4544 *Organometallics* **1998,** *17,* 4544−4550

Articles

Palladium(II) Complexes of Monoaryliminophosphorane Derivatives of 1,2-Bis(Diphenylphosphino)methane. Crystal Structure of $[Pd\{\kappa^2\text{-}C_6H_3(N{=}N{-}C_6H_4Me\text{-}4')\text{-}2\text{-}(C_6H_4Me\text{-}4'')\text{-}5\text{-}C,N'\}\{\kappa^2\text{-}PPh_2CH_2P({=}NC_6H_4Me\text{-}4)Ph_2\text{-}P,N\}]$[†]

José Vicente,*[,‡] Aurelia Arcas, Delia Bautista, and
M. Carmen Ramírez de Arellano

Grupo de Química Organometálica,[§] Departamento de Química Inorgánica, Facultad de Química, Universidad de Murcia, Apartado 4021, Murcia, 30071 Spain

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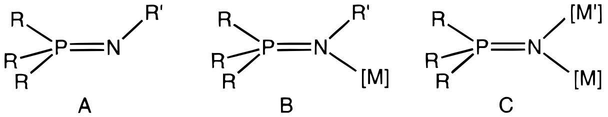
The complex [Pd(azoMe)(κ^1-dppm)(κ^2-dppm)]TfO (azoMe = 2-(4′-tolylazo)-5-methylphenyl, dppm = bis(diphenylphosphino)methane, TfO = CF_3SO_3) reacts at room temperature with aryl azides N_3Ar to give, in moderate to high yields, iminophosphorane complexes [Pd(κ^2-azoMe-*C*,*N*′){κ^2-$PPh_2CH_2P({=}NAr)Ph_2$-*P*,*N*}]TfO [Ar = C_6H_4R, R = H (**1**), MeO-2 (**2a**), Me-2 (**2b**), NO_2-2 (**2c**), MeO-3 (**3a**), NO_2-3 (**3c**), MeO-4 (**4a**), Me-4 (**4b**), NO_2-4 (**4c**)]. In all cases, there is a linear correlation between δ(P) (ppm) of both phosphorus atoms and temperature T (°C) [$\delta(P_1) = \delta_1(0) + a_1T$; $\delta(P_2) = \delta_2(0) + a_2T$]. In the ortho-substituted complexes **2a**−**c** and the nitro derivatives **3c** and **4c**, crossing of the two δ/T plots of each complex is not observed and the change in chemical shift with temperature is small or nil, $|a_1|$, $|a_2|$ = (0−12) × 10^{-3} ppm/°C. In the other complexes, the gradient of one of the straight lines is positive ($a_1 \approx 26 \times 10^{-3}$ ppm/°C) and that of the other is negative ($a_2 \approx -7.5 \times 10^{-3}$ ppm/°C). Both lines cross in the range 0−25 °C. **4b** reacts with [Au(acac)PPh_3] (1:2) to give [Pd(azoMe-C,N′){$PPh_2C(AuPPh_3)_2P({=}NAr)Ph_2$-*P*,*N*}] [Ar = Me-4 (**5b**)]. [Pd(azoMe-*C*,*N*′)(κ^2-dppm)]TfO reacts with NaN_3 to give [$Pd_2(azoMe)_2(\mu_2\text{-}N_3)(\mu_2\text{-}dppm)_2$]TfO (**6**). The crystal structure of **4b** is reported.

Introduction

Iminophosphoranes [also called phosphoranimines, phosphinimines, or phosphazenes; (A) in Scheme 1] are interesting intermediates in the synthesis of natural products[1−3] and of nitrogen-containing organic compounds.[4]

Scheme 1



Metallic derivatives of iminophosphoranes can be classified into three groups: phosphiniminates (R′ = metallic moiety in A, Scheme 1), N-coordinated iminophosphorane complexes (M = metallic moiety in B), and mixed complexes (M and M′ metallic moieties in C).[4−7] In this paper, we describe palladium(II) complexes of type B. Most of these complexes are prepared starting from the ligand (see Scheme 2 to see this and other[8−13] methods of synthesis). We have reported the synthesis of iminophosphorane platinum complexes by reacting ylides with nitrile complexes.[14,15] In this paper, we report a new method which uses the attack of organic azides on the noncoordinated phosphorus atom of a

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[†] Dedicated to Professor Pascual Royo on the occasion of his 60th birthday.

[‡] E-mail: jvs@fcu.um.es.

[§] WWW: http://www.scc.um.es/gi/gqo/.

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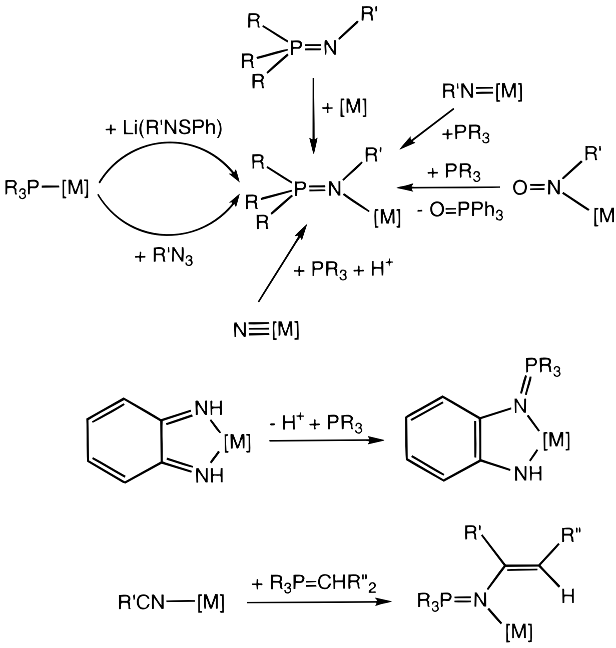
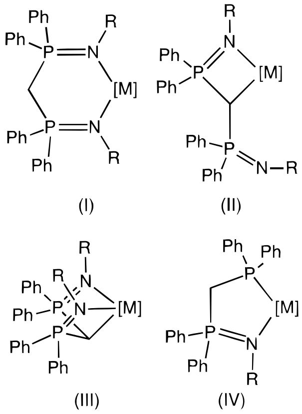
S0276-7333(98)00445-2 CCC: $15.00

