Bis(2-pyridyl)silane ligands. 2. Structural characterization and catalytic applications of palladium complexes in organostannane cross-coupling reactions

Michael E. Wright, and Charlotte K. Lowe-Ma

Organometallics, **1990**, 9 (2), 347-352• DOI: 10.1021/om00116a009 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Organometallics **1990,** *9,* 347-352

Bis(2-pyridyl)silane Ligands. 2. Structural Characterization and Catalytic Applications of Palladium Complexes in Organostannane Cross-Coupling Reactions†

Michael E. Wright*

Department of Chemistry & Biochemistry, Utah State University, Logan, Utah 84322-0300

Charlotte K. Lowe-Ma‡

Research Department, Naval Weapons Center, China Lake, California 93555

Received April 21, 1989

The synthesis and characterization of $[R^1R^2Si(2\text{-pyridyl})]PdCl_2$ (R^1 = Me, R^2 = phenyl; **3**) are presented. Complex **3** crystallizes in the monoclinic space group $P2_1/n$ ($Z = 4$) with $\beta = 99.98\ (1)°$ and $a = 12.208\ (2)$ Å, $b = 12.651\ (3)$ Å, $c = 14.079\ (2)$ Å. The single-crystal study showed the six-membered chelate ring to be in a boat conformation with the palladium and silicon atoms as the apexes out of plane. Cross-coupling reactions of organostannanes catalyzed by $[Me_2Si(2\text{-pyridyl})]PdCl_2$ (**2**) were examined. Vinyltributylstannane undergoes cross coupling in high yield when treated with benzoyl chloride and 1 mol % of **2** in dichloromethane, whereas treatment with iodobenzene results in formation of $[Me_2Si(2\text{-pyridyl})PdI_2$ (**4**) with only a minor amount of cross coupling observed. A solvent change to dimethylformamide, an increase in the reaction temperature, and the addition of lithium chloride or sodium iodide gave clean cross coupling with a relative rate 3 times that of $(Ph_3P)_2PdCl_2$. Lithium chloride eliminated homocoupling of the vinylstannane partner, whereas addition of sodium iodide accelerated the reaction but still allowed homocoupling of the stannane partner (~10%). The addition of LiCl did not affect the cross-coupling reaction when $(PPh_3)_2PdCl_2$ was used as the precatalyst. When trimethyl(phenylethynyl)stannane was used, the addition of lithium chloride did not decrease homocoupling of the organostannane reagent for precatalyst **2**, whereas for $(Ph_3P)_2PdCl_2$ homocoupling of the stannane partner was not observed with or without added lithium chloride. Attempts to employ (*E*)-1,2-$[R^1IC{=}CIR^2]$ ($R^1 = R^2$ = H; R^1 = H, R^2 = Ph; $R^1 = R^2$ = Ph) in the cross-coupling reaction with trimethyl(phenylethynyl)stannane resulted in complete homocoupling of the stannane reagent and conversion of the (*E*)-diiodoalkenyl compounds to acetylenes ($R^1C{\equiv}CR^2$).

Introduction

The formation of carbon-carbon bonds under mild conditions can be carried out by using a wide variety of coupling partners and transition-metal catalysts (eq 1).[1]

$$\text{R'-M} \quad + \quad \text{R-X} \xrightarrow{\text{Group 10 Catalyst}} \text{R-R'} \quad + \quad \text{M-X} \qquad (1)$$

M = SnR_3, ZnR, BR_2, Zr(Al), MgX'

X = Halide or Triflate

The cross-coupling reactions often produce good to excellent yields of cross-coupled products and can proceed with a high degree of stereospecificity.[2]

The ligands usually found in group 10 catalytic systems utilize phosphorus as the coordinating atom or atoms. Many of the phosphorus-containing ligands are bidentate (hereafter referred to as P-P ligands), forming chelate rings ranging from five to seven atoms, including the transition metal. Although bidentate nitrogen-based ligands (i.e. N-N type) such as 2,2′-bipyridine and 1,10-phenanthroline are ubiquitous in coordination chemistry,[3] much less attention has been paid to their use as ligands for cross-coupling catalysts. Recent examples demonstrate that both nickel[4] and palladium[5] complexes of 2,2′-bipyridine are efficient catalysts in cross-coupling reactions.

The N-N type ligands appear to have significantly different electronic properties in comparison to P-P type ligands. The stronger σ-donation by the nitrogen ligands tends to favor oxidative-addition and slow reductive-elimination processes.[6] This behavior was exemplified by the reaction of platinum complexes with triethylsilane where the P-P ligand did not undergo oxidative addition whereas a closely related phosphorus-nitrogen ligand on the platinum readily gave oxidative addition of the silicon-hydride bond.[7]

Several reviews and papers exist that cover the synthetic and mechanistic aspects of cross-coupling chemistry,[1,8-10]

---

† Dedicated to the memory of John K. Stille.

‡ To whom correspondence should be addressed concerning the crystallographic study.

