

Synthesis of *cis*-Dichloro(2-pyridiniumyl)(di-2-pyridylphenylphosphine)palladium(II) and Structural Aspects of Precursors^{1a}

George R. Newkome,*^{1b} David W. Evans, and Frank R. Fronczek

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Palladium(II) complexes of 2-pyridylphosphines were synthesized. Two unique aspects of these complexes were observed: first, formation of *cis*-dichlorobis(di-2-pyridylphenylphosphine)palladium(II) (**2**), which is the first example of an isolated, nonchelated *cis*-bis(triarylphosphine)palladium(II) complex; second, sequential extrusion of a phosphorus moiety leading to *cis*-dichloro(2-pyridiniumyl)(di-2-pyridylphenylphosphine)palladium(II) (**3**), and ultimately to (2,2'-bipyridine)PdCl₂ (**4**). X-ray crystallographic data have been collected on these complexes and indicate that charge transfer may be the driving force for the formation of the *cis* geometry. Complexes **2**, 2-C₆H₆, and 3-C₆H₆ crystallized in the triclinic space group *P* $\bar{1}$. The unit cell dimensions are as follows: for **2**, *a* = 10.462 (2), *b* = 11.148 (3), and *c* = 14.644 (1) Å with α = 96.18 (2), β = 90.48 (1), and γ = 115.34 (1)° and *Z* = 2; for 2-C₆H₆, *a* = 10.707 (1), *b* = 11.846 (1) and *c* = 14.100 (3) Å with α = 80.33 (1), β = 85.34 (1), and γ = 87.57 (1)° and *Z* = 2; for 3-C₆H₆, *a* = 8.9812 (13), *b* = 10.1553 (9), and *c* = 14.4363 (13) Å with α = 91.322 (7), β = 95.671 (10), and γ = 91.630 (10)° and *Z* = 2. An extension of this study into Pd(II) complexes of 2,6-bis(diphenylphosphino)pyridine led to the isolation of chloro-bridged dimer **7**, derived from an oxidative byproduct of the ligand. Complex **7** (Pd₂Cl₄C₃₈H₄₆N₂O₂P₄) crystallized in the monoclinic space group *P*₂₁/*n*. The unit cell dimensions are *a* = 17.276 (6), *b* = 13.703 (2), and *c* = 23.178 (4) Å with β = 92.04 (3)° and *Z* = 4.

Introduction

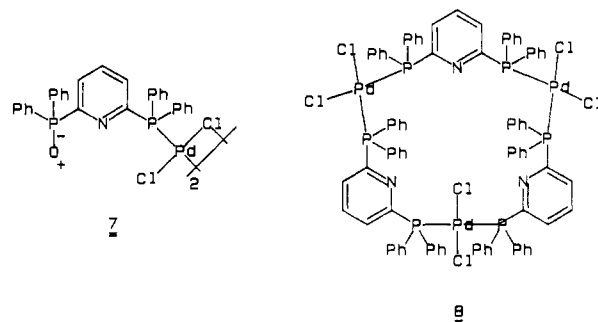
Even though there are examples of palladium(II)-phosphine complexes,² of those involving nonchelating triarylphosphines, only two papers mention the presence of the "cis isomer", based on solution ³¹P NMR spectral data.³ Despite the overwhelming evidence² for Pd(II)-triarylphosphine complexes preferring the trans geometry, the lack of examples of isolated cis isomers remains a curious anomaly, especially considering the preponderance of corresponding Pt(II) examples.⁴ Therefore, the isolation of cis complex **2** provided us with insight into the potential interactions, which may permit the formation of new cis-Pd(II) complexes. X-ray crystallographic data have been collected on all new complexes synthesized in this study and their structural data correlated.

The rearrangement of **2** (Scheme I), with concurrent extrusion of phosphinite **6**, leading to the formation of **3** will be described in detail elsewhere,^{5b} as the subsequent rearrangement to **4** has been.⁵ A detailed discussion of their solid-state structure, as determined by single-crystal X-ray analysis, will be herein provided.

An extension of this study led us to investigate the reaction of 2,6-bis(diphenylphosphino)pyridine with Pd(II) salts. The major product was the previously observed cyclic *cis,cis,trans* trimer (**8**),⁶ but another unanticipated complex was isolated, as a minor byproduct. Single-crystal X-ray analysis of this minor byproduct showed it to be the chloro-bridged dimer **7**, which arose from an autoxidation impurity in the bis(phosphine) ligand.

Experimental Section

General Comments. All melting points were taken in a capillary tube on a Thomas-Hoover Uni-Melt apparatus and are uncorrected. ¹H



NMR spectra were determined on an IBM NR/80 spectrometer with CDCl₃ used as solvent, with TMS (0.1%) as the internal standard. ³¹P NMR spectra were determined by M. Nauman on a Bruker WP200 spectrometer with CDCl₃ used as solvent, unless otherwise noted, and H₃PO₄ used as an external standard. Mass spectral (MS) data (70eV) were determined by H. Land on a Hewlett-Packard 5985 GC/mass spectrometer and reported herein as *m/e* (relative intensity, assignment). Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Complex Formation. Procedure A. A solution of ligand (2.1 equiv) and Na₂PdCl₄ (1.0 equiv) in anhydrous MeOH was warmed for 3-6 h. The solution was then cooled to 25 °C overnight. The orange/yellow precipitate was filtered and recrystallized.

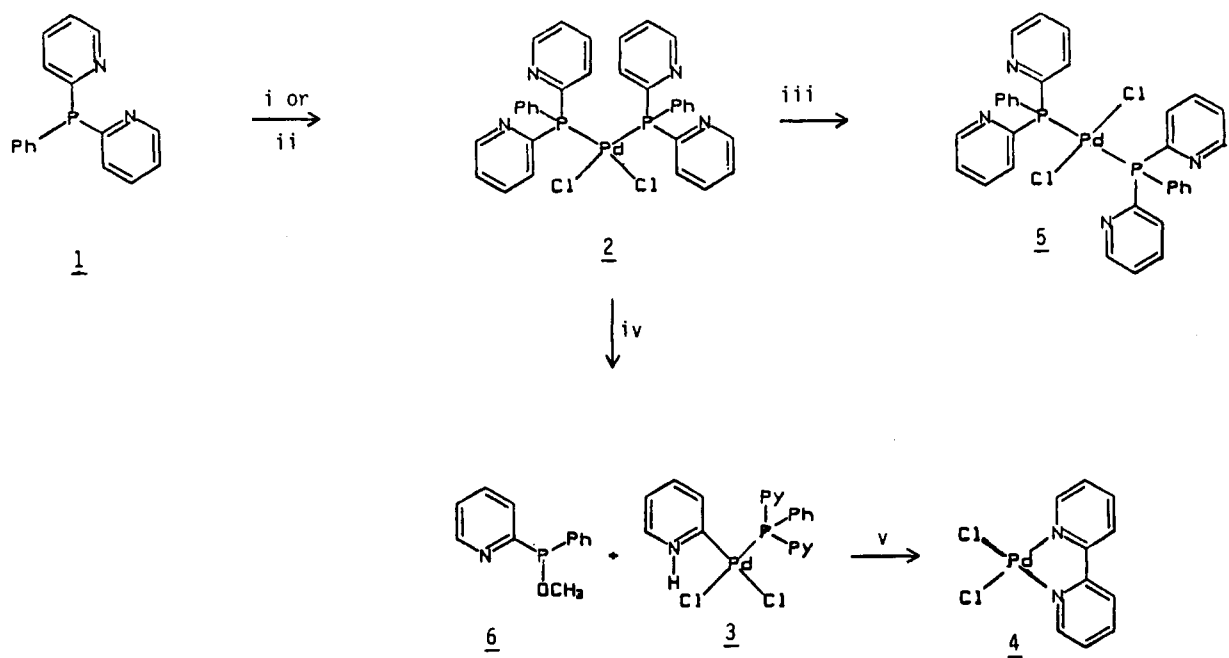
Procedure B. A slurry of PdCl₂ (1.0 equiv) in MeCN was warmed to 50 ± 10 °C until dissolution was complete. A solution of the ligand (2.1 equiv) in MeCN was then added and the resulting yellow solution stirred for 20 h at 25 °C. If any precipitate was present, the solution was filtered and the filtrate concentrated in vacuo. Recrystallization gave the pure complex.

