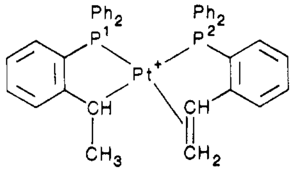
(27) Wilke, G.; Schott, H.; Heimbach, P. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 92.

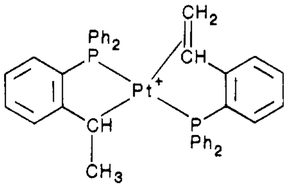
(28) Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1977**, *99*, 8337.

vinyl groups. The solid products isolated by addition of hexane show broad ν(CO) absorption in the 2000 cm^{-1} region, but pure compounds could not be obtained. Ethylene (1 atm) does not react with **1** or **2** and has no effect on the ^{1}H or ^{31}P NMR spectra of these complexes.

The protonation of zerovalent metal complexes of the d^{10} triad is well-known.[29] For example, $Pt(PPh_3)_3$ is protonated at the metal atom to give either $[PtH(PPh_3)_3]X$ or $PtHX(PPh_3)_2$, depending on the coordinating ability of X,[30] and the nickel(0) complexes $Ni(Ph_2PCH_2CH_2PPh_2)_2$ and $Ni\{P(OEt)_3\}_4$ react with acids to form cationic nickel(II) hydrides.[31] In contrast, Pt(1,5-COD)$_2$ is protonated at one of the double bonds to give the cyclooctenylplatinum(II) complex $[Pt(C_8H_{12})(1,4,5\text{-}\eta\text{-}C_8H_{13})]Y$ (Y = BF_4, PF_6).[32] Addition of 1 mol equiv of aqueous HBF_4 or HPF_6 to a solution of **2** in ether gives an immediate white precipitate of the chelate σ-alkyl salt $[Pt\{CH(CH_3)C_6H_4PPh_2\text{-}o\}(SP)]Y$ (Y = BF_4, PF_6) (**3**), formed by addition of a proton to one of the coordinated vinyl groups of Pt(SP)$_2$. The salt is isolated as a mixture of cis and trans isomers **3a** and **3b**, respectively, in variable proportions; these have been identified on the basis of their NMR spectra. Prolonged heating in dichloromethane gives exclusively the more stable trans isomer, which also has been made independently by reaction of *trans*-$PtHCl(AsPh_3)_2$ with SP to give $PtCl\{CH(CH_3)C_6H_4PPh_2\text{-}o\}(AsPh_3)$ and subsequent treatment of the latter with SP in the presence of $AgBF_4$.[33] Treatment of the mixture of **3a** and **3b** with potassium *tert*-butoxide does not re-form **2**.



3a



3b

The ^{1}H NMR spectrum of the cis isomer **3a** shows its methyl proton resonance at δ 1.65 as a triplet with ^{195}Pt satellites ($^3J_{PtCH_3}$ = 30 Hz), the multiplicity arising from coincidentally equal couplings to the methine proton and to the trans phosphorus atom of 7.5 Hz. The methine proton resonance is a multiplet at δ 3.50 with ^{195}Pt satellites ($^2J_{PtCH}$ = 68 Hz), and a pair of doublets in the ^{1}H{^{31}P} NMR spectrum at δ 5.85 and δ 4.80 with ^{195}Pt satellites can be assigned to coordinated vinyl protons H^2 and H^3 ($^2J_{PtH^2}$ = 63 Hz, $^2J_{PtH^3}$ = 59 Hz). The signal due to H^1 is not observed, presumably because it is underneath the aromatic resonances. The ^{31}P{^{1}H} NMR spectrum of **3a** consists of a pair of doublets at δ 44.1 and 30.0 ($^2J_{PP}$ = 16 Hz), each with ^{195}Pt satellites ($^1J_{PtP}$ = 4200, 1633 Hz, respectively). The magnitude of $^2J_{PP}$ is typical of cis tertiary phosphine ligands in planar platinum(II) complexes, and the magnitudes of $^1J_{PtP}$ suggest that the less shielded resonance is due to P^1, trans to the olefin, while the more shielded resonance is due to P^2, trans to the σ-bonded carbon atom.[34] In the product mixture there is also a minor amount (ca. 10%) of an isomer having very similar ^{31}P chemical shifts and coupling constants to those of **3** (see Experimental Section). The likely nature of this compound is discussed below.