(1) Organostannane: Stille, J. K. *Pure Appl. Chem.* **1985,** *57,* 1771. Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986,** *25,* 508. Scott, W. J.; McMurry J. E. *Acc. Chem. Res.* **1988,** *21,* 47. Vinylborate compounds: Suzuki, A. *Acc. Chem. Res.* **1982,** *15,* 178. Suzuki, A. *Pure Appl. Chem.* **1985,** *57,* 1749. Vinylzinc compounds: Jabri, N.; Alexakis, A.; Normant, J. F. *Tetrahedron Lett.* **1981,** *22,* 959. Vinylalane and -zirconium compounds: Negishi, E. *Acc. Chem. Res.* **1982,** *15,* 340. Grignard reagents: Hayashi, T.; Kumada, M. *Acc. Chem. Res.* **1982,** *15,* 395. Tamao, K.; Sumitani, K.; Kiso, Y.; Zembayashi, M.; Fijioka, A.; Kodama, S-I.; Nakajima, I.; Minato, A.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1976,** *49,* 1958.

(2) For recent examples of stereospecific cross-coupling reactions see: (a) Stille, J. K.; Simpson, J. H. *J. Am. Chem. Soc.* **1987,** *109,* 2138. (b) Negishi, E.; Takahashi, T.; Baba, S.; Van Horn, D. E.; Okukado, N. *J. Am. Chem. Soc.* **1987,** *109,* 2393 and references cited therein.

(3) Yale, H. L. *Pyridine and Its Derivatives*; Interscience: New York, 1961; Part 2, Chapter 7.

(4) Yamamoto, T.; Yasuhiro, H.; Yamamoto, R. *Bull. Chem. Soc. Jpn.* **1978,** *51,* 2091. Yamamoto, T.; Sanechika, K.; Yamamoto, A. *J. Polym. Sci., Polym. Lett. Ed.* **1980,** *18,* 9. Tanaka, S.; Sato, M.; Kaeriyama, K.; Kanetsuna, H. *Chem. Abstr.* **1985,** *103,* 88278.

(5) Sustmann, R.; Lau, J.; Zipp, M. *Tetrahedron Lett.* **1986,** *27,* 5207.

(6) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organometallic Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987.

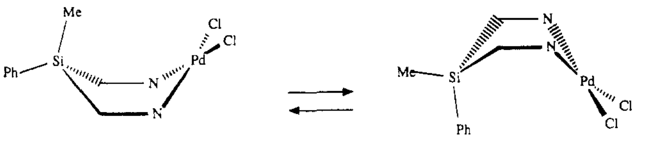
(7) Cullen, W. R.; Evans, S. V.; Han, N. F.; Trotter, J. *Inorg. Chem.* **1987,** *26,* 514.

(8) For a detailed mechanistic study on the Kumada cross-coupling reaction see: Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979,** *101,* 7547. For a more recent paper dealing primarily with the reductive-elimination step in cross-coupling reactions see: Ozawa, F.; Kurihara, K.; Fujimori, M.; Hidaka, T.; Toyoshima, T.; Yamamoto, A. *Organometallics* **1989,** *8,* 180.

(9) For a mechanistic study on the use of vinyl triflates and organostannane reagents see: Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1986,** *108,* 3033.

(10) For recent mechanistic studies with platinum analogues see: (a) Stang, P. J.; Kowalski, M. H.; Schiavelli, M. D.; Longford, D. *J. Am. Chem. Soc.*, in press. (b) Stang, P. J.; Kowalski, M. H. *J. Am. Chem. Soc.*, in press.

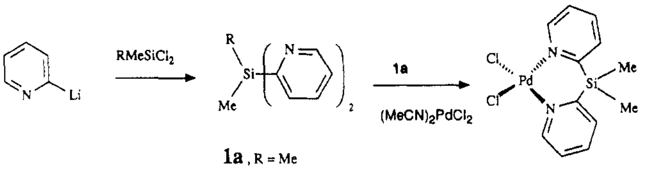
0276-7333/90/2309-0347$02.50/0



3(e) 3(a)

Figure 1. Possible boat conformations for complex 3.

but more information would be valuable concerning the use of catalysts containing N-N type ligands. Our current interest in cross-coupling chemistry stems from programs utilizing palladium-catalyzed cross-coupling reactions for the synthesis of new organometallic polymers[11] and the modification of polymer backbones.[12] With the recent synthesis of a new class of bis(2-pyridyl)silane ligands (eq 2),[13] we thought it would be of interest to examine their utility as ligands for cross-coupling catalysts. In this paper we present full details on the synthesis and characterization of the palladium complexes [R^1R^2Si(2-pyridyl)]$PdCl_2$ and their application as ligands in selected cross-coupling reactions.