Complex 2 was prepared by procedure A using **1** (132 mg, 0.5 mmol) and Na₂PdCl₄ (71 mg, 0.24 mmol) in anhydrous MeOH (25 mL). Recrystallization (MeOH) of the resultant solid gave (5%) an insoluble white solid, which was shown to be pure **3**: mp > 240 °C dec; ¹H NMR (DMSO-*d*₆) δ 6.97 (m, 5-pyH, 1 H), 7.05-8.50 (m, Ar H, 16 H), 10.2 (br s, NH, 1 H); ³¹P NMR (DMSO-*d*₆) δ 30.5. Anal. Calcd for C₂₇H₂₄N₃PCl₂Pd: C, 54.16; H, 4.04; N, 7.02. Found: C, 54.37; H, 4.41; N, 6.83. Crystals of 3-C₆H₆ suitable for X-ray analysis were obtained by crystallization from CH₂Cl₂/C₆H₆/C₆H₁₂.

Cooling to 25 °C gave (70%) **2**, as yellow microcrystals: 119 mg; mp 157-159 °C dec; ¹H NMR δ 7.04-8.28 (m, PhH + 3,3',5,5'-pyH, 9 H), 8.40 (br d, 4,4'-pyH, *J* = 7.1 Hz, 2 H), 8.79 (d, 6,6'-pyH, *J* = 9.4 Hz, 2 H); ³¹P NMR δ 29.4. Anal. Calcd for C₃₂H₂₆N₄P₂Cl₂Pd: C, 54.45; H, 3.71; N, 7.94. Found: C, 54.31; H, 3.90; N, 8.01. Crystals of 2-C₆H₆ suitable for X-ray analysis were obtained by crystallization from CH₂Cl₂/C₆H₆/C₆H₁₂. Crystallization from C₆H₆/petroleum ether (bp 30-60 °C) gave **2** as a nonsolvate.

Complex 2 was also prepared by procedure B using **1** (106 mg, 0.4 mmol) and PdCl₂ (35 mg, 0.20 mmol) in anhydrous MeCN (25 mL). Workup yielded (100%) crude **2**, which was recrystallized (CH₂Cl₂/

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Scheme 1^a

^a i = Na₂PdCl₄/CH₃OH/25 °C; ii = PdCl₂/CH₃CN/25 °C; iii = excess 1/CH₃CN/50 °C; iv = CH₃OH/Δ; v = excess Cl⁻/CH₃OH/50 °C.

Table I. Crystal Data for 2, 2·C₆H₆, 3·C₆H₆, and 7

	2	2·C ₆ H ₆	3·C ₆ H ₆	7
formula:	PdCl ₂ C ₃₂ H ₂₆ N ₄ P ₂	PdCl ₂ C ₃₈ H ₃₂ N ₄ P ₂	PdCl ₂ C ₂₇ H ₂₄ N ₃ P	Pd ₂ Cl ₄ C ₅₈ H ₄₆ N ₂ O ₂ P ₄
fw	705.82	783.93	598.76	1281.50
cryst syst	triclinic	triclinic	triclinic	monoclinic
space group	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$	P ₂ ₁ /n
a, Å	10.462 (2)	10.707 (1)	8.9812 (13)	17.276 (6)
b, Å	11.148 (3)	11.846 (1)	10.1553 (9)	13.703 (2)
c, Å	14.644 (1)	14.100 (3)	14.4363 (13)	23.178 (4)
α, deg	96.18 (2)	80.33 (1)	91.322 (7)	
β, deg	90.48 (1)	85.34 (1)	95.671 (10)	92.04 (3)
γ, deg	115.34 (1)	87.57 (1)	91.630 (13)	
V, Å ³	1531.7 (11)	1756.4 (6)	1309.3 (6)	5483 (4)
d, g/cm ³	1.526	1.335	1.429	1.553
Z	2	2	2	4
μ(MoKα), cm ⁻¹	5.91	5.37	8.80	10.03
min transmissn, %	92.93	94.70	94.73	95.44
cryst size, mm	0.28 × 0.36 × 0.36	0.12 × 0.20 × 0.20	0.24 × 0.24 × 0.48	0.20 × 0.24 × 0.32
θ limits, deg	1 < θ < 25	1 < θ < 25	1 < θ < 25	1 < θ < 22
scan rates, deg/min	0.80–4	1.54–4	0.43–4	0.91–5
precision	I ≈ 25σ(I)	I ≈ 25σ(I)	I ≈ 25σ(I)	I ≈ 25σ(I)
max scan time, s	45	90	60	60
no. of unique data	5382	6171	4598	5309
no. of obsd data	3597	5259	4073	3646
variables	396	426	310	385
R	0.0398	0.0283	0.0313	0.0462
R _w	0.0394	0.0325	0.0357	0.0472
max. residual, e/Å ³	1.12	0.34	0.70	0.47
color	yellow	yellow	colorless	orange
temp, °C	21.5	21	18.5	22

C₆H₁₂) to give pure **2**, as a yellow crystalline solid: 140 mg; identical with the above sample.

Complex 3 was prepared by refluxing a solution of **2** (1.41 g, 2.0 mmol) in anhydrous MeOH (100 mL) for 24 h. The cooled solution was filtered, and the resultant white solid was recrystallized as above to give (30%) **3**: 360 mg; mp > 240 °C.

Concentration of the filtrate yielded a mixture of **2** and **6**, which was chromatographed (silica; CH₂Cl₂); the phosphinite fraction was distilled in vacuo to give **6** as a colorless oil: bp 120 °C (1 mmHg); ¹H NMR δ 3.71 (d, OCH₃, J_{3P-H} = 16.7 Hz, 3 H), 7.0–8.1 (m, PhH + 3,5-pyH, 7 H), 8.32 (br d, 4-pyH, J = 7.0 Hz, 1 H), 8.75 (br d, 6-pyH, J = 9.0 Hz, 1 H); ³¹P NMR δ 110.2; MS m/e 217 (63, M⁺), 202 (100, M⁺ - CH₃), 124 (27, M⁺ - C₆H₇N). Anal. Calcd for C₁₂H₁₂NOP: C, 66.35; H, 5.57; N, 6.45. Found: C, 66.07; H, 5.38; N, 6.41.