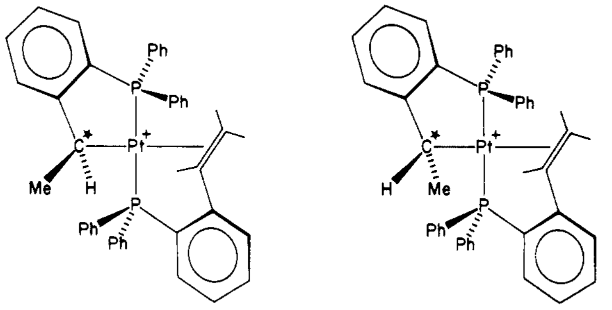


Figure 3. Diastereomers of *cis*-$[Pt(o\text{-}CH_3CHC_6H_4PPh_2)(SP)]Y$ (Y = BF_4, PF_6) (**3b**).

The methyl resonance of the trans isomer **3b** is a doublet at δ 1.40 with ^{195}Pt satellites ($^3J_{HH}$ = 7.5 Hz, $^3J_{PtCH_3}$ = 60 Hz) and the methine resonance appears as a multiplet at δ 3.65 with ^{195}Pt satellites ($^2J_{PtCH}$ = 75 Hz). In the ^{1}H{^{31}P} NMR spectrum there is a pattern typical of a coordinated vinyl group in the region δ 5.5–4.0, although the ^{195}Pt satellites could not be located. The trans- and cis-interproton coupling constants of 15 and 8 Hz, respectively, in the vinyl groups of both **3a** and **3b** are only slightly less than those of free SP, suggesting that the olefin is not greatly perturbed on binding to platinum(II) in these cationic complexes. The ^{31}P{^{1}H} NMR spectrum of **3b** shows two AB quartets, in ca. 3:1 ratio, having very similar chemical shifts (δ_P 47.2, 33.9 and 48.2, 35.6) and identical coupling constants ($^2J_{PP}$ = 367 Hz). The magnitude of $^2J_{PP}$ is characteristic of trans tertiary phosphine ligands in planar platinum(II) complexes.[34] Coincidentally, the inequivalent phosphorus atoms in each trans species are coupled equally to ^{195}Pt and the magnitude of $^1J_{PtP}$ (2883 Hz) in both cases is also diagnostic of mutually trans phosphines.[34] Since the ^{1}H NMR spectrum of **3b** gives no evidence of the presence of an isomer containing the six-membered ring $PtCH_2CH_2C_6H_4PPh_2\text{-}o$, we suggest that the isomers of **3b** are diastereomers arising from the presence of two chiral centers, namely, the σ-bonded carbon atom and the coordinated vinyl group (Figure 3). A similar explanation may account for the isomers of **3a**.

The reaction of 1 mol equiv of aqueous HBF_4 with Ni(SP)$_2$ in ether at −30 °C often gave white or pale green paramagnetic solids, but occasionally an air-sensitive, orange precipitate was obtained. This product was insoluble in toluene and ether but dissolved in CH_2Cl_2, $CHCl_3$, chlorobenzene, and acetone to give highly air-sensitive solutions which rapidly darkened. The IR spectrum, measured in a KBr disk at 0 °C, was broad, but its general features were similar to those of **3b**; there were no bands in the 1700–2000 cm^{-1} region assignable to ν(NiH). The ^{31}P{^{1}H} NMR spectrum in acetone-d_6 at −90 °C showed only the presence of **1** and decomposition products. The microanalytical and IR data suggest that the compound may be *trans*-$[Ni\{CH(CH_3)C_6H_4PPh_2\text{-}o\}(SP)]BF_4$, analogous to the corresponding platinum(II) and palladium(II) complexes.[16] As such, it may be a rare example of a cationic nickel(II)–olefin complex, cf. $[NiX\{CH_2{=}CHCH_2CH_2As(CH_2CH_2CH_2AsMe_2)_2\}]^+$ (X = Cl, Br),[35] $[Ni(\eta\text{-}C_5H_5)(PMe_2Ph)(C_2H_4)]ClO_4$,[36] and $[Ni(\eta\text{-}C_5H_5)(diene)]^+$ (diene = 1,5-COD, NBD).[37]