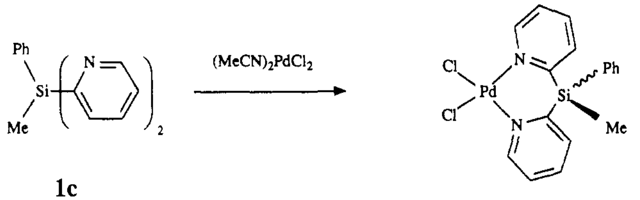
1a, R = Me
1b, R = CH=CH₂

2

(2)

Results and Discussion

Synthesis and Characterization of Ligands and Complexes. Ligand 1c (prepared as in eq 2) reacts with $(CH_3CN)_2PdCl_2$ in dichloromethane to afford the new palladium complex 3 (eq 3). Analytically pure 3 appears by spectroscopic data to exist as a mixture of conformational isomers.



1c

3

(3)

The silyl methyl resonances in the ^1H NMR spectrum were utilized to assign a ratio of 1:8 for 3(a) and 3(e), respectively (Figure 1). The two methyl resonances were very similar in chemical shift to those observed previously for complex 2 (SiMe's δ 1.70 and 0.96). Isomer 3(e) was isolated by recrystallization from the isomeric mixture. Heating a sample of 3(e) to 65 °C in $CDCl_3$ did not cause any broadening of the methyl resonances; hence, the energy barrier for the conversion of isomers 3(e) to 3(a) is substantial. Other neutral N-N ligand systems having six-membered chelate rings are known to be fluxional.[14]

Table I. Summary of Pertinent Crystallographic Data for the Single-Crystal X-ray Diffraction Study on 3(e)

formula	$C_{17}H_{16}Cl_2N_2PdSi$
fw	453.72
unit cell	a = 12.208 (2) Å, b = 12.651 (3) Å, c = 14.079 (2) Å, β = 99.98 (1)°, V = 2141.51 (63) $Å^3$
space group	$P2_1/n$, $Z = 4$
D_{calcd}, g/cm^3	1.671 (includes 1 CH_2Cl_2/formula unit)
cryst size, mm	0.40 × 0.44 × 0.22
faces	{100}, {01$\bar{1}$}, {011}
μ(Moα), cm^{-1}	14.20
data collecn	$2\theta/\theta$
scan speed, deg/min	variable, 5–15
scan range, deg	1 < $2\theta(K\alpha_1)$ to 1 > $2\theta(K\alpha_2)$
octants	$\bar{h}k\bar{l}$, $\bar{h}kl$ (partial $hk\bar{l}$, hkl)
range, deg	4–50 (2θ, Mo Kα)
total no. of observations	4694
no. of unique data	3779 (R_{merge} = 0.015)
no. of obsd data	3390 with $\lvert F_0\rvert > 3\sigma_F$
transmissn min, max.	0.638, 0.727
refinement	280 params
R	0.033[a]
R_w	0.044[b]
GOF	1.38

[a] $R = \sum\lvert\lvert F_o\rvert - k\lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$. [b] $R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$.

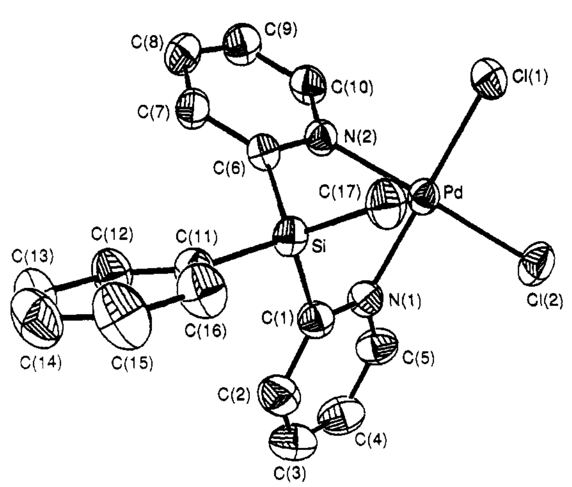
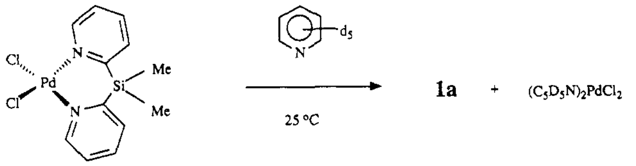


Figure 2. Plot of complex 3(e) with 50% probability thermal ellipsoids and the labeling scheme. Hydrogens have been omitted for clarity.

The ^1H NMR spectra of 2, which also exists as a rigid chelate ring,[13] have been obtained in the coordinating solvents acetone-d_6, acetonitrile-d_3, and pyridine-d_5. The first two solvents gave virtually identical spectra with only minor differences in peak positions due to changes in the polarity and viscosity of the NMR solvents. In contrast, the pyridine-d_5 ^1H NMR spectrum showed signals corresponding *only* to free ligand after 30 min (eq 4)! This reaction brings to light a somewhat unexpected liability for this new class of ligands.



(4)

To better understand the coordination geometry of these new ligands, we have investigated the molecular structure of 3 by single-crystal X-ray analysis. Single crystals of 3(e) were grown by diffusion of ether into a dichloromethane solution containing 3(e). The results of the single-crystal X-ray diffraction study are summarized in Table I, and

---

[11] Wright, M. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, *29*, 294. Wright, M. E. *Macromolecules*, in press.