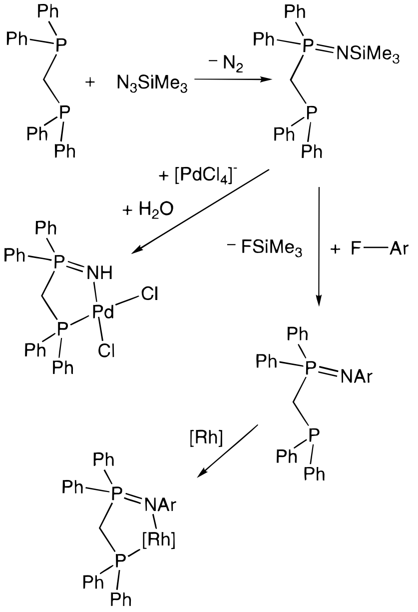
Scheme 2



Scheme 3



Scheme 4



monocoordinated 1,2-bis(diphenylphosphino)methane palladium(II) complex (Staudinger reaction).

The reported iminophosphorane complexes can be classified into two groups depending on the number of P atoms of the ligand. Those from monophosphines are known for Mo,[16] W,[9,12] Os,[10] Co,[11,17,18] Rh,[19−23] Ir,[13,20,21] Ni,[8] Pd,[23,24] Pt,[14,15] Zn, Cd, Hg,[23] and B.[25] With only a few exceptions,[26−29] most complexes containing iminophosphorane ligands with two phosphorus atoms are bis(diphenylphosphino)methane (dppm) derivatives. Of this family, complexes of Mo,[12] Rh,[30−35] Ir,[30−32,36] Pd,[7,27,37,38] and Pt[37−39] have been reported. The different types of coordination of these ligands are shown in Scheme 3. The most abundant are those from diphosphinodiimine derivatives (I−III). In this paper, we report the synthesis of a family of palladium complexes of type IV containing *N*,*P*-diphosphinomonoimine ligands. In most cases, the reported synthesis of these complexes requires two or three steps from dppm to prepare first the ligand. In addition, the nature of the N-substituent is limited to H,[27] aryl groups containing several F, CN, or NO_2 substituents, a polyfluoropyridyl group, or 8-quinoline (Schemes 4 and 5).[12,33−35] Only one palladium complex of this type has previously been reported, $[PdCl_2(PPh_2CH_2P({=}NH)Ph_2\text{-}P,N)]$.[27] During the preparation of this article, a new derivative of the type $[PdCl_2(PPh_2CH_2P({=}NR)Ph_2\text{-}P,N)]$, where R is a group containing a ferrocenyl unit, was reported.[40]

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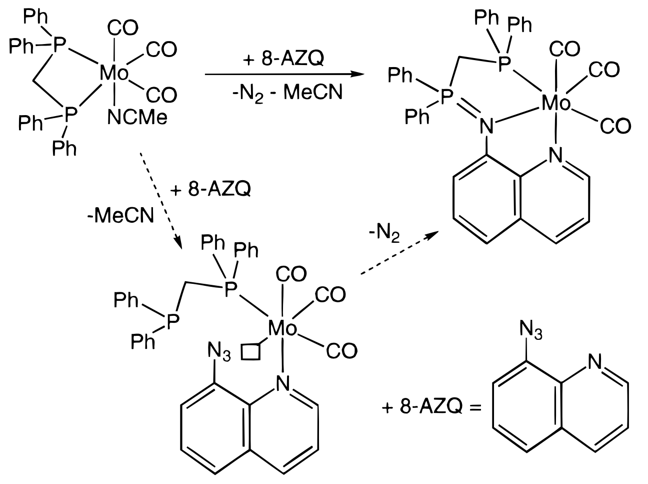
Scheme 5



Experimental Section

^{1}H and ^{31}P{^{1}H} NMR spectra ($CDCl_3$ solutions, room temperature) were measured on a Varian Unity 300 spectrometer. Chemical shifts are referred to TMS (^{1}H) and H_3PO_3 (^{31}P). All solvents were distilled before use, and unless otherwise stated, the reactions were carried out under normal laboratory conditions. [Pd(azoMe)(κ^1-dppm)(κ^2-dppm)]TfO, [Pd(κ^2-azoMe-*C*,*N′*)(κ^2-dppm)]TfO, and [Pd(azoMe)Cl(κ^1-dppm)$_2$] were prepared as previously reported.[15]

[Pd(κ^2-azoMe-*C*,*N′*)(PPh$_2$CH$_2$P(=NAr)Ph$_2$-*P*,*N*] [Ar = C$_6$H$_4$R, R = H (1), MeO-2 (2a), Me-2 (2b), NO$_2$-2 (2c), MeO-3 (3a), NO$_2$-3 (3c), MeO-4 (4a), Me-4 (4b), NO$_2$-4 (4c)]. To a suspension of [Pd(azoMe)(κ^1-dppm)(κ^2-dppm)]TfO in THF was added the corresponding R-phenyl azide [Pd:azide = 1 (R = p-Me), 2 (R = p-MeO, o-Me, o-MeO, m-MeO), and 2.5 (R = H, p-NO$_2$, o-NO$_2$, m-NO$_2$)]. The solution was stirred for 15 (**4b**), 30 (**2c**), 90 (**2a**, **4c**) min or 4 (**4a**, **3a**), 5 (**1, 2b, 3c**) h. The resulting solutions were evaporated to dryness. Complexes were isolated as follows.

1. The solid was washed with diethyl ether (4 mL) and the oily residue was stirred with diethyl ether (4 mL) to obtain **1** as an orange solid. Yield: 112 mg, 58%. Anal. Calcd for $C_{46}H_{40}F_3N_3O_3P_2PdS$: C, 58.76; H, 4.29; N, 4.47; S, 3.41. Found: C, 58.47; H, 4.31; N, 4.49; S, 3.72. Mp (°C): 154. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 136. ^{1}H NMR: δ, 7.89−7.25 (m, aromatic protons), 6.99−6.23 (m, aromatic protons), 4.21 (dd, CH$_2$, $^2J_{PH}$ = 10.8, 9.00 Hz), 2.23 (s, 3H, Me), 1.88 (s, 3H, Me). ^{31}P{^{1}H} NMR: δ, 31.39, 30.59 (AB, $^2J_{PP}$ = 18.33 Hz).