Complex 4 was prepared by warming (50–60 °C) a solution of **2** (35 mg, 0.05 mmol) and saturated aqueous NaCl (0.1 mL) in 95% EtOH

for 18 h. After the initially orange solution turned yellow, the mixture was concentrated in vacuo; the residue was dissolved in CH₂Cl₂ (25 mL), filtered, and concentrated to give (97%) **4** (H = Y), as orange crystals, 34 mg. Crystals suitable for X-ray analysis were obtained from acetone/CHCl₃ (2:1).

Complex 5 was prepared by refluxing a solution of **2** (35 mg, 0.05 mmol) and **1** (1.2 mg, 5 μmol) in MeCN (15 mL) for 24 h. The solution was concentrated in vacuo and chromatographed (silica; CH₂Cl₂) to give (95%) **5** as orange microcrystals: 33 mg; mp 171–173 °C dec; ³¹P NMR δ 17.7.

Complex 7. Procedure A. A mixture of 2,6-bis(diphenylphosphino)pyridine⁷ (45 mg, 0.1 mmol) and Na₂PdCl₄ (29 mg, 0.1 mmol) in absolute EtOH (25 mL) was refluxed for 20 h under an argon atmosphere.

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Table II. ^{31}P NMR Data for Pyridylphosphines and Their Pd(II) and Pt(II) Complexes

compd	chem shift, δ		ref
	CD_2Cl_2	CDCl_3	
	Ligands		
PPh_3	-4.9	-4.2	11
(2-pyr) PPh_2	-3.4	-2.7	11
(2-pyr) $_2\text{PPh}$		-1.9	<i>b</i>
	Pd(II) Complexes		
<i>trans</i> -(PPh_3) $_2\text{PdCl}_2$		23.6/24.1	11
[(2-pyr) PPh_2] PdCl_2^a	23.8	22.9	3
[(2-pyr) PPh_2] PdCl_2^a	29.3	28.5	3
<i>cis</i> -[(2-pyr) $_2\text{PPh}$] PdCl_2		29.4	<i>b</i>
<i>trans</i> -[(2-pyr) $_2\text{PPh}$] PdCl_2		17.7	<i>b</i>
	Pt(II) Complexes		
<i>cis</i> -(PPh_3) $_2\text{PtCl}_2$		14.7	11
<i>trans</i> -(PPh_3) $_2\text{PtCl}_2$		20.6	11
<i>cis</i> -[(2-pyr) PPh_2] PtI_2		6.7	11
<i>trans</i> -[(2-pyr) PPh_2] PtI_2		9.8	11

^aNo assignments were made by the authors. ^bThis work.

Cooling to 25 °C yielded a bright yellow precipitate, which was filtered to give *cis,cis,trans*-Pd $_3$ [μ -((Ph_2P) $_2$ -2,6-pyr)] $_3\text{Cl}_6$ (2-pyr = 2-pyridyl) (**8**):³ 57 mg. Concentration of the filtrate gave **7** as orange microcrystals: 5 mg; mp > 240 °C; ^{31}P NMR δ 21.6, 31.0. Crystals suitable for X-ray analysis were obtained by crystallization from EtOH/petroleum ether (bp 30–60 °C).

X-ray Experiments. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer equipped with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) and a graphite monochromator. The ω - 2θ scans were made at variable rates, designed to yield measurements of equal precision for all significant data. A maximum was placed on the scan time spent on each reflection. Crystal data and specifics for each data set are given in Table I. One hemisphere of data was measured for each triclinic crystal and one quadrant for the monoclinic crystal, within the specified angular limits. Redundant data were merged for **7**. Data reduction included corrections for background, Lorentz, polarization, and absorption, the latter based upon ψ scans of reflections near $\chi = 90^\circ$, by using the program EAC of the Enraf-Nonius SDP programs.⁸ Reflections having $I > 3\sigma(I)$ were considered observed and used in the refinements.

All structures were solved by the heavy-atom method and refined by full-matrix least squares based upon F , except **2**· C_6H_6 , which was refined by blocked-matrix least squares, with weights $w = \sigma^{-2}(F_o)$, using the SHELX system, scattering factors of Cromer and Waber,⁹ and anomalous dispersion coefficients of Cromer.¹⁰ Non-hydrogen atoms were refined anisotropically, except for the phenyl carbons of **7**; hydrogen atom positions were calculated and included as fixed contributions.

For **2**, hydrogen atom thermal parameters were refined individually, whereas, in **2**· C_6H_6 and **3**· C_6H_6 , those of the ligand hydrogens were refined as one common variable and those at the solvate hydrogens as another variable. The thermal parameters of the pyridinium hydrogens of **3** were refined as one variable as well. The thermal parameters of **7** were allowed to ride upon their respective carbons. Secondary extinction effects were not a problem for any of these refinements. Final R factors and residual densities are included in Table I. The coordinates of non-hydrogen atoms for **2** (nonsolvate and solvate), **3**, and **7** are given in Tables IV–VI and VIII, respectively.

Results and Discussion

Complex Formation. The reaction of phosphine **1** with $\text{Na}_2\text{-PdCl}_4$ in anhydrous MeOH at 25 °C led to the formation of two products. The major product was **2**, with **3** present as a very minor byproduct (74% overall; 95% **2** and 5% **3**). The formation of **3**, as well as its further rearrangement to **4**, was via a phosphorus extrusion procedure, which was discussed in a preliminary communication.⁷ When this reaction was run above 50–60 °C, **5** was formed. The temperature dependence of this extrusion process was further supported by the observation that **2** can be readily

Table III. Important Bond Lengths (\AA) and Angles (deg) in Complexes **2**, **2**· C_6H_6 , and **3**· C_6H_6^a

	2	2 · C_6H_6	3 · C_6H_6
Pd–Cl(1)	2.3573 (14)	2.3495 (9)	2.3807 (9)
Pd–Cl(2)	2.3485 (22)	2.3550 (9)	2.3498 (8)
Pd–P(1)	2.2469 (18)	2.2624 (8)	2.2433 (8)
Pd–P(2)	2.2569 (13)	2.2623 (8)	
Pd–C(1)			1.980 (3)
P–C av	1.835 (13) ^b	1.835 (10) ^b	1.829 (9) ^b
C–N av	1.350 (19) ^b	1.348 (16) ^b	1.336 ^c
C–C av	1.374 (15) ^b	1.372 (17) ^b	1.376 (16) ^b
Cl(1)–Pd–Cl(2)	91.86 (6)	92.18 (3)	91.04 (3)
Cl(1)–Pd–P(1)	83.91 (6)	84.79 (3)	90.47 (3)
Cl(1)–Pd–P(2)	168.73 (11)	171.76 (6)	
Cl(1)–Pd–C(1)			176.8 (3)
Cl(2)–Pd–P(1)	167.87 (8)	170.87 (5)	177.07 (16)
Cl(2)–Pd–P(2)	85.82 (6)	87.54 (3)	
Cl(2)–Pd–C(1)			86.59 (9)
P(1)–Pd–P(2)	100.46 (6)	96.69 (2)	
P(1)–Pd–C(1)			91.99 (9)
C–N–C av	117.2 (6) ^b	117.5 (2) ^b	117.0 (3)
N–C–C av	122.8 (8) ^b	122.8 (6) ^b	123.4 ^c
C–C–C av	119.5 (12) ^b	119.6 (9) ^b	119.7 (10) ^b

^aDisordered atoms are excluded. ^bRoot-mean-square standard deviation. ^cAverage of two values.