[12] Wright, M. E.; Pulley, S. R. *Molecules*, in press.

[13] Wright, M. E. *Tetrahedron Lett.* **1987**, *28*, 3233.

[14] For example see: House, D. A.; Steel, P. J.; Watson, A. A. *Aust. J. Chem.* **1986**, *39*, 1525. Calderon, J. L.; Cotton, F. A.; Shaver, A. *J. Organomet. Chem.* **1972**, *38*, 105. Onishi, M.; Hiraki, K.; Shironita, M.; Yamaguchi, Y.; Nakagawa, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 961. For a related example of a fluxional six-membered cyclopalladated complex see: Hiraki, K.; Fuchita, Y.; Takechi, K. *Inorg. Chem.* **1981**, *20*, 4316.

Table II. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for Non-Hydrogen Atoms in Crystalline 3(e)[a]

atom type[b]	fractional coordinates *x*	*y*	*z*	U_{eq},[c] Å^2
Pd	0.13261 (2)	0.68630 (2)	0.81441 (2)	0.0347 (1)
Cl(1)	0.19798 (8)	0.69522 (7)	0.67063 (6)	0.0496 (1)
Cl(2)	−0.03123 (7)	0.61197 (7)	0.74016 (6)	0.0531 (3)
Si	0.29025 (7)	0.57628 (6)	0.99333 (6)	0.0344 (2)
N(1)	0.0812 (2)	0.6694 (2)	0.9428 (2)	0.040 (1)
N(2)	0.2747 (2)	0.7561 (2)	0.8814 (2)	0.036 (1)
C(1)	0.1461 (3)	0.6137 (2)	1.0143 (2)	0.038 (1)
C(2)	0.1078 (3)	0.5940 (3)	1.0996 (2)	0.051 (1)
C(3)	0.0064 (3)	0.6330 (3)	1.1143 (3)	0.059 (1)
C(4)	−0.0563 (3)	0.6918 (3)	1.0428 (3)	0.058 (1)
C(5)	−0.0178 (3)	0.7068 (3)	0.9564 (3)	0.049 (1)
C(6)	0.3413 (3)	0.7084 (2)	0.9565 (2)	0.035 (1)
C(7)	0.4383 (3)	0.7583 (3)	0.9997 (2)	0.042 (1)
C(8)	0.4671 (3)	0.8561 (3)	0.9667 (3)	0.050 (1)
C(9)	0.3985 (3)	0.9021 (3)	0.8901 (3)	0.053 (1)
C(10)	0.3032 (3)	0.8508 (3)	0.8491 (2)	0.045 (1)
C(11)	0.3755 (3)	0.5265 (3)	1.1074 (2)	0.040 (1)
C(12)	0.4165 (3)	0.5921 (3)	1.1859 (2)	0.048 (1)
C(13)	0.4830 (3)	0.5519 (3)	1.2668 (3)	0.058 (1)
C(14)	0.5096 (3)	0.4465 (4)	1.2729 (3)	0.064 (1)
C(15)	0.4705 (4)	0.3812 (3)	1.1984 (3)	0.067 (1)
C(16)	0.4041 (3)	0.4195 (3)	1.1159 (3)	0.053 (1)
C(17)	0.2886 (3)	0.4796 (3)	0.8942 (3)	0.047 (1)

[a] The numbers in parentheses are the estimated standard deviations in the last digit(s). [b] Atoms are labeled in agreement with Figure 2. [c] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Bond Lengths and Angles for Non-Hydrogen Atoms in Crystalline 3(e)[a]