2a. The solid was washed with *n*-hexane (15 mL) and the oily residue was stirred with diethyl ether (4 mL) to obtain **1** as an orange solid. The mixture was stirred to obtain **2a** as a solid. Yield: 86 mg, 63%. Anal. Calcd for $C_{47}H_{42}F_3N_3O_4P_2PdS$: C, 58.18; H, 4.36; N, 4.33; S, 3.30. Found: C, 58.30; H, 4.56; N, 4.16; S, 3.13. Mp (°C): 220. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 124. ^{1}H NMR: δ, 8.0−6.02 (m, aromatic protons), 3.87 [dd, CH$_2$, $^2J_{PH}$ = 11.7, 8.7 Hz], 3.01 [s, 3H, MeO], 2.27, 1.84 [s, 3H, Me (azoMe)]. ^{31}P{^{1}H} NMR: δ, 41.42 (d, $^2J_{PP}$ = 22.95 Hz), 33.80 (d).

2b. Dichloromethane (1 mL), diethyl ether (10 mL), and *n*-hexane (5 mL) were successively added to the solid, and the mixture was stirred to obtain **2b** as an orange solid. Yield: 103 mg, 67%. Anal. Calcd for $C_{47}H_{42}F_3N_3O_3P_2PdS$: C, 59.15; H, 4.44; N, 4.40; S, 3.36. Found: C, 59.67; H, 4.77; N, 3.93; S, 3.32. Mp (°C): 124. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 121. ^{1}H NMR: δ, 7.86−7.33 (m, aromatic protons), 7.03−6.85 (m, aromatic protons), 6.63−6.26 (m, aromatic protons), 4.0−3.8 [m, CH$_2$], 2.26 (s, 6H, Me), 1.82 (s, 3H, Me). ^{31}P{^{1}H} NMR: δ, 40.67 (d, $^2J_{PP}$ = 24.65 Hz), 32.12 (d).

2c. Dichloromethane (1 mL) and diethyl ether (10 mL) were successively added to the solid and the mixture was stirred to obtain **2c** as a yellow solid. Yield: 101 mg, 75%. Anal. Calcd for $C_{46}H_{39}F_3N_4O_5P_2PdS$: C, 56.08; H, 3.99; N, 5.69; S, 3.25. Found: C, 56.22; H, 4.08; N, 5.54; S, 3.06. Mp (°C): 216. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 124. ^{1}H NMR: δ, 7.93−6.23 (m, aromatic protons), 4.6−3.6 (m, CH$_2$), 2.25, 1.79 (s, 3H, Me). ^{31}P{^{1}H} NMR: δ, 44.93 (d, $^2J_{PP}$ = 22.5 Hz), 31.32 (d).

3a. The solid was washed with diethyl ether (5 mL) and then recrystallized three times from dichloromethane (1 mL)/diethyl ether (20 mL). The resulting solid was dissolved in dichloromethane and chromatographed on a silica gel TLC plate (ca. 30 × 30 cm) with a dichloromethane/diethyl ether (1:3) mixture. The elution gave only one yellow wide band, which was collected to give a solution that was evaporated to give complex **3a** as an orange solid. Yield: 40 mg, 24%. Anal. Calcd for $C_{47}H_{42}F_3N_3O_4P_2PdS$: C, 58.18; H, 4.36; N, 4.33; S, 3.30. Found: C, 57.16; H, 4.45; N, 4.11; S, 3.73. Although this complex was spectroscopically pure, the elemental analyzer always gave a low C content (1.75% relative error). Mp (°C): 125. ^{1}H NMR: δ, 7.81−5.90 (m, aromatic protons), 4.21 [t, CH$_2$, $^2J_{PH}$ = 9.00 Hz], 3.30 [s, 3H, MeO], 2.15, 1.81 [s, 3H, Me (azoMe)]. ^{31}P{^{1}H} NMR: δ, 35.08 (s) (see Discussion).

3c. The solid was washed with diethyl ether (4 × 4 mL) and the oily residue was stirred with diethyl ether (4 mL) to obtain **3c** as an orange solid. Yield: 44 mg, 30%. Anal. Calcd for $C_{46}H_{39}F_3N_4O_5P_2PdS$: C, 56.08; H, 3.99; N, 5.69; S, 3.25. Found: C, 56.19; H, 4.19; N, 5.72; S, 3.07. Mp (°C): 119. ^{1}H NMR: δ, 8.2−6.21 (m, aromatic protons), 4.31 (t, CH$_2$, $^2J_{PH}$ = 9.3 Hz), 2.14, 1.87 [s, 3H, Me (azoMe)]. ^{31}P{^{1}H} NMR: δ, 39.10 (d, $^2J_{PP}$ = 17.85 Hz), 34.29 (d).

4a. The orange solid was treated as for **1**. Yield: 150 mg, 91%. Anal. Calcd for $C_{47}H_{42}F_3N_3O_4P_2PdS$: C, 58.18; H, 4.36; N, 4.33; S, 3.30. Found: C, 58.13; H, 4.44; N, 4.28; S, 3.18. Mp (°C): 290. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 131. ^{1}H NMR: δ, 7.89−7.26 (m, aromatic protons), 6.97 (d, 1 H, aromatic protons, $^3J_{HH}$ = 8.1 Hz), 6.85 (d, 2 H, aromatic protons, $^3J_{HH}$ = 8.1 Hz), 6.50 (dd, aromatic protons, $^3J_{HH}$ = 8.1, $^4J_{HH}$ = 1.5 Hz), 6.26−6.18 (m, 3H, aromatic protons), 4.17 [dd, CH$_2$, $^2J_{PH}$ = 11 Hz, 9 Hz], 3.57 [s, 3H, MeO], 2.25, 1.88 [s, 3H, Me (azoMe)]. ^{31}P{^{1}H} NMR: δ, 35.65, 35.14 (AB, $^2J_{PP}$ = 20.15 Hz).