Table IV. Atomic Positional Parameters ($\times 10^4$) and Isotropic Temperature Factors ($\text{\AA}^2 \times 10^3$) for **2**

atom	x	y	z	U^a
Pd(1)	1508.8 (4)	4346.0 (4)	2402.8 (3)	29.3 (2)
Cl(1)	-645.4 (15)	2394.6 (15)	2170.7 (12)	49.6 (6)
Cl(2)	322.1 (16)	5724.9 (16)	2515.2 (12)	56.5 (7)
P(1)	2478.3 (14)	2934.9 (13)	1982.0 (9)	28.9 (5)
N(1)	4731 (5)	4353 (5)	1107 (3)	47 (2)
C(1)	4363 (5)	3558 (5)	1776 (3)	29 (2)
C(2)	5286 (6)	3180 (5)	2213 (4)	39 (2)
C(3)	6654 (6)	3613 (6)	1918 (5)	52 (3)
C(4)	7021 (6)	4390 (7)	1219 (4)	53 (3)
C(5)	6045 (7)	4734 (7)	834 (4)	58 (3)
N(2)	2301 (5)	1237 (5)	473 (4)	54 (2)
C(6)	1811 (5)	2138 (5)	793 (4)	36 (2)
C(7)	1047 (6)	2559 (6)	249 (4)	44 (2)
C(8)	713 (7)	2010 (7)	-655 (4)	56 (3)
C(9)	1161 (7)	1071 (7)	-996 (4)	56 (3)
C(10)	1933 (7)	693 (7)	-422 (4)	55 (3)
C(11)	2135 (5)	1684 (5)	2760 (4)	35 (2)
C(12)	2026 (9)	2042 (7)	3677 (5)	75 (4)
C(13)	1795 (11)	1116 (8)	4303 (5)	101 (5)
C(14)	1667 (8)	-134 (7)	4005 (5)	76 (4)
C(15)	1761 (7)	-497 (6)	3098 (5)	59 (3)
C(16)	2001 (6)	413 (6)	2466 (4)	45 (3)
P(2)	3468.5 (14)	6216.0 (14)	2917.7 (9)	29.6 (5)
N(3)	4852 (6)	8802 (5)	2515 (4)	65 (3)
C(17)	3893 (6)	7551 (5)	2183 (4)	36 (2)
C(18)	3223 (8)	7263 (7)	1321 (4)	60 (3)
C(19)	3503 (9)	8298 (8)	782 (5)	76 (4)
C(20)	4465 (8)	9561 (7)	1115 (5)	66 (3)
C(21)	5156 (8)	9810 (7)	1955 (5)	61 (3)
N(4)	5080 (5)	5428 (5)	3844 (3)	47 (2)
C(22)	5166 (5)	6180 (5)	3178 (4)	34 (2)
C(23)	6412 (6)	6877 (6)	2769 (4)	48 (3)
C(24)	7638 (7)	6830 (7)	3089 (5)	58 (3)
C(25)	7564 (7)	6093 (7)	3790 (4)	63 (3)
C(26)	6271 (7)	5403 (7)	4146 (4)	62 (3)
C(27)	3201 (6)	6874 (5)	4079 (4)	37 (2)
C(28)	1975 (7)	6238 (7)	4509 (4)	60 (3)
C(29)	1863 (7)	6772 (8)	5392 (5)	70 (3)
C(30)	2933 (8)	7874 (7)	5823 (5)	66 (3)
C(31)	4157 (9)	8434 (7)	5368 (5)	71 (3)
C(32)	4296 (7)	7949 (6)	4498 (4)	45 (2)

^aEquivalent isotropic temperature factor: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, p 316.

converted to **5** by warming a solution of **2** above 50 °C in the presence of excess free phosphine **1**. The unexpected appearance

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(9) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(10) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

Table V. Atomic Positional Parameters ($\times 10^4$) and Isotropic Temperature Factors ($\text{\AA}^2 \times 10^3$) for $2\text{-C}_6\text{H}_6$

atom	x	y	z	U^a
Pd(1)	4181.6 (2)	2318.0 (2)	2562.9 (1)	30.5 (1)
Cl(1)	5542.4 (7)	3783.0 (7)	2687.1 (6)	46.9 (3)
Cl(2)	5863.3 (7)	1003.4 (7)	2388.2 (6)	49.7 (3)
P(1)	2674.4 (6)	3720.4 (6)	2492.6 (5)	32.9 (2)
P(2)	2882.0 (6)	837.4 (6)	2676.4 (5)	33.4 (2)
C(1)	1145 (3)	3386 (2)	2112 (2)	41 (1)
N(1)	1275 (3)	2861 (3)	1335 (2)	57 (1)
C(2)	197 (5)	2602 (4)	982 (3)	88 (2)
C(3)	-939 (5)	2831 (4)	1374 (5)	104 (2)
C(4)	-1061 (4)	3365 (4)	2199 (4)	92 (2)
C(5)	27 (3)	3657 (3)	2572 (3)	71 (1)
C(6)	2380 (3)	4319 (3)	3598 (2)	40 (1)
N(2)	1559 (3)	5234 (3)	3589 (3)	74 (1)
C(7)	1350 (4)	5682 (4)	4427 (4)	90 (2)
C(8)	1947 (5)	5252 (5)	5238 (4)	97 (2)
C(9)	2754 (5)	4331 (4)	5234 (3)	85 (2)
C(10)	2974 (3)	3848 (3)	4403 (2)	55 (1)
C(11)	3118 (3)	4918 (2)	1529 (2)	38 (1)
C(12)	3238 (3)	4698 (3)	608 (2)	53 (1)
C(13)	3569 (4)	5557 (4)	-139 (3)	71 (2)
C(14)	3773 (3)	6635 (3)	36 (3)	64 (1)
C(15)	3672 (4)	6822 (3)	965 (3)	78 (2)
C(16)	3337 (4)	5957 (3)	1720 (3)	61 (1)
C(17)	1365 (3)	1053 (2)	3353 (2)	37 (1)
N(3)	1550 (2)	1565 (2)	4102 (2)	48 (1)
C(18)	551 (3)	1747 (3)	4700 (3)	55 (1)
C(19)	-632 (3)	1446 (3)	4567 (3)	64 (1)
C(20)	-819 (3)	935 (3)	3793 (3)	63 (1)
C(21)	205 (3)	710 (3)	3168 (3)	51 (1)
C(22)	2639 (3)	414 (3)	1517 (2)	40 (1)
N(4)	1691 (3)	-260 (3)	1472 (2)	63 (1)
C(23)	1524 (4)	-557 (4)	612 (3)	74 (2)
C(24)	2280 (4)	-220 (4)	-201 (3)	71 (2)
C(25)	3252 (4)	459 (4)	-146 (3)	77 (2)
C(26)	3443 (4)	789 (3)	725 (2)	62 (1)
C(27)	3436 (3)	-464 (2)	3438 (2)	37 (1)
C(28)	3507 (4)	-1499 (3)	3130 (3)	60 (1)
C(29)	3840 (5)	-2479 (3)	3768 (4)	84 (2)
C(30)	4098 (4)	-2420 (3)	4692 (3)	66 (1)
C(31)	4025 (3)	-1384 (3)	4995 (3)	61 (1)
C(32)	3691 (3)	-399 (3)	4367 (2)	49 (1)
C(33)	732 (7)	2283 (7)	7604 (5)	121 (3)
C(34)	1846 (9)	1785 (5)	7336 (5)	119 (3)
C(35)	2919 (7)	2205 (7)	7535 (5)	129 (3)
C(36)	2883 (8)	3110 (7)	8007 (6)	145 (4)
C(37)	1786 (10)	3593 (5)	8298 (6)	152 (4)
C(38)	678 (8)	3187 (7)	8109 (5)	128 (3)

^a See footnote a in Table IV.

of **2** with this ligand led us to examine carefully the factors involved; the results will be discussed in the next section.