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Structures of $M(SP)_2$ [M = Ni (1), Pt (2)]. The molecular structures are illustrated in Figures 1 and 2. The SP ligands in both compounds are bidentate, the coordination geometry being approximately tetrahedral. The dihedral angle between the plane containing the metal atom and the two phosphorus atoms and the plane containing the metal atom and the midpoints of the two double bonds is 69.0 (1)° (Ni) and 61.8° (Pt), compared with the ideal tetrahedral value of 90°. The angles formed by the two olefin midpoints with the metal as vertex and by the two phosphorus atoms with the metal as vertex are 113.2 (2)° and 109.30 (4)° (Ni) and 112.1 (2)° and 110.08 (4)° (Pt), these angles deviating slightly from the tetrahedral value of 109°27′. If MPV is the midpoint of the olefinic bond, the chelate bite angles, P–M–MPV, are 95.5 (1)° and 91.6 (1)° (Ni) and 90.6 (1)° and 88.7 (1)° (Pt); again, these values are considerably less than the ideal value of 109°27′.

The M–P distances in each complex differ significantly, i.e. Ni–P(1) = 2.194 (1) Å, Ni–P(2) = 2.204 (1) Å in 1, Pt–P(1) = 2.278 (1) and 2.290 (1) Å in **2**. The average M–P distances in **1** [2.199 Å] and **2** [2.284 Å] fall at the long end of the ranges of 2.15–2.20 (Ni) and 2.26–2.29 Å (Pt) observed in trigonal-planar tertiary phosphine complexes of nickel(0)[38] and platinum(0),[39] respectively, containing variously substituted olefins. The most valid comparison is probably that between the tetrahedral $M(SP)_2$ complexes and the trigonal metal(0) ethylene complexes $M(C_2H_4)(PPh_3)_2$. For both nickel and platinum, the M–P bond lengths in the latter [2.153 (4) Å (M = Ni);[40] 2.268 (4) Å (M = Pt)][41] are significantly less than in the former, a trend that is to be expected as the coordination number of the metal is reduced. The Ni–P distance in **1** is also marginally greater than the Ni–P(PPh_3) separation of 2.180 (1) Å in $Ni(C_2H_4)(Me_2PCH_2CH_2PMe_2)(PPh_3)$, the only tetrahedral nickel(0) ethylene complex to be studied by X-ray crystallography.[12,42]

In **1** one vinyl group is bound symmetrically to nickel [Ni–C(19) = 2.033 (4) Å, Ni–C(20) = 2.037 (5) Å] and the other vinyl group is asymmetrically coordinated, the Ni–C_β bond being significantly shorter than the Ni–C_α bond [Ni–C(40) = 2.034 (5) Å, Ni–C(39) = 2.059 (4) Å (Δ/σ = 4.2)]. This behavior has also been observed in the Pt^{II}–SP complexes $PtR_2(SP)$ (R = CH_3, CF_3).[43] In **2** both vinyl groups are asymmetrically coordinated, although the difference between the Pt–C separations in each vinyl group is only just statistically significant [Pt–C(19) = 2.139 (4) Å, Pt–C(20) = 2.165 (7) Å (Δ/σ = 3.3); Pt–C(39) = 2.152 (4) Å, Pt–C(40) = 2.179 (7) Å (Δ/σ = 3.4)]. In this case, in contrast to **1**, the shorter bonds are those to C_α.