4b. The orange solid was treated as for **1**. Yield: 270 mg, 94%. Anal. Calcd for $C_{47}H_{42}F_3N_3O_3P_2PdS$: C, 59.15; H, 4.44; N, 4.40; S, 3.36. Found: C, 59.47; H, 4.56; N, 4.47; S, 3.39. Mp (°C): 260. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 135. ^{1}H NMR: δ, 7.89−7.35 (m, aromatic protons), 7.25 (d, 2H, H$_{22,26}$, $^3J_{HH}$ = 8.4 Hz), 6.97 (d, 1H, H$_{14}$, $^3J_{HH}$ = 8.15 Hz), 6.81 (d, 2H, H$_{23,25}$, $^3J_{HH}$ = 8.4 Hz), 6.50, 6.44 (AB, 4H, Ar, J_{AB} = 8.4 Hz), 6.25 (d, 1H, H$_{16}$, $^4J_{HP}$ = 6.6 Hz), 4.21 [t, CH$_2$, $^2J_{PH}$ = 9.00 Hz], 2.24, 2.02, 1.88 [s, 3H, Me]. ^{31}P{^{1}H} NMR: δ, 35.17 (s, see Discussion).

Crystal Structure. A crystal of **4b** was mounted in inert oil on a glass fiber and transferred to the diffractometer (Siemens P4). The crystal data are summarized in Table 1. Unit cell parameters were determined from a least-squares fit of 63 accurately centered reflections (5.6° < 2θ < 25.0°). The structure was solved by the heavy atom method and refined anisotropically on F^2 (program SHELXL 93).[41] Hydrogen atoms were included using a riding model. The final R1 was 0.0344 [$I > 2\sigma(I)$], for 660 parameters. Maximum Δ/σ = 0.036; maximum $\Delta\rho$ = 0.30 e Å^{-3}.

The programs use the neutral atom scattering factors, $\Delta f'$ and $\Delta f''$ and absorption coefficients from International Tables for Crystallography.[42]

4c. The orange solid was washed with dichloromethane (4 mL), the suspension was filtered, and to the resulting solution were added diethyl ether (15 mL) and *n*-hexane (10 mL) to give **4c**. Yield: 84 mg, 72%. Anal. Calcd for $C_{46}H_{39}F_3N_4O_5P_2$-

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[42] *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C, Tables 6.1.1.4 (pp 500−502), 4.2.6.8 (pp 219−222), and 4.2.4.2 (pp 193−199).

Table 1. Crystal Data for 4b

molecular formula	$C_{47}H_{42}F_3N_3O_3P_2PdS$
source	slow diffusion Et_2O/*n*-hexane
crystal habit	orange cube
a (Å)	18.439(2)
b (Å)	14.505(1)
c (Å)	18.754(2)
β (deg)	117.019(7)
Z	4
λ (Å)	0.71073
T (K)	298(2)
radiation used	Mo Kα
monochromator	graphite
space group	$P2_1/n$
crystal size (mm)	0.46 × 0.36 × 0.33
μ (mm^{-1})	0.590
abs correction	ψ scans
max/min transmission (%)	0.82/0.75
diffractometer	Siemens P4
data collection method	ω scans
2θ range (deg)	6.1−50.0
reciprocal lattice segment	$+h, +k, \pm l$
reflns measd	18 750
independent reflns	7858
R_{int}	0.024
R1[a]	0.0344
wR2[b]	0.0785

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ for reflections with $I > 2\sigma(I)$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$ and a and b are constants set by the program.

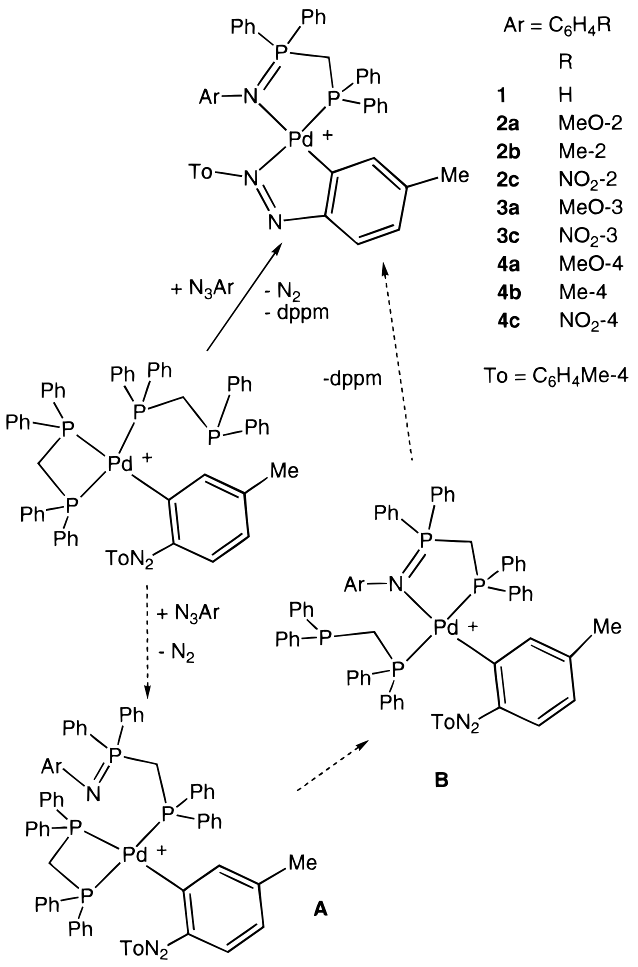
Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound 4b