The reaction of 2,6-bis(diphenylphosphino)pyridine⁷ with Pd(II) salts was of interest, since Balch and co-workers^{3,6} have shown this ligand to be capable of forming trinuclear complexes containing at least two metal-metal bonds. Their attempts to synthesize the Pd₂ dinuclear intermediate led to the formation of the thermodynamically stable cyclic trimer **7**.⁶ Under their reaction conditions, Pd(II) usually exists, however, in a monomeric form.

The use of an alcoholic solution of Na₂PdCl₄, where the chloro-bridged dimer Pd₂Cl₆²⁻ is the predominate Pd(II) species, should favor dimer formation. Under these conditions the cyclic cis,cis,trans trimer **8** was also formed, in addition to a small amount of an orange solid **7**. X-ray analysis determined this to be a chloro-bridged dimer containing 2 equiv of 2,6-bis(diphenylphosphino)pyridine *P*-oxide, a trace impurity in the phosphine ligand (undetected by ³¹P NMR) arising from the autoxidation of the diphosphine.

³¹P NMR Spectral Results. The ³¹P NMR data for complexes **2**, **3**, **5**, and **7** show interesting trends, which relate to results recently reported,^{3,6,11,12} in addition to those herein reported. Thus,

Table VI. Atomic Positional Parameters ($\times 10^4$) and Isotropic Temperature Factors ($\text{\AA}^2 \times 10^3$) for $3\text{-C}_6\text{H}_6$

atom	x	y	z	U^a
Pd(1)	2011.6 (2)	986.3 (2)	4284.1 (1)	33.1 (1)
Cl(1)	1308.2 (10)	3221.9 (8)	4397.4 (6)	53.7 (3)
Cl(2)	1758.3 (9)	701.1 (8)	5872.1 (5)	46.1 (3)
P(1)	2166.3 (8)	1175.1 (8)	2751.1 (5)	34.6 (2)
C(1)	2666 (3)	-859 (3)	4257 (2)	35 (1)
N(1)	1679 (3)	-1831 (3)	4398 (2)	40 (1)
C(2)	4135 (3)	-1241 (3)	4161 (2)	42 (1)
C(3)	4501 (4)	-2544 (3)	4203 (3)	50 (1)
C(4)	3423 (4)	-3504 (3)	4334 (3)	55 (1)
C(5)	2004 (4)	-3124 (3)	4437 (3)	49 (1)
C(6)	2886 (3)	-239 (3)	2139 (2)	36 (1)
N(2)	4220 (3)	-97 (3)	1824 (2)	59 (1)
C(7)	2069 (4)	-1414 (3)	2065 (2)	47 (1)
C(8)	2648 (5)	-2484 (4)	1645 (3)	60 (1)
C(9)	4019 (5)	-2350 (4)	1300 (3)	71 (2)
C(10)	4746 (5)	-1153 (4)	1400 (3)	77 (2)
C(11)	339 (3)	1333 (3)	2078 (2)	37 (1)
N(3)	308 (3)	1177 (3)	1150 (2)	50 (1)
C(12)	-930 (3)	1518 (3)	2541 (2)	54 (1)
C(13)	-2311 (4)	1513 (4)	1996 (3)	58 (1)
C(14)	-2353 (4)	1378 (4)	1064 (3)	62 (1)
C(15)	-1027 (4)	1212 (4)	632 (3)	63 (1)
C(16)	3378 (3)	2536 (3)	2461 (2)	40 (1)
C(17)	3307 (5)	2967 (4)	1572 (3)	50 (2)
C(18)	4294 (5)	3940 (4)	1358 (3)	74 (2)
C(19)	5349 (4)	4484 (4)	2010 (3)	67 (2)
C(20)	5414 (4)	4053 (4)	2904 (3)	65 (1)
C(21)	4426 (4)	3076 (4)	3137 (3)	53 (1)
C(22)	694 (5)	5074 (4)	8543 (4)	76 (2)
C(23)	1209 (5)	4169 (5)	9191 (3)	72 (2)
C(24)	1720 (4)	2982 (4)	8890 (3)	66 (2)
C(25)	1709 (4)	2706 (4)	7966 (3)	63 (1)
C(26)	1204 (4)	3607 (4)	7324 (3)	66 (2)
C(27)	678 (5)	4783 (4)	7615 (3)	70 (2)

^a See footnote a in Table IV.

Table VII. Important Bond Lengths (\AA) and Angles (deg) in Complex **7**^a

Pd(1)-Cl(1)	2.411 (3), 2.425 (3)	Pd(1)-Cl(2)	2.324 (2)
Pd(1)-Cl(3)	2.268 (2)	Pd(1)-P(1)	2.228 (2)
P(2)-O(2)	1.479 (6)	P-C av	1.812 (12) ^b
C-N av	1.335 (16) ^b	C-C av	1.381 (25) ^b
Cl(1)-Pd(1)-Cl(2)	85.01 (7)	Cl(2)-Pd(1)-P(1)	95.24 (10), 96.44 (10)
Cl(1)-Pd(1)-Cl(3)	91.32 (10), 91.96 (11)	Cl(3)-Pd(1)-P(1)	88.34 (10), 86.86 (11)
Cl(2)-Pd(1)-Cl(3)	175.78 (19), 174.00 (16)	C-N-C av	118.0 (6) ^b
Cl(1)-Pd(1)-P(1)	178.41 (24)	N-C-C av	122.9 (6) ^b
		C-C-C av	119.8 (14) ^b

^a **7** is treated as being symmetrical. Dual values indicate statistical non-equivalency. ^b Root-mean-square standard deviation.

the chemical shifts due to the sequential replacement of phenyl with 2-pyridyl (2-pyr) needs to be addressed. The chemical shift of Ph₃P is reported to be δ -4.94 in CD₂Cl₂, while (2-pyr)Ph₂P has a relative downfield shift (δ -8.36),¹² whereas (2-pyr)₂PhP (**1**), used in this study, shows a resonance at δ -1.90 in CDCl₃. In order to take solvent effects into account, the ³¹P NMR spectra of these 2-pyridyl/phenylphosphines were determined in CDCl₃, as a common solvent. The results shown in Table II indicate that the solvent effect is -0.7 ppm. The resulting shift due to the replacement of a phenyl group with 2-pyridyl is thus in the range 0.8-1.5 ppm.