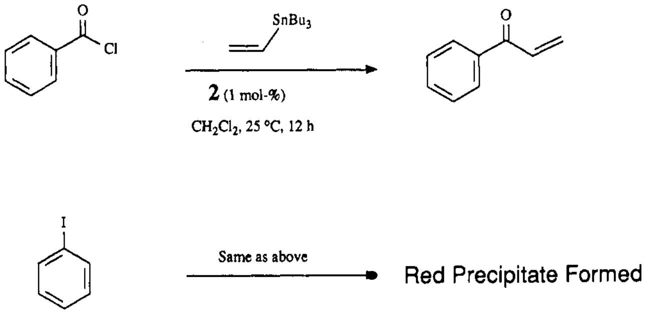
	Bond Lengths (Å)		
Pd–Cl(1)	2.304 (1)	Pd–Cl(2)	2.292 (1)
Pd–N(1)	2.025 (3)	Pd–N(2)	2.027 (2)
Si–C(1)	1.895 (3)	Si–C(6)	1.888 (3)
Si–C(11)	1.865 (3)	Si–C(17)	1.853 (4)
N(1)–C(1)	1.363 (4)	N(1)–C(5)	1.343 (5)
N(2)–C(6)	1.359 (4)	N(2)–C(10)	1.349 (4)
C(1)–C(2)	1.386 (5)	C(2)–C(3)	1.380 (6)
C(3)–C(4)	1.373 (5)	C(4)–C(5)	1.390 (6)
C(6)–C(7)	1.385 (4)	C(7)–C(8)	1.389 (5)
C(8)–C(9)	1.375 (5)	C(9)–C(10)	1.369 (5)
C(11)–C(12)	1.404 (4)	C(11)–C(16)	1.397 (5)
C(12)–C(13)	1.376 (5)	C(13)–C(14)	1.371 (6)
C(14)–C(15)	1.356 (6)	C(15)–C(16)	1.384 (5)
	Bond Angles (deg)		
Cl(1)–Pd–Cl(2)	91.6	Cl(1)–Pd–N(1)	176.1 (1)
Cl(2)–Pd–N(1)	89.0 (1)	Cl(1)–Pd–N(2)	89.3 (1)
Cl(2)–Pd–N(2)	178.1 (1)	N(1)–Pd–N(2)	90.2 (1)
C(1)–Si–C(6)	100.4 (1)	C(1)–Si–C(11)	110.2 (1)
C(6)–Si–C(11)	111.9 (1)	C(1)–Si–C(17)	113.2 (2)
C(6)–Si–C(17)	109.8 (2)	C(11)–Si–C(17)	110.9 (2)
Pd–N(1)–C(1)	118.9 (2)	Pd–N(1)–C(5)	121.1 (2)
C(1)–N(1)–C(5)	119.9 (3)	Pd–N(2)–C(6)	121.2 (2)
Pd–N(2)–C(10)	118.7 (2)	C(6)–N(2)–C(10)	120.1 (3)
Si–C(1)–N(1)	116.8 (2)	Si–C(1)–C(2)	123.5 (2)
N(1)–C(1)–C(2)	119.5 (3)	C(1)–C(2)–C(3)	120.7 (3)
C(2)–C(3)–C(4)	119.0 (4)	C(3)–C(4)–C(5)	119.0 (4)
N(1)–C(5)–C(4)	121.7 (3)	Si–C(6)–N(2)	115.1 (2)
Si–C(6)–C(7)	125.5 (2)	N(2)–C(6)–C(7)	119.4 (3)
C(6)–C(7)–C(8)	120.4 (3)	C(7)–C(8)–C(9)	118.9 (3)
C(8)–C(9)–C(10)	119.2 (3)	N(2)–C(10)–C(9)	122.0 (3)
Si–C(11)–C(12)	123.2 (2)	Si–C(11)–C(16)	119.6 (2)
C(12)–C(11)–C(16)	117.1 (3)	C(11)–C(12)–C(13)	120.8 (3)
C(12)–C(13)–C(14)	120.7 (3)	C(13)–C(14)–C(15)	119.7 (3)
C(14)–C(15)–C(16)	120.9 (4)	C(11)–C(16)–C(15)	120.8 (3)

[a] The numbers in parentheses are the estimated standard deviations in the last digit(s). Atoms are labeled in agreement with Figure 2.

a plot of 3(e) with thermal ellipsoids is displayed in Figure 2. Final atomic coordinates and selected bond lengths and angles for crystaline 3(e) can found in Tables II and III, respectively.

The coordination sphere about the palladium is square planar, having reasonable angles (~90°) and coplanarity of the chlorine, nitrogen, and palladium atoms (see Table A in the supplementary material). The six-membered chelate ring as anticipated exists in a boat conformation with the silicon and palladium being the ends out of plane.[15]

Cross-Coupling Reactions Catalyzed by 2. The palladium-catalyzed cross coupling of aryl halides or acid chlorides with either vinyl or acetylenic stannane reagents is a well-established synthetic procedure. As mentioned earlier, the catalytic sequence often employs phosphine-containing palladium catalysts, with the use of $(CH_2CN)_2PdCl_2$ as one of the more common exceptions.[16] The question we seek to answer is as follows: How efficiently will the bis(pyridyl)silane palladium complexes perform as catalysts in the Stille reaction?



Reaction of benzoyl chloride with vinyltributylstannane produced the cross-coupling product in excellent yield after 12 h of reaction at 25 °C. However, reaction of iodobenzene with vinyltributylstannane at 25 °C in dichloromethane gave only a minor amount of cross-coupling product prior to a red precipitate appearing in the reaction vessel. On the basis of the ^1H NMR spectrum and elemental analysis data the complex was identified as $[Me_2Si(2\text{-pyridyl})]PdI_2$ (4).

We have prepared 4 in a stoichiometric fashion from 2, vinyltributylstannane, and iodobenzene in 95% yield in either dichloromethane or tetrahydrofuran (THF) solutions. Analysis of the dichloromethane reaction mixture by gas chromatography did not show any detectable amounts of chlorobenzene, hence ruling out phenyl radicals.[17] The THF reaction produced a significant amount of $(Bu_3Sn)_2$. Analogous results were obtained when the reactions were carried out in the dark. These data are consistent with atom abstraction occurring from iodotributylstannane.