Lengths (Å)			
N(1)−N(2)	1.267(3)	N(1)−C(2)	1.396(3)
N(2)−C(11)	1.446(3)	Pd−C(1)	1.988(3)
Pd−N(2)	2.104(2)	Pd−N(3)	2.159(2)
Pd−P(1)	2.2303(8)	P(2)−N(3)	1.607(2)
N(3)−C(61)	1.430(3)		
Angles (deg)			
N(2)−N(1)−C(2)	112.8(2)	N(1)−N(2)−C(11)	114.6(2)
N(1)−N(2)−Pd	117.1(2)	C(11)−N(2)−Pd	128.3(2)
C(1)−Pd−N(2)	78.62(10)	N(2)−Pd−N(3)	100.71(8)
C(1)−Pd−P(1)	97.71(8)	N(3)−Pd−P(1)	84.33(6)
C(61)−N(3)−P(2)	122.0(2)	C(61)−N(3)−Pd	117.0(2)
P(2)−N(3)−Pd	120.71(12)	C(2)−C(1)−Pd	111.4(2)
N(1)−C(2)−C(1)	120.0(2)		

PdS: C, 56.08; H, 3.99; N, 5.69; S, 3.25. Found: C, 55.89; H, 4.14; N, 5.67; S, 3.17. Mp (°C): 290. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 130. ^{1}H NMR: δ, 8.0−7.26 (m, aromatic protons), 7.00 (d, aromatic protons, $^3J_{HH}$ = 7.5 Hz), 6.80−6.71 (m, aromatic protons), 6.19 (dd, aromatic protons, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 0.9 Hz), 4.38 [dd, CH$_2$, $^2J_{PH}$ = 11.4, 9 Hz], 2.17, 1.87 [s, 3H, Me]. ^{31}P{^{1}H} NMR: δ, 38.27 (d, $^2J_{PP}$ = 15.2 Hz), 34.46 (d).

[Pd(κ^2-azoMe-*C,N′*)(PPh$_2$C(AuPPh$_3$)$_2$P(=NAr)Ph$_2$-*P,N*]-TfO (Ar = C$_6$H$_4$Me-4) (5b). To a suspension of [Pd(κ^2-azoMe-*C,N′*)(PPh$_2$CH$_2$P(=NAr)Ph$_2$-*P,N*]TfO [Ar = C$_6$H$_4$Me-4 (**4b**)] (90 mg, 0.09 mmol) in dichloromenthane (10 mL) was added [Au(acac)PPh$_3$] (106 mg, 0.19 mmol). The suspension was stirred for 36 h and then concentrated (2 mL). Addition of diethyl ether (5 mL) and *n*-hexane (5 mL) gave **3** as a red solid. Yield: 146 mg, 88%. Anal. Calcd for $C_{83}H_{70}Au_2F_3N_3O_3P_4PdS$: C, 53.28; H, 3.78; N, 2.25; S, 1.71. Found: C, 52.96; H, 3.96; N, 2.14; S, 1.82. Mp (°C): 143. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 125 Ω^{-1} mol^{-1} cm^2. ^{1}H NMR (300 MHz): 8.09−8.02 (m, aromatic protons), 7.75−7.64 (m, aromatic protons), 7.5−6.9 (m, aromatic protons), 6.77−6.64 (m, aromatic protons), 6.42−6.30 (m, aromatic protons), 2.23, 1.98, 1.83 [s, 2Me (azoMe) and 1Me (*p*-methylphenyl)]. ^{31}P NMR (121 MHz): 60.3 [dt, P^V, $^2J_{AM}$ = 33.0 Hz, $^2J_{AX}$ = 11.4 Hz], 43.3 [d, P^{III}, $^2J_{AM}$ = 33.0 Hz], 37.1 [d, PPh$_3$, $^2J_{AX}$ = 11.4 Hz)].

Scheme 6



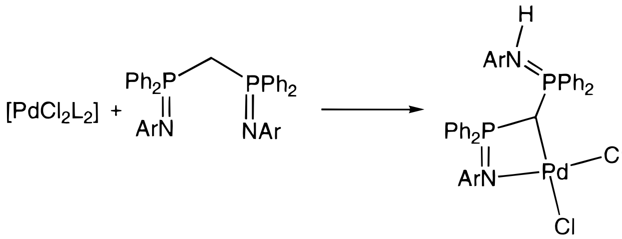
[Pd$_2$(μ_2−N$_3$)(azoMe)$_2$(μ_2-dppm)$_2$]TfO (6). To a suspension of [Pd(azoMe)(κ^2-dppm)]TfO (165 mg, 0.19 mmol) in acetone (15 mL) was added NaN$_3$ (14 mg, 0.215 mmol), and the reaction mixture stirred for 8 h. The solvent was removed, and dichloromethane (10 mL) added. Concentration (2 mL) and addition of diethyl ether (20 mL) and *n*-hexane (10 mL) gave **6** as an orange solid. Yield: 126 mg, 83%. Anal. Calcd for $C_{79}H_{70}F_3N_7O_3P_4Pd_2S$: C, 59.63; H, 4.43; N, 6.16; S, 2.01. Found: C, 59.34; H, 4.40; N, 6.11; S, 2.19. Mp (°C): 186. IR (cm^{-1}): $\nu_{asymmetric}$(N$_3$), 2070 cm^{-1}. ^{1}H NMR: δ, 7.54−6.83 (m, aromatic protons), 6.34 (d, 2 H aromatic protons, J = 8.1 Hz), 4.25−3.57 [dm, 4H, CH$_2$], 2.46, 1.94 (s, 6H, Me). ^{31}P{^{1}H} NMR: δ, 9.79 (s).

Results and Discussion

Synthesis and Reactivity of Complexes. The complex [Pd(azoMe)(κ^1-dppm)(κ^2-dppm)]TfO (azoMe = 2-(4′-tolylazo)-5-methylphenyl, dppm = bis(diphenylphosphino)methane, TfO = CF$_3$SO$_3$)[43] reacts, at room temperature, with aryl azides N$_3$Ar to give moderate to high yields of iminophosphorane complexes [Pd(κ^2-azoMe-*C,N′*){PPh$_2$CH$_2$P(=NAr)Ph$_2$-*P,N*}]TfO [Ar = C$_6$H$_4$R, R = H (**1**), MeO-2 (**2a**), Me-2 (**2b**), NO$_2$-2 (**2c**), MeO-3 (**3a**), NO$_2$-3 (**3c**), MeO-4 (**4a**), Me-4 (**4b**), NO$_2$-4 (**4c**)] (Scheme 6). The reaction with N$_3$C$_6$H$_4$Me-3 gives the corresponding complex, but we were unable to separate it from traces of bis(diphenylphosphino)methane dioxide (by ^{31}P NMR).