In the bis(triarylphosphine)palladium series, data can be found for *trans*-(Ph₃P)₂PdCl₂ (δ 23.6 in CDCl₃)¹¹ and [(2-pyr)-Ph₂P]₂PdCl₂ [δ 23.8 and 29.3 (CD₂Cl₂); δ 22.9 and 28.5 (CDCl₃)].³ We tentatively assigned the δ 23.8 (δ 22.9) signal to the *cis* isomer and the δ 29.3 (δ 28.5) signal to the *trans* isomer. These data indicate that the solvent effect for the complexes is approximately -0.85 ppm. The resonance for **2** occurs at δ 29.4

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Table VIII. Non-Hydrogen Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$) for **7**

atom	x	y	z	U^a
Pd(1)	644.7 (5)	1942.8 (6)	3321.6 (4)	35.7 (3)
Pd(2)	-682.3 (5)	3851.2 (6)	3448.2 (4)	37.3 (3)
Cl(1)	635 (2)	3702 (2)	3299 (2)	60 (1)
Cl(2)	-672 (2)	2083 (2)	3481 (1)	55 (1)
Cl(3)	1941 (2)	1911 (2)	3205 (2)	66 (1)
Cl(4)	-1990 (2)	3901 (2)	3509 (2)	65 (1)
P(1)	658 (2)	315 (2)	3324 (1)	34 (1)
N(1)	1139 (4)	71 (6)	2240 (4)	37 (3)
C(11)	1321 (5)	-150 (7)	2791 (5)	33 (4)
C(12)	2008 (6)	-636 (7)	2962 (4)	42 (4)
C(13)	2505 (6)	-894 (7)	2528 (6)	53 (4)
C(14)	2316 (6)	-686 (8)	1966 (5)	52 (5)
C(15)	1629 (6)	-208 (7)	1836 (5)	43 (4)
P(2)	3644 (2)	5058 (3)	3908 (1)	55 (1)
O(2)	1895 (4)	-402 (6)	689 (3)	72 (3)
P(3)	-714 (2)	5474 (2)	3447 (1)	35 (1)
N(2)	-1110 (4)	5483 (6)	2340 (4)	35 (3)
C(21)	-1317 (6)	5883 (7)	2824 (5)	35 (4)
C(22)	-1923 (6)	6537 (8)	2863 (5)	54 (4)
C(23)	-2323 (6)	6787 (8)	2363 (5)	53 (5)
C(24)	-2117 (6)	6383 (7)	1850 (5)	46 (4)
C(25)	-1515 (5)	5722 (7)	1851 (4)	36 (4)
P(4)	-1223 (2)	5139 (2)	1191 (1)	49 (1)
O(4)	-1752 (4)	5407 (6)	703 (3)	63 (3)

^aSee footnote *a* in Table IV.

in CDCl_3 ; therefore, for the series of complexes, the replacement of a phenyl group with 2-pyridyl results in no trend, based on the preliminary geometric assignment. However, when our initially assigned geometry of the complexes, originally synthesized by Balch et al.,³ is reversed, the trends become apparent. Substitution of 2-pyridyl for phenyl causes an average *upfield* shift of 1.2 ppm for the trans complexes, while the cis isomers shift *downfield* by 0.9 ppm. As with the ligands, these shifts are small and indicate that the ³¹P NMR shifts are insensitive to the electronics of phosphorus' aromatic substituents, at least in this case. This effect has been noted previously¹³ where the main factor affecting ³¹P chemical shifts is the interaction with the d orbitals on phosphorus. In order to verify these assignments, trans isomer **5** was prepared and its ³¹P NMR spectrum determined. The observed shift of δ 17.7 clearly supports the proposed trend. It should be noted that the shifts due to 2-pyridyl for phenyl substitution are on the order of magnitude of errors due to concentration and spectrometer frequency difference, as herein shown for *trans*-(Ph₃P)₂PdCl₂ (24.1 vs. 23.6 ppm). This rather large relative difference makes any statements about trends tenuous.

The difficulties with ³¹P NMR assignments lie in the scarcity of literature examples of nonchelating *cis*-[(aryl)₃P]₂Pd(II) complexes. Balch's mixture³ was indicative of two isomers, and the one present in lower concentration can reasonably be expected to be the heretofore unobserved isomer. In addition, the Pt analogues had been synthesized and were available in both isomeric forms. The chemical shifts of these complexes (L₂PtX₂) showed that the cis isomer was always at a higher field [i.e. L = Ph₃P, X = Cl, δ = 5.9; L = (2-pyr)Ph₂P, X = Cl, δ = 3.1].¹² The rationale for the observed reversed trend within these palladium complexes is not obvious.

The ³¹P NMR spectrum of **7** was very encouraging, based on the above trends, since two equally intense signals (δ 31.0 and 21.6) were observed. These chemical shifts could have arisen from a dimer (or higher-ordered oligomer), possessing a cis-palladium center and a trans-palladium center. The X-ray analysis confirmed the structure (**7**); thus, the coordinated phosphorus appears at δ 31.0 and the free phosphorus *P*-oxide at δ 21.6.

Solid-State Structure of 2. Both the nonsolvate and benzene solvate single crystals of **2** were obtained. A perspective drawing

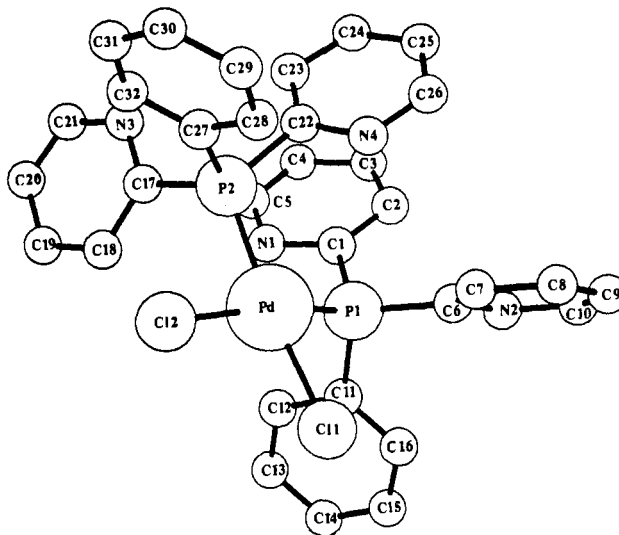


Figure 1. Perspective drawing of *cis*-dichlorobis(di-2-pyridylphenylphosphine)palladium(II) (**2**).

of the nonsolvate, along with the atom-labeling scheme, is shown in Figure 1. Table III contains selected bond lengths and angles for **2**, 2-C₆H₆, and the pyridinium complex 3-C₆H₆. The atomic positional parameters for **2** are listed in Table IV. The coordination sphere of the palladium in **2** consists of Pd-Cl and Pd-P distances within the normal ranges for bonds to palladium (Pd-Cl, 2.357–2.348 Å; Pd-P, 2.247–2.257 Å) and are similar to those reported for *cis*-(Ph₃P)₂PtCl₂ acetone solvate (Pt-Cl, 2.333–2.355 Å; Pt-P, 2.250–2.264 Å).¹² The PdCl₂ plane forms a dihedral angle of 14.6° with the PdP₂ plane. A remarkable feature of **2** is that the N(1) and N(4) rings are approximately coplanar, with a dihedral angle of 7.1° and an interring distance (center to center) of 3.40 Å. A possible explanation for the formation of the cis complex and the coplanar arrangement of these two rings lies in the potential for charge transfer to occur. Careful examination of the geometry shows that a dihedral angle of 74.4° exists between the PdP(Cl) plane and the N(1) ring, which corresponds to an angle of 15.6° between the Pd-P bonding orbital and the pyridine π -system. Application of the cos² relationship for orbital overlap¹⁴ indicates this to be equivalent to an overlap of 92.8%. This would suggest that back-donation of Pd-P bonding electron density is probable, yielding a relatively electron-rich N(1) pyridine ring. Conversely, the dihedral angle between the PdP(C(17)) plane and the N(4) ring is 43.7°, which corresponds to a dihedral angle between orbitals of 46.3° and has a calculated orbital overlap of 47.7%. Thus, the N(4) pyridine ring can be considered to be relatively electron poor as compared to the N(1) pyridine ring. Additional facts, suggestive of a charge-transfer mechanism, are that the atoms of each ring overlap in such a way as to align relatively electron-rich and relatively electron-poor atoms. The forces, described here, are apparently weak and support the ease with which **2** can be isomerized to **5** at slightly elevated (50–60 °C) temperatures.