The cross-coupling reaction of iodobenzene and vinyltributylstannane catalyzed by 2 was in part successful (~70% conversion prior to catalyst decomposition) if a solvent change was made to dimethylformamide (DMF) and the reaction temperature was increased. Homocoupling of vinyltributylstannane was observed as a side reaction. The addition of lithium chloride to the reaction mixture caused a 6-fold increase in the relative reaction

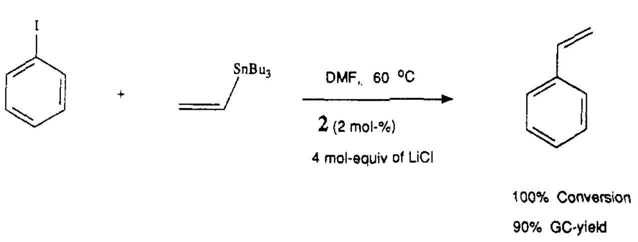
---

(15) Newkome, G. R.; Gupta, V. K.; Taylor, H. C. R.; Fronczek, F. R. *Organometallics* **1984**, *3*, 1549 and references cited therein. Steel, P. J. *Acta Crystallogr., Sect. C.* **1983**, *39*, 1623. House, D. A.; Steel, P. J.; Watson, A. A. *Aust. J. Chem.* **1986**, *39*, 1525.

(16) Beletskaya, I. P. *J. Organomet. Chem.* **1983**, *250*, 551. The nitrile ligand has found widespread use in the synthetic applications of (η^2-olefin)palladium(II) complexes: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organometallic Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987; pp 831–41 and references cited therein.

(17) Kuivila, H. G. *Acc. Chem. Res.* **1968**, *1*, 299.

rate as well as affording 100% conversion of the cross-coupling partner *without* homocoupling byproduct (eq 5).

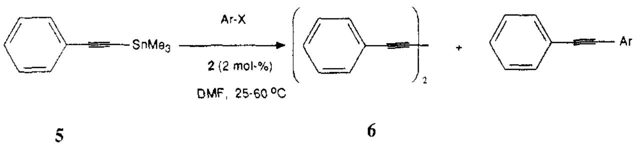


(5)

The relative reaction rate for precatalyst **2** was found to be 3 times that of $(Ph_3P)_2PdCl_2$. The addition of lithium chloride had no effect on reactions employing the latter precatalyst.

Interestingly, the addition of sodium iodide produced the same increase in the relative rate of cross-coupling reaction as did lithium chloride (eq 5); however, the amount of homocoupling byproduct remained consonant (~10%). A previous study by Kumada and co-workers pointed out that (2,2′-bipyridine)$NiCl_2$ was *not* an effective cross-coupling catalyst because the catalytic cycle was interrupted by the formation of stable diorganonickel complexes (i.e. stable toward reductive elimination).[18] The role of the added salt may be to enhance the reductive elimination of the diorganopalladium intermediate through formation of a pentacoordinate species. There are reported cases where reductive elimination was favored in d^8 complexes by prior *coordination* of a ligand (usually an olefin containing electron-withdrawing groups,[19a] but phosphine ligands have also been used[19b]). A halobenzene has also been observed to accelerate reductive-elimination reactions.[20]

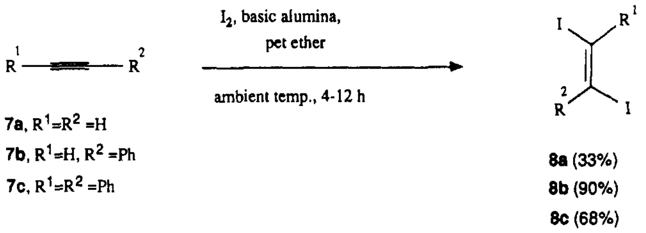
We have also examined the effect of added LiCl on the cross-coupling reaction of aryl halides and an acetylenic stannane reagent (eq 6). The reaction of trimethyl(phenylethynyl)stannane with iodobenzene at 60 °C in DMF was complete within 15 min. The shorter reaction time is consistent with the transmetalation step being rate determining since acetylenic groups are known to transfer faster than vinyl moieties from tin.[21] For both reactions with and without added LiCl we found a significant amount of homocoupling had occurred (~20%). Similar results were obtained for reactions run at 25 °C for longer reaction times and those with $(CH_3CN)_2PdCl_2$ on the precatalyst. Utilization of 2-chloropyridine or (η^6-C_6H_5Cl)$Cr(CO)_3$ eliminated the homocoupling byproduct because the source of iodine atoms (i.e. the Bu_3SnI) has been deleted.



(6)

The result that added LiCl did not decrease the percentage of homocoupling for the alkynylstannane reagent would indicate that the transmetalation step was faster than halide metathesis, but yet iodine atom abstraction from iodotrimethylstannane was competitive with oxidative addition of iodobenzene to the catalytically active palladium(0) species. Because the reactions were completed in very short time periods, relative rates were not obtained. It is also noteworthy to mention that $(PPh_3)_2PdCl_2$ did *not* produce significant amounts (>5%) of the homocoupling byproduct. The amount of iodine atom abstraction observed was clearly catalyst-dependent.