We propose a reaction pathway (see Scheme 6) that assumes formation of the iminophosphorane **A** through the classical Staudinger reaction.[4] A chelating *N,P*-

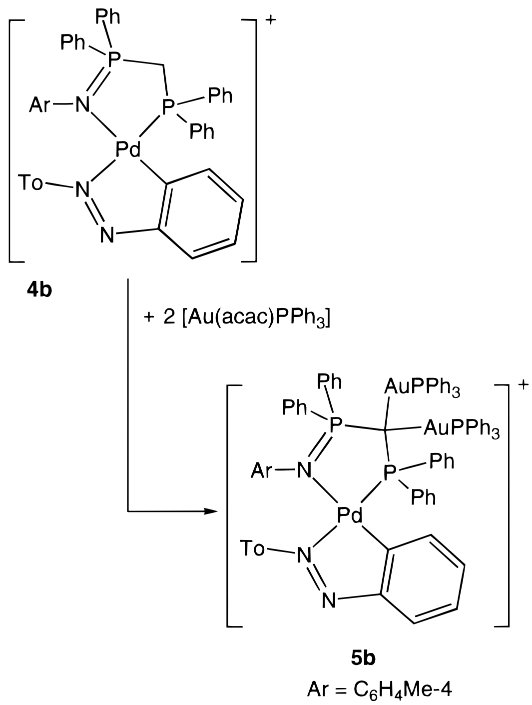
Scheme 7



iminophosphorane is formed by replacement of the P−Pd bond trans to the aryl group in **A**. Finally, the resulting intermediate (**B**) gives complexes **1**−**4** by replacement of the monocoordinate dppm by the N atom of the aryl ligand. The formation of the iminophosphorane **A** requires the presence of the uncoordinated P atom, as the complex [Pd(κ^2-azoMe-*C*,*N′*)(κ^2-dppm)]TfO[43] does not react with $N_3C_6H_4Me$-4. In the only process reported in the literature similar to our reaction, the dissociation of one of the phosphorus atoms of a chelating diphosphine was proposed as an essential step in the reaction mechanism (Scheme 5).[12] In this case, the previous coordination of the 8-azidoquinoline could help the cleavage of the P−Mo bond. The **A** → **B** process is facilitated by (i) the strained nature of the four-membered ring of dppm compared to the very stable five-membered ring that results in **B** and (ii) the destabilizing effect that an aryl group exerts on the trans P−Pd bond (*transphobia*).[43] Finally, the chelate effect can explain the transformation of **B** into **1**−**4**.

Complex **4b** reacts with KOBu^t to give a mixture of two compounds (observed by ^{31}P NMR) that could not be separated. However, it does not react with Et_2NH (neat or in a dichloromethane solution, room temperature, 3 days). The behavior of the *N*,*P*-diphosphinomonoimine ligand in **4a** contrasts with that of the free diphosphinodiimine ligands ArN=PPh_2CH_2P(=NAr)-Ph_2. These react with [$PdCl_2L_2$] (L = PhCN, MeCN, L_2 = COD) to give products resulting from the migration of one of the methylene protons to one of the nitrogen atoms and coordination through the other nitrogen and the methine carbon atoms (Scheme 7).[37] The acidic character of the CH_2 group in **4b** was shown by its reaction with [Au(acac)PPh_3]. The 1:2 reaction gives

Scheme 8



complex [Pd(κ^2-azoMe-*C*,*N′*){$PPh_2C(AuPPh_3)_2P$(=NAr)-Ph_2-*P*,*N*}] [Ar = Me-4 (**5b**); Scheme 8]. The 1:1 reaction gives a mixture that contains **4b**, the starting palladium complex, and another complex that, according to ^{31}P NMR, could be the monoaurated complex [Pd(κ^2-azoMe-*C*,*N′*)($PPh_2CH(AuPPh_3)P$(=NAr)Ph_2-*P*,*N*]. Many attempts to separate this mixture were unsuccessful. We have shown the synthetic utility of [Au(acac)PPh_3] to prepare gold(I) complexes with C-,[44−52] N-,[53−55] and S-[56] donor ligands. This reagent has also been used to prepare other gold(I) complexes containing the moiety $Ph_2PC(AuPPh_3)_2PPh_2$.[57−61]

We also attempted to prepare phosphiniminates of palladium (R′ = metallic moiety in A, Scheme 1) by reacting NaN_3 with [Pd(azoMe)(κ^1-dppm)(κ^2-dppm)]TfO, [Pd(azoMe)Cl(κ^1-dppm)$_2$], or [Pd(κ^2-azoMe-*C*,*N′*)(κ^2-dppm)]TfO.[43] The starting materials were recovered in the first two cases, but in the last reaction, the complex [Pd_2(azoMe)$_2$(μ_2-N_3)(μ_2-dppm)$_2$]TfO (**6**) was isolated (Scheme 9). This complex does not decompose after being refluxed in THF for 1 h. Traces of **6** were also obtained in the reaction between [Pd(azoMe)(κ^1-dppm)(κ^2-dppm)]TfO and N_3SiMe_3. This result can be explained if formation of $TfOSiMe_3$ is asumed.

We have attempted unsuccessfully to react **4b** with H_2O_2, PPh_3, or 2,2′-bipyridine.