The structure of 2-C₆H₆ (atomic positional parameters in Table V) reveals several, not entirely unexpected, features. Due to the fact that the benzene solvate is situated roughly orthogonal to the Pd coordination plane on the phosphine side of the molecule, the Pd-Cl bond lengths and angles are not altered to a significant extent, with the exception of the Cl-Pd-Cl angle, which widens slightly (0.32°). The Pd-P coordination is altered, however, since the bond lengths become longer [from 2.252 (average) to 2.262 Å] and the P-Pd-P angle narrows (from 100.46 to 96.69°). The Cl-Pd-P angles all widen as a result of this narrowing. In addition, the interring interactions noted in the nonsolvate are weakened via an increase in distance between the two (3.5 Å and a dihedral

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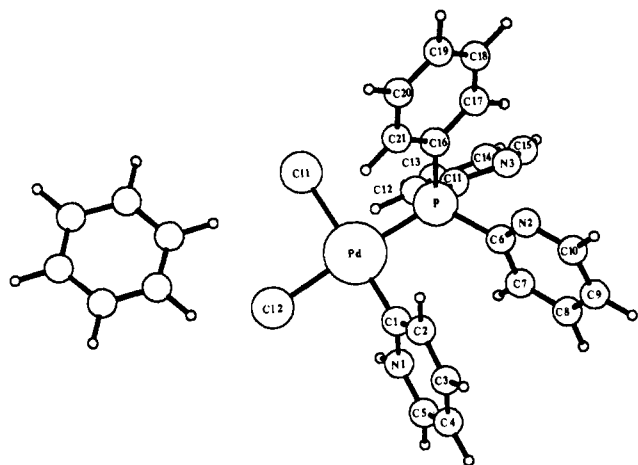


Figure 2. Perspective drawing of *cis*-dichloro(2-pyridiniumyl)(di-2-pyridylphenylphosphine)palladium(II) benzene solvate (**3**).

angle of 8.1°) and a decrease in overlap with the Pd–P bonding electrons (51.2 and 38.4% for the N(1) and N(3) pyridine rings, respectively).

A feature of **2**, **3**, and **5**, which needs to be addressed, is the assignment of the pyridine rings, as well as the nitrogen atoms, in the phosphine ligand. For **2**, this was a moot problem, since the precision of the X-ray experiment was not sufficient for differentiating between carbon and nitrogen atoms, though the bond lengths and angles allowed the assignment of the pyridines. The data collected for **2**·C₆H₆ were of sufficient precision. The model used for the final refinements involved N(1) ring disorder, with N(1) and C(5) present in a 1:1 ratio in those two positions. Rotational disorder between the three aromatic rings of the phosphine did not seem to be operative in this compound, since the bond lengths and angles as well as thermal parameters of the "phenyl" ring suitably fit the observed data.

For both **2** and **2**·C₆H₆, an ortho H is oriented toward the Pd, but as in *cis*-(Ph₃P)₂PtCl₂¹² and *trans*-(Ph₃P)₂PdCl₂,¹⁵ the closest Pd–H distances are too long for any significant interaction (2.83 and 2.90 Å, respectively).

The Pd-coordination sphere of **3**·C₆H₆ (atomic positional parameters in Table VI; perspective drawing with numbering scheme in Figure 2) consists of two *cis*-chlorine atoms with significantly different bond lengths. The atom trans to P(1) is at a distance of 2.350 Å from Pd, as opposed to 2.381 Å for the chlorine trans to the pyridinium C. This is due to the trans influence of the pyridinium ligand, since the 2.350 Å length is very near the lengths observed in **2**. This increased trans influence of an sp² C over that of P has recently been documented in several cases.¹⁶ The benzene solvate does not perturb the coordination sphere in a manner similar to **2**, since it is located on the chlorine side of the molecule rather than the triarylphosphine side. The Pd–C bond length is 1.98 Å, which is in the normal range for (sp²)C–Pd bonds.^{15,17} Angles about Pd reflect the diminished size of pyridinium as compared to the P ligand. The Cl–Pd–P angles widen (83.9–90.5 and 167.9–177.1°) with concurrent narrowing of the Cl–Pd–P angle (from 100.5–92.0°).

The assignment of the ring bound directly to palladium as a C-bonded pyridine ylide, rather than an N-bonded pyridine was based on bond lengths and angles found in the model as the refinement was nearing completion, in addition to the thermal parameters. The Hamilton *R* factor ratio test¹⁸ indicated that

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 (16) Wiege, M.; Brune, H. A.; Klein, H.-P.; Thewalt, U. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 718. Canziani, F.; Galimberti, L.; Garlaschelli, L.; Malatesta, M. C.; Albinati, A.; Ganazolli, F. *J. Chem. Soc., Dalton Trans.* **1983**, 827. Constable, A. G.; McDonald, W. S.; Shaw, B. L. *Ibid* **1980**, 2282.
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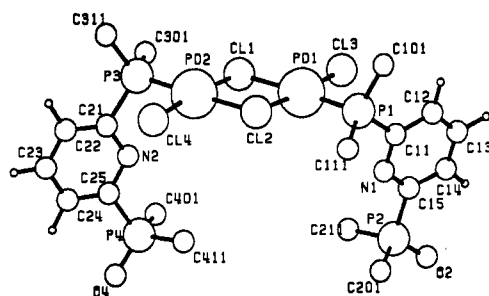


Figure 3. Perspective drawing of complex **7**. (The phenyl rings have been omitted for clarity purposes.)

the N-bonded model could be rejected at the 0.005 confidence level.¹⁹ As in the **2**·C₆H₆ structure, the precision of this X-ray experiment allowed us to assign unambiguously the pyridine rings. The N(3) pyridine ring was treated as being disordered in the same manner as described above. An intermolecular H bond is formed between the pyridinium proton and Cl(1) of an adjacent molecule. The bond length is 2.286 (3) Å and the N(1)–C(1)–Cl(1) angle is 158.4 (2)°. This bond is roughly orthogonal to the palladium coordination plane at an angle of 83.9 (1)°. The coordination plane of palladium is the least distorted within this series of (2-pyr)₂PhP complexes with a dihedral angle of 3.3° between the PdCl₂ and PdP(Cl) planes, another artifact of the diminished steric bulk of pyridinium versus phosphine.