The Ni–C distances in **1** are equal, within experimental error, to those in tetrahedral $Ni(C_2H_4)(Me_2PCH_2CH_2PMe_2)(PPh_3)$ [2.050 (3), 2.045 (3) Å][12] but are significantly longer than the average Ni–C bond lengths in comparable trigonal nickel(0) olefin complexes, e.g. $Ni(C_2H_4)(PPh_3)_2$ [1.970 (5) Å],[40] $Ni(Me_2C{=}CMe_2)\{(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2\}$,[38d] and $Ni(C_2H_4)_2\{P(C_6H_{11})_3\}$ [1.987–2.042 Å].[38e] This is the same trend as observed in the Ni–P bond lengths (see above). A similar comparison cannot be made between the Pt–C bond lengths in $Pt(SP)_2$ and those in trigonal platinum(0) olefin complexes; the latter lie in the range 2.03–2.17 Å, but the quoted standard errors are, as expected, higher than those for nickel. As usual in olefin complexes, the C=C distances of the coordinated vinyl groups in **1** and **2** are substantially greater than that for a free vinyl group [1.335 (5) Å].[44] Those in **1** are equal within experimental error [1.397 (6), 1.401 (6) Å] and are comparable with corresponding distances in other nickel(0) olefin complexes, e.g. $Ni(C_2H_4)(PPh_3)_2$ [1.391 (5) Å][40] and $Ni(Me_2C{=}CMe_2)\{(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2\}$ [1.421 (3) Å].[38e] Similar statements can be made about the C=C distances in **2** [1.404 (11), 1.429 (11) Å], cf. $Pt(C_2H_4)(PPh_3)_2$ [1.434 (13) Å][41] and $Pt\{(Z)\text{-}(C_6H_4NO_2\text{-}p)CH{=}CH(C_6H_4NO_2\text{-}p)\}(PPh_3)_2$ [1.416 (15) Å].[39c]

The bend-back angles α, β, and β'[45] for the hydrogen atoms of the C(19)–C(20) vinyl group in $Ni(SP)_2$ are 36 (4)°, 71°, and 73°, respectively, while the corresponding angles for the C(39)–C(40) vinyl group are 37 (4)°, 73°, and 71°. The corresponding angles for the C(19)–C(20) vinyl group in $Pt(SP)_2$ are 47 (6)°, 63°, and 71° and for the C(39)–C(40) vinyl group they are 51 (5)°, 65°, and 64°. Unfortunately, owing to the difficulty of locating light atoms with high-precision by X-ray diffraction, the differences between these values for **1** and **2** are not statistically significant. The same is true for the difference between the C=C bond lengths of **1** and **2**.

Discussion

Compounds **1** and **2** are rare examples of tetrahedrally coordinated, 18-electron complexes to nickel(0) and platinum(0) in which two phosphorus atoms and two olefins are bound to the metal atom. As such, they model the intermediate proposed for ethylene exchange in the trigonal, 16-electron complexes $M(C_2H_4)(PPh_3)_2$. Sixteen-electron species of formula $M(SP)_2$ in which one of the vinyl groups is free probably are intermediates in the reactions of the 18-electron complexes with ligands such as CO and PPh_3.

Various measures of stability and bond strength for zerovalent metal complexes of the nickel triad give the order Ni > Pt > Pd.[1,46] This presumably reflects variations in the ability of the metal atom to form σ- and π-bonds with the ligands. Nyholm[47] has suggested that the

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(38) For example: (a) $Ni((Z)\text{-}PhCH{=}CHPh)\{P(C_6H_4Me\text{-}p)_3\}_2$, 2.181 (4) Å: Ittel, S. D.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *74*, 121. (b) $Ni((E)\text{-}PhCOCH{=}CHCO_2Me)(PPh_3)_2$, 2.184 (1) Å: Andreetti, G. D.; Bocelli, G.; Sgarabotto, P.; Chiusoli, G. P.; Costa, M.; Terenghi, G.; Biavati, A. *Transition Met. Chem. (Weinheim, Ger.)* **1980**, *5*, 129. (c) $Ni\{CH_2{=}CMe(CO_2Et)\}(PPh_3)_2$, 2.180 (2) Å: Komiya, S.; Ishizu, J.; Yamamoto, A.; Yamamoto, T.; Takenaka, A.; Sasada, Y. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1283. (d) $Ni(Me_2C{=}CMe_2)\{(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2\}$, 2.156 (6) Å: Brauer, D. J.; Krüger, C. *J. Organomet. Chem.* **1974**, *77*, 423. (e) $Ni(C_2H_4)_2\{P(C_6H_{11})_3\}$, 2.196 (2) Å: Krüger, C.; Yi-Hung Tsay *J. Organomet. Chem.* **1972**, *34*, 387.