We also investigated that cross-coupling chemistry of (*E*)-diiodoalkenyl compounds with trimethyl(phenylethynyl)stannane. The (*E*)-diiodoalkenyl compounds were easily obtained through a slight modification of the procedure developed by Larson, Luidhart, Kabalka, and Pagni.[22] We found that employing basic alumina (Brockmann I, basic) without any special treatment produced an isolated yield comparable to that previously reported (eq 7).[22c] Compound **8c** exhibited surprisingly low solubility in chloroform and required several hot extractions from the alumina to obtain a reasonable yield (68% yield after a final recrystallization from hot chloroform).



(7)

Reaction of **8a** with trimethyl(phenylethynyl)stannane (**5**) in DMF and 1 mol % of **2** afforded almost exclusively compound **6** (eq 8). The reaction was performed at ambient temperature and was complete within 15 min. Compound **6** arises from the homocoupling of the stannane partner; hence, complex **2** has catalyzed the homocoupling of **5** and *not* the cross-coupling reaction! Under the same reaction conditions but with **8b**, compounds **6** and **7b** were isolated in near-quantitative yields. Use of other palladium(II) precatalysts such as $(CH_2CN)_2PdCl_2$ and $(PPh_3)_2PdCl_2$ in DMF gave similar results.

---

(18) The stable diorganonickel complexes were noted for the cross coupling of chlorobenzene and alkyl Grignard reagents. See Kumada and co-workers (1976) in ref 1.

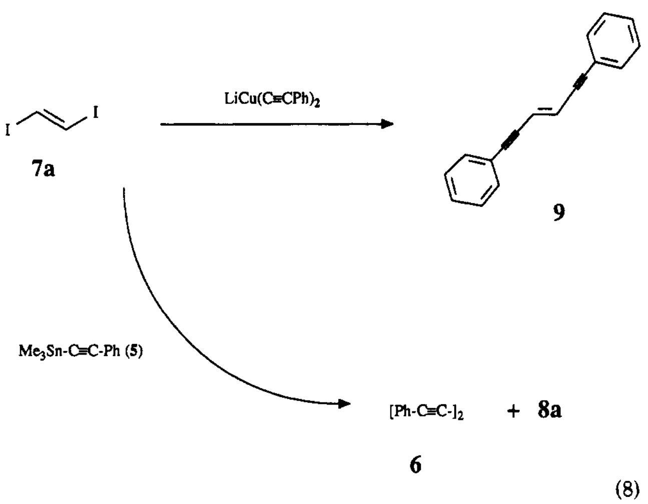
(19) (a) Yamamoto, T.; Yamamoto, A.; Ikeda, S. *J. Am. Chem. Soc.* **1971**, *93*, 3350. Binger, P.; Doyle, M. J. *J. Organomet. Chem.* **1978**, *162*, 195. Goliaszewski, A.; Schwartz, J. *J. Am. Chem. Soc.* **1984**, *106*, 5028; *Organometallics* **1985**, *4*, 417. Kurosawa, H.; Emoto, M.; Urabe, A.; Miki, K.; Kasai, N. *J. Am. Chem. Soc.* **1985**, *107*, 8253 and references cited therein. Komiya, S.; Akai, Y.; Tanaka, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1985**, *4*, 1130. (b) Braterman, P. S.; Cross, R. J.; Young, G. B. *J. Chem. Soc., Dalton Trans.* **1977**, 1892. Bayer, U.; Brune, H. A. *Z. Naturforsch.* **1983**, *38B*, 226 and references cited therein. Komiya, S.; Abe, Y.; Yamamoto, A.; Yamamoto, T. *Organometallics* **1983**, *2*, 1466. Tatsumi, K.; Nakamura, A.; Komiya, S.; Yamamoto, A.; Yamamoto, T. *J. Am. Chem. Soc.* **1984**, *106*, 8181. McKinney, R. J.; Roe, C. D. *J. Am. Chem. Soc.* **1985**, *107*, 261 and references cited therein.

(20) Fahey, D. R. *J. Am. Chem. Soc.* **1970**, *92*, 402; *Organomet. Chem. Rev., Sect. A* **1972**, *2*, 245. Hidai, M.; Kashiwagi, T.; Ikeda, T.; Uchida, Y. *J. Organomet. Chem.* **1971**, *30*, 279. Geriach, D. H.; Kane, A. R.; Parshall, G. W.; Jesson, J. P.; Muetterties, E. L. *J. Am. Chem. Soc.* **1971**, *93*, 3543. Parshall, G. W. *J. Am. Chem. Soc.* **1974**, *96*, 2360. Cundy, C. S. *J. Organomet. Chem.* **1971**, *69*, 305. Uchino, M.; Yamamoto, A.; Ikeda, S. *J. Organomet. Chem.* **1970**, *24*, C63. Uchino, M.; Asagi, K.; Yamamoto, A.; Ikeda, S. *J. Organomet. Chem.* **1975**, *84*, 93.

(21) Logue, M. W.; Teng, K. *J. Org. Chem.* **1982**, *47*, 2549.