Spectroscopic Properties. The ^{31}P{^{1}H} NMR spectra of complexes **1**−**4** show an AB system (**1**, **4a**), two

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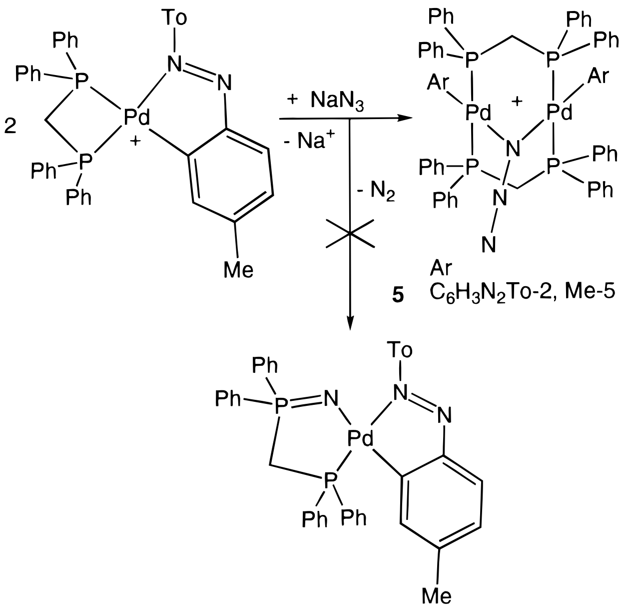
Scheme 9



doublets (**2a**, **2b**, **2c**, **3c**, **4c**) or a singlet (**3a**, **4b**) in the range 30−45 ppm with $^3J_{PP}$ = 15−25 Hz. The ^{31}P chemical shifts of $Ph_3P{=}NC_6H_4R$-4 (R = H, NO_2, CN, CF_3, Cl, F, Me, OMe, NMe_2) are in the range 2.6−7.8 ppm and follow the expected order $\delta(NO_2) > \delta(CN) > \delta(CF_3) > \delta(Cl) > \delta(F) > \delta(H) > \delta(Me) > \delta(OMe) > \delta(NMe_2)$.[62] Therefore, N-coordination leads to deshielding of the P^V nucleus. When we prepared the first complex of this family (**4b**), we were surprised to find a singlet for the two different phosphorus atoms. In the only family of related complexes, $[RhCl(CO)(PPh_2CH_2P(=NAr)Ph_2\text{-}P,N]$ [Ar = $C_6F_n(CN)_m(NO_2)_pH_q$], the P^{III} and P^V resonances were unequivocally assigned because of the different J_{PRh} values.[33−35] In all cases, the P^V resonance appeared at a lower field (2−4 ppm; range, 42−44 ppm) than the P^{III} resonance (range, 39−40 ppm) with $^3J_{PP}$ in the range 28−32 Hz. Therefore, we undertook a variable-temperature $^{31}P\{^1H\}$ NMR study to see if a scrambling process was making both phosphorus atoms in **4b** equivalent. At −60 °C two doublets were observed that changed to an AB quartet when the temperature was raised to give a singlet at 24 °C and again an AB quartet at 30 °C. No coalescence was observed. Therefore, the conclusion was that both resonances were temperature dependent. To see if this phenomenon had some electronic and/or steric origin, we prepared the rest of the family containing substituents of different electronic effects in the three possible positions on the aryl group. The data are represented in Figures 1 and 2. In all cases, a linear correlation between δ(P) (ppm) of both phosphorus atoms and temperature *T* (°C) was observed [$\delta(P_1) = \delta_1(0) + a_1T$; $\delta(P_2) = \delta_2(0) + a_2T$]. Complexes **1**−**4** can be divided into two groups. In the first one, including the ortho-substituted complexes **2a**−**c** and the nitro derivatives **3c** and **4c** (Figure 2), there is no crossing of the two δ/T plots of each complex. In addition, the changes in chemical shift with temperature are small or nil, $|a_1|$, $|a_2|$ = (0−12) × 10^{-3} ppm/°C. According to the data found in the above-mentioned Rh complexes, the low-field resonance in the range 37−45 ppm should be assigned to the P^V atom and those in the range 31−35 ppm to the P^{III} atom. In the second group of complexes, there is a crossing of the two straight lines of each complex (Figure 1). Of the two straight lines corresponding to each complex, one is of a positive gradient and the other is negative. Those with a positive gradient have $a_1 \approx 26 \times 10^{-3}$ ppm/°C, while those with a negative gradient have $a_2 \approx -7.5 \times 10^{-3}$ ppm/°C. The crossing points are in the range 0−25 °C. This behavior is similar to that found for the Me or CH_2 and OH protons of methanol or ethylene glycol, respectively, and is used to measure the temperature within the sample NMR tube.[63] Correspondingly, our complexes could also have the same application in ^{31}P NMR spectroscopy. Although we cannot assign the P^V and P^{III} resonances in the second group of complexes, the observed order $\delta(P^VNO_2\text{-}4) > \delta(P^VMe\text{-}4) \approx \delta(P^VOMe\text{-}4) > \delta(H)$ at room temperature means that, in this case, the chemical shift is dependent on other more important contributions than the electronic one.

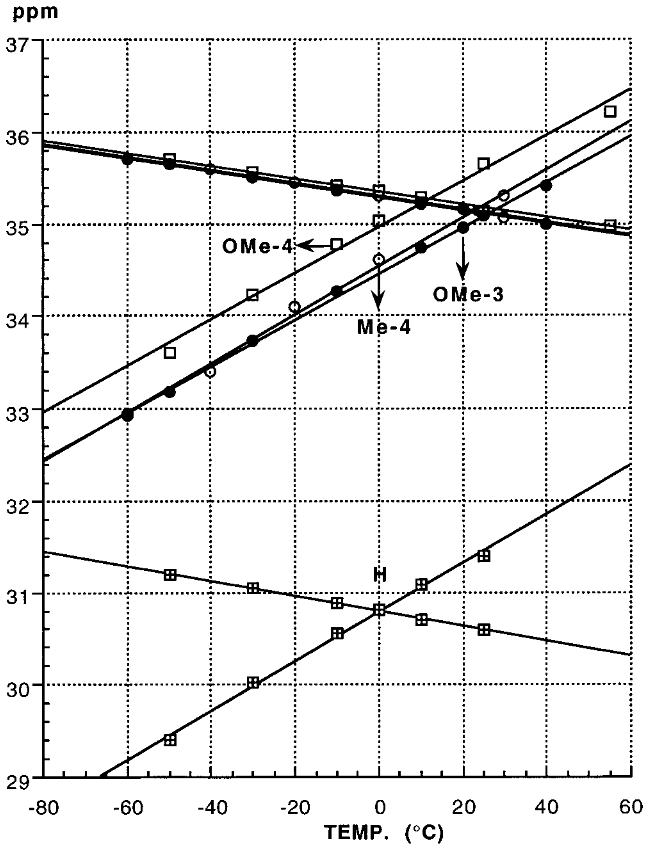


Figure 1. Correlation between δ(P) (ppm) of both phosphorus nuclei and temperature *T* (°C) of complexes **1** (R = H), **3a** (R = OMe-3), **4a** (R = OMe-4), and **4b** (R = Me-4).