(39) For example: (a) $Pt\{(NC)_2C{=}C(CN)_2\}(PPh_3)_2$, 2.289 (8) Å: Bombieri, G.; Forsellini, E.; Panattoni, C,; Graziani, R.; Bandoli, G. *J. Chem. Soc. A* **1970**, 1313. (b) $Pt(Cl_2C{=}CCl_2)(PPh_3)_2$, 2.286 (7) Å: Francis, J. N.; McAdam, A.; Ibers, J. A. *J. Organomet. Chem.* **1971**, *29*, 131. (c) $Pt\{(Z)\text{-}(C_6H_4NO_2\text{-}p)CH{=}CH(C_6H_4NO_2\text{-}p)\}(PPh_3)_2$, 2.280 (4) Å: Baraban, J. M.; McGinnety, J. A. *Inorg. Chem.* **1974**, *13*, 2864. (d) $Pt(CH_2{=}C{=}CH_2)(PPh_3)_2$, 2.282 (9) Å: Kadonaga, M.; Yasuoka, N.; Kasai, N. *J. Chem. Soc., Chem. Commun.* **1971**, 1597.

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(42) The average Ni-P distance of 2.25 Å in $Ni(C_2F_4)\{(PPh_2CH_2)_3CMe\}$[13] is anomalously long, perhaps reflecting differences in the nature of M–C_2F_4 and M–C_2H_4 bonds.

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(46) The $M(PF_3)_4$ complexes appear to be exceptional. Although their thermal stability follows the order M = Ni > Pt > Pd, the M–P force constants are in the order Pt > Pd > Ni [Edwards, H. G. M.; Woodward, L. A. *Spectrochim. Acta, Part A* **1970**, *26A*, 897] and the relative ordering of both σ- and π-bonding derived from He I photoelectron spectra is Pt ≈ Pd > Ni [Bassett, P. J.; Higginson, B. R.; Lloyd, D. R.; Lynaugh, N.; Roberts, P. J. *J. Chem. Soc., Dalton Trans.* **1974**, 2316].

ability to form a strong σ-bond should be related to the electron affinity (EA) of the d^{10} metal atom, whereas the tendency to engage in π-back-bonding should be related to the $d^{10} \rightarrow d^9$ ionization potential (IP). De Kock[48] has pointed out that the difference (EA − IP) parallels the usual stability trend for the complexes, i.e. Ni > Pt > Pd; the σ-bond strength is in the order Pt > Pd $\approx$ Ni, whereas the π-bond strength is in the order Ni > Pt $\approx$ Pd.[48] This nicely accounts for the trend in equilibrium constants for eq 1: the fragment $M(PPh_3)_2$ preferentially binds the stronger π-acceptor ethylene rather than the stronger σ-donor PR_3 when M = Ni, whereas the reverse is true for Pt. The same feature also emerges from the behavior of the tetrahedral complexes $M(PPh_3)_2(SP)$ (M = Ni, Pt);[49] the platinum(0) complex undergoes reversible dissociation of the coordinated vinyl group at low temperature, whereas the nickel(0) complex preferentially undergoes exchange of one of its PPh_3 ligands. Similarly, in this work, we find that the ease of exchange of $M(SP)_2$ with SP is the order Pt > Ni.