The phenyl ortho H is oriented toward Pd, but even though this is the closest to the Pd of all the (2-pyr)₂PhP complexes, at 2.80 Å it is clearly too far away for any significant interaction.

Solid-State Structure of 7. Single crystals of **7** were obtained by crystallization from EtOH/C₆H₆/petroleum ether. A perspective drawing with numbering scheme is shown in Figure 3. Table VII contains the important bond lengths and angles, while Table VIII shows the atomic coordinates and thermal parameters. The Pd-coordination spheres are typical of Cl-bridged dimers containing phosphine, as a neutral ligand.²⁰ The Pd–Cl bond lengths are very similar to those found in the chloro-bridged complex containing two dimethyl 2-chloro-3-(diphenylphosphino)maleate²⁰ (free, 2.268 vs. 2.273 Å; bridging-"bound", 2.324 vs. 2.327 Å; bridging-"coordinated", 2.411–2.425 vs. 2.408 Å). The angles within the Pd-coordination sphere are also within the normal range found for bridged chloro-dimers (internal Cl–Pd–Cl, 85.0°; external Cl–Pd–Cl, 91.3–92.0°; internal Cl–Pd–P, 95.2–96.4°; external Cl–Pd–P, 88.3–86.9°). The P–O bond is also typical with a bond length of 1.479 Å (compared to 1.483 Å for Ph₃PO²¹).

The Pd(1)P(1)Cl(3) plane forms a dihedral angle of 2.6° with the Pd(1)Cl(1)Cl(2) plane, which in turn forms an angle of 5.4° with the Pd(2)P(3)Cl(4) plane. The PdCl₂ planes involved in the bridge form an angle of 0.7°. The Pd–N contacts are well outside of the ranges considered to indicate any interactions (3.71 Å).

Conclusion

The formation of the first isolated, nonchelated *cis*-bis(triarylphosphine)–Pd(II) complex indicates that this geometry is not necessarily unfavorable for Pd(II). The rationale for the formation of **2** involves the existence of a weak charge-transfer interaction between two pyridine rings on adjacent phosphines. This interaction in effect locks the geometry of the complex. The weakness of this interaction can be seen by the ease of isomerization. Warming **2** with an excess of ligand **1** to 50–60 °C leads to the formation of **5**. The apparent weakness of this interaction leads to the conclusion that the *cis* isomer is the kinetic product whereas the *trans*-isomer is the thermodynamically more stable

- (19) The ylide model was refined to an *R* factor of 0.0268, whereas the N-pyridine model was refined to 0.0313. With 3763 degrees of freedom (4073 data – 310 parameters), the *R* ratio of 1.1679 is greater than the required 1.0013 for rejection at the 0.005 confidence level.
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 (21) Ruban, G.; Zabel, V. *Cryst. Struct. Commun.* **1976**, *5*, 671.

product. However, in the Pd(II) series the thermal barrier leading to the formation of the trans product must lie near or below the energy level of the typical complex formation reaction conditions, since the trans isomer is the one usually observed.

The inclusion of the phosphorus extrusion process into the series of organometallic preparative reactions will provide a novel alternative to those presently available.²² Considering the number of phosphines commercially available, this method of preparation should lead to the synthesis of many new complexes heretofore inaccessible by standard routes.

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Registry No. 1, 68469-71-6; 2, 110173-82-5; 2-C₆H₆, 110173-84-7; 3, 110173-83-6; 3-C₆H₆, 110173-85-8; 4, 14871-92-2; 5, 110222-28-1; 6, 110144-23-5; 7, 110191-20-3; 8, 87039-36-9; PdCl₂, 7647-10-1; (Ph₂P)₂-2,6-pyr, 64741-27-1; Na₂PdCl₄, 13820-53-6.

Supplementary Material Available: Listings of bond distances and angles (Tables S1, S4, S7, and S10), calculated hydrogen coordinates and refined isotropic thermal parameters (Tables S2, S5, S8, and S11), and anisotropic thermal parameters (Tables S3, S6, S9, and S12) for complexes 2, 2-C₆H₆, 3-C₆H₆, and 7 and additional atomic coordinates and thermal parameters for 7 (Table S17) (40 pages); listings of observed and calculated structure factors (Tables S13-S16) (98 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of Minnesota, Minneapolis, Minnesota 55455

Heterobimetallic Au-Ir, Ag-Ir, and Au-Ru Bis(μ -hydrido) Complexes. X-ray Crystal and Molecular Structures of [AuRu(H)₂(dppm)₂(PPh₃)]PF₆ and [Ir(H)₂(bpy)(PPh₃)₂]PF₆

Bruce D. Alexander, Brian J. Johnson, Steven M. Johnson, Paul D. Boyle, Nina C. Kann, Ann M. Mueting, and Louis H. Pignolet*

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Several new heterobimetallic hydrides containing Au or Ag have been synthesized. [AuRu(H)₂(dppm)₂(PPh₃)]PF₆ (3) was made by the reaction of AuPPh₃NO₃ with Ru(H)₂(dppm)₂ with the use of acetone as solvent. [AgIr(H)₂(bpy)(PPh₃)₂](O₃SCF₃)(BF₄) (5), [AgIr(H)₂(bpy)(PPh₃)₂(NO₃)](BF₄) (6), and [AuIr(H)₂(bpy)(PPh₃)₂(CH₃CN)](BF₄)₂ (7) were synthesized by the reaction of the BF₄⁻ salt of [Ir(H)₂(bpy)(PPh₃)₂](PF₆) (4) with AgO₃SCF₃, AgNO₃, and Au(CH₃CN)₂BF₄, respectively, and [AgIr(H)₂(bpy)(PPh₃)₂](O₃SCF₃)(BF₄) (8) was made by the reaction of PPh₃ with 5. Compounds 3 and 4 were characterized by single-crystal X-ray diffraction in the solid state (3, *P*2₁/*n*, *a* = 19.456 (7) Å, *b* = 15.049 (5) Å, *c* = 23.843 (4) Å, β = 113.41 (3)°, *T* = -91 °C, *R* = 0.050; 4, *P*2₁/*c*, *a* = 11.677 (3) Å, *b* = 21.723 (7) Å, *c* = 17.680 (1) Å, β = 92.70 (4)°, *T* = -85 °C, *R* = 0.041) and by ³¹P and ¹H NMR spectroscopy in solution. In both complexes the hydride ligands were directly observed by X-ray diffraction and in 3 were found to bridge the Ru-Au bond. The average Ru-H and Au-H distances in 3 are 1.71 (6) and 1.98 (6) Å, respectively, and the Ru-Au separation is 2.694 (1) Å. The average Ir-H and Ir-N distances in 4 are 1.51 (6) and 2.150 (5) Å, respectively. Comparison of the Ir-N distances in 4 and those of the previously characterized AuPPh₃ adduct of 4 [AuIr(H)₂(bpy)(PPh₃)₂](BF₄)₂ (2) provides further support for a bridging dihydride formulation of the latter. Compounds 5-8 were also determined to have bridging hydrides by NMR and IR spectroscopy.

Introduction

There has been considerable interest recently in the synthesis and structural characterization of mixed transition-group 1B (11⁶⁴) clusters.¹⁻³¹ These compounds are important because of

their intrinsically novel structures and properties, their potential use as bimetallic catalysts, and their potential to aid in under-

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