Iminophosphorane complexes related to **1**−**4** exhibit an IR band in the range 1230−1285 cm^{-1} assigned to the ν(P=N) mode.[14,19,26,31,37] The IR spectra of complexes **1**−**4** in such a region are not different from that in the complex $[Pd(\kappa^2\text{-azoMe-}C,N')(\kappa^2\text{-dppm})]^+$.[43] Probably, in our complexes the band assigned to the ν(P=N) mode is overlapped by others due to the azophenyl group.

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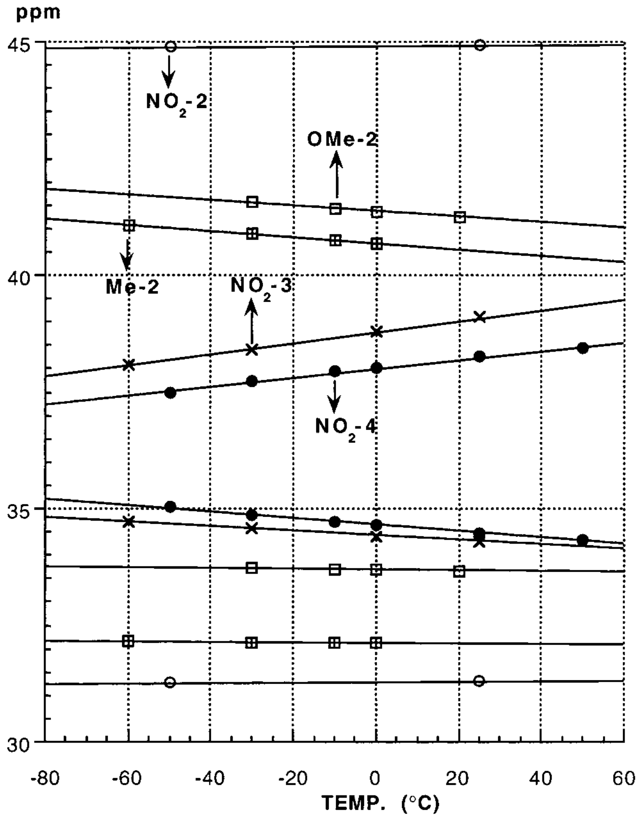

Figure 2. Correlation between δ(P) (ppm) of both phosphorus nuclei and temperature T (°C) of complexes **2a** (R = OMe-2), **2b** (R = Me-2), **2c** (R = NO$_2$-2), **3c** (R = NO$_2$-3), and **4c** (R = NO$_2$-4).

Complex **6** shows a singlet in the $^{31}P\{^1H\}$ NMR spectrum, suggesting the symmetrical structure shown in Scheme 9. When the azido ligand bridges two metal centers, there are two coordination modes for this ligand: through a single N atom (1,1 mode) or through the two terminal N atoms (1,3 mode). IR spectroscopy can be used to distinguish between these modes.[64] The ν_{sym}(NNN) mode appears as a band of medium intensity at around 2060 cm^{-1} for the 1,1-N$_3$ mode. In complex **6**, a strong band at 2070 cm^{-1} indicates the 1,1-coordination mode for the N$_3$ ligand.

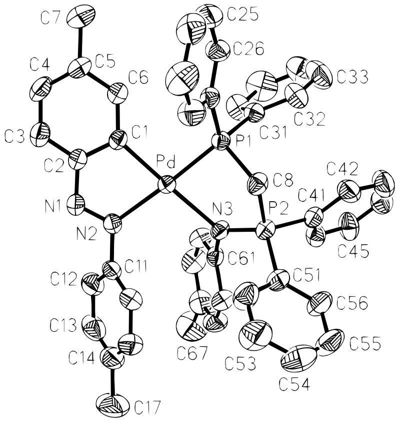

Figure 3. ORTEP plot of **4b** with the labeling scheme.

Crystal Structure of [Pd(κ^2-azoMe-C,N′)(PPh$_2$CH$_2$P(=NC$_6$H$_4$Me-4)Ph$_2$-*P*,*N*)] (4b). There are only two reported crystal structures of iminophosphorane complexes of Pd, [PdCl$_2$(PPh$_2$CH$_2$P(=NR)Ph$_2$-*P*,*N*)], with R being H,[27] or Fe(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$CH=C(CO$_2$Et).[40] In **4b**, the coordination plane is strongly distorted because the Pd−C(1)−C(2)−N(1)−N(2) plane forms an angle of 13.9° with the Pd−N(3)−P(1) plane (see Figure 3). This distortion seems necessary to avoid contact between the aryl groups bonded to the cis nitrogen atoms. The Pd−N$_{imine}$ bond distance [2.159(2) Å] is longer than the Pd−N$_{azo}$ bond length [2.104(2) Å]. Both distances are much longer than Pd−N$_{imine}$ in [PdCl$_2$(PPh$_2$CH$_2$P(=NH)Ph$_2$-*P*,*N*)] [2.021(6) Å].[27] The different Pd−N$_{imine}$ and Pd−N$_{azo}$ distances could reflect the greater strength of the Pd−NH bond compared to the Pd−NAr bond and/or be due to a difference in the trans influence [C(1) versus P(1)].

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Supporting Information Available: An X-ray crystallographic file in CIF format for compound **4b** is available on the Internet only. Access information is given on any current masthead page.

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