Unfortunately, neither X-ray nor spectroscopic results for **1** and **2** give any clear indication of the relative strength of the metal–olefin interaction in these compounds. The C=C bond lengths and the average bend-back angle of the vinyl hydrogen atoms tend to be greater, and the bond length differences (M–P)–(M–C) to be less, for **2** than for **1**, but in no case are the differences statistically significant ($\Delta/\sigma \approx 1.8$–$2.4$). The shielding of the ^1H and ^{13}C nuclei of the coordinated vinyl groups is uniformly greater for **2** than for **1**, and since such shieldings often seem to correlate with the expected degree of π-back-bonding to the olefin,[50,51] it could be argued that π-back-bonding to the vinyl group is greater in $Pt(SP)_2$ than in $Ni(SP)_2$; however, skepticism has been expressed about such simple interpretations, at least in the case of ^{13}C chemical shifts.[52] The interproton coupling constants of the vinyl groups are smaller for **2** than for **1**, consistent with a closer approach to a metallacycloalkane structure, hence greater π-back-bonding, in the former; on the other hand, the C–H coupling constants do not differ significantly. We suggest that the metal–olefin bond strengths in **1** and **2** probably are not greatly different and that the differences in chemical behavior noted above arise largely from the increase in M–P σ-bond strength in going from nickel(0) to platinum(0).

Not much is known about the behavior of tertiary phosphine–olefin complexes of nickel(0) or platinum(0) with acids. Addition of HCN to $Ni(C_2H_4)L_2$ [L = $P(O\text{-}o\text{-}C_6H_4Me)_3$] at low temperature is reported to give an ethylnickel(II) complex $Ni(C_2H_5)(CN)L_2$, which decomposes on warming to give C_2H_5CN, $NiH(CN)L_3$, and $Ni(CN)_2$.[53] Reaction of triflic acid or sulfuric acid with $Pt(C_2H_4)(PPh_3)_2$ gives up to 70% of the calculated quantity of ethane, presumably formed by protolytic cleavage of the Pt–C bond of an intermediate ethylplatinum(II) cation, though this was not isolated or detected.[54] This assumption is obviously supported by the isolation of the stable chelate complex **3**. Formation of a five-membered ring chelate σ-alkyl by protonation of a low-valent metal complex has been observed previously in the reaction of the d^8 complexes $M(CO)_3(SP)$ (M = Fe, Ru) with HCl or HBr.[55]

The instability of the nickel(II) complex **4** compared with its platinum(II) and palladium(II) analogues, and especially its tendency to revert to **1** in solution, are not surprising. Ab initio calculations have confirmed the low metal–olefin bond energy in neutral complexes of the type NiX_2(olefin), though cationic nickel(II)–olefin complexes are predicted to be more stable.[56] For divalent metal–olefin complexes, such as Zeise's Salt, σ-bonding is expected to predominate over π-back-bonding,[57,58] and the second ionization potentials of the metals, which should reflect the tendency of the divalent metal ions to form strong σ-bonds, are in the order Pt > Pd > Ni.

Acknowledgment. We thank K. D. Griffiths for computational assistance.

Registry No. 1, 113509-30-1; **2**, 104437-86-7; **2**·$0.5C_6H_5CH_3$, 113509-36-7; **3a**·BF_4 (isomer 1), 113509-33-4; **3a**·BF_4 (isomer 2), 113565-45-0; **3a**·PF_6 (isomer 1), 113565-43-8; **3a**·PF_6 (isomer 2), 113625-65-3; **3b**·BF_4 (isomer 1), 113565-42-7; **3b**·BF_4 (isomer 2), 113565-47-2; **3b**·PF_6 (isomer 1), 113625-64-2; **3b**·PF_6 (isomer 2), 113625-66-4; **4**, 113509-35-6; SP, 17165-18-3; $Ni(1,5\text{-}COD)_2$, 1295-35-8; $Ni(acac)_2$, 3264-82-2; $Pt(1,5\text{-}COD)_2$, 12130-66-4; $PtCl_2(SP)$, 113509-31-2.

Supplementary Material Available: A table of comparative bond lengths and bond angles for $M(o\text{-}CH_2{=}CHC_6H_4PPh_2)_2$ (M = Ni, Pd, Pt) and tables of anisotropic thermal parameters and hydrogen atom parameters for $Ni(SP)_2$ (**1**) and $Pt(SP)_2$ (**2**) (10 pages); listings of structure factor amplitudes for **1** and **2** (49 pages). Ordering information is given on any current masthead page.

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