(22) (a) Larson, S.; Luidhardt, T.; Kabalka, G. W.; Pagni, R. M. *Tetrahedron Lett.* **1988**, *29*, 35. (b) Pagni, R. M.; Kabalka, G. W.; Boothe, R.; Gaetano, K.; Stewart, L. J.; Conaway, R.; Dial, C.; Gray, D.; Larson, S.; Luidhardt, T. *J. Org. Chem.* **1988**, *53*, 4477. (c) During the review of this article a paper appeared on the use of "out-of-the-bottle alumina": Hondrogiannis, G.; Lee, L. C.; Kabalka, G. W.; Pagni, R. M. *Tetrahedron Lett.* **1989**, *30*, 2069.

(23) Ukhin, L. Y.; Sladkov, A. M.; Gorshkov, V. I. *Zh. Org. Khim.* **1968**, *4*, 25. For the same preparation but higher yield (>100%?) see: Burdon, J.; Coe, P. L.; Marsh, C. R.; Tatlow, J. C. *J. Chem. Soc., Perkin Trans. 1* **1972**, 639. Also see: Coe, P. L.; Milner, N. E.; Smith, J. A. *J. Chem. Soc., Perkin Trans. 1* **1975**, 654. For an example with 1,2-dichloroethene see: Guillerm, D.; Linstrumelle, G. *Tetrahedron Lett.* **1986**, *27*, 5857. For examples of acetylenic zinc reagents and palladium catalysis see: Negishi, E.; Okukado, N.; Lovich, S. F.; Luo, F.-T. *J. Org. Chem.* **1984**, *49*, 2629. Carpita, A.; Rossi, R. *Tetrahedron Lett.* **1986**, *27*, 4351.



(8)

In the case of the (*E*)-1,2-diiodoalkenyl compounds homocoupling of the organostannane reagent was most likely mediated through the palladium(II) iodide species 4; however, the source of iodine atoms has shifted to a cross-coupling partner.[24] The role of 8 can be viewed as a very efficient oxidant for the conversion of the palladium(0) species to the palladium(II) complex 4.[25]

In conclusion, the present study demonstrates that indeed the new complex [Me_2Si(2-pyridyl)]$PdCl_2$ (2) is an effective catalyst for the Stille cross-coupling reaction with added lithium chloride. A drawback to the use of N-N-type ligands is competing reaction with the iodotrialkylstannane product, which can lead to homocoupling of the organostannane partner. Addition of lithium chloride will diminish the amount of homocoupling, but only if the transmetalation step is slow relative to halide metathesis. This was found to be the case for tributylvinylstannane.

Experimental Section

General Considerations. All manipulations of compounds and solvents were carried out by using standard Schlenk techniques. Solvents were degassed and purified by distillation under nitrogen from standard drying agents.[26] Spectroscopic measurements utilized the following instrumentation: ^1H NMR, Varian XL 300; ^{13}C NMR, Varian XL 300 (at 75.4 MHz); infrared, Perkin-Elmer 1750 FT-IR spectrometer. Gas chromatographic analyses utilized a Varian 3700 chromatograph coupled with a HP 3390A recorder/integrator. Retention times and response factors were obtained from the average of three independent runs. NMR chemical shifts are reported in δ vs Me_4Si (^1H) and the $CDCl_3$ resonance (^{13}C, 77.0 ppm). 2-Bromopyridine was purchased from Lancaster Synthesis Inc. and used as received. *n*-BuLi (2.5 M in hexane), methylphenyldichlorosilane, Brockmann I alumina (basic), phenylacetylene, styrene, iodobenzene, 2-chloropyridine, and diphenylacetylene were purchased from Aldrich Chemical Co. and used as received. $(CH_3CN)_2PdCl_2$,[27] $(PPh_3)_2PdCl_2$,[28] (phenylethynyl)trimethylstannane,[29] vinyltributylstannane,[30] and (η^6-C_6H_5Cl)$Cr(CO)_3$[31] were prepared by literature methods. Elemental analyses were performed by Atlantic Microlab, Norcross, GA.

Bis(2-pyridyl)methylphenylsilane (1c). To a chilled (−90 °C) ether (30 mL) solution containing 2-bromopyridine (5.0 g, 31.7 mmol) was added *n*-BuLi 13 mL) dropwise by syringe. The mixture was stirred at −90 °C for an additional 4 h, and then the dichloromethylphenylsilane (3.0 g, 15.9 mmol) was added in one portion. The mixture was warmed to room temperature and then diluted with ether (100 mL). The mixture was washed with H_2O (2 × 150 mL) and brine (100 mL), and then the organic layer was dried (K_2CO_3). Removal of the solvent under reduced pressure afforded crude 1c as a light brown solid. Final purification of 1c was achieved by recrystallization from a mixture of hot pentane (15 mL) and CH_2Cl_2 (8 mL) cooled to −25 °C to afford 1c (3.1 g, 70%) as a light brown powder. ^1H NMR ($CDCl_3$): δ 8.86 (m, 2 H), 7.71–7.66 (m, 2 H), 7.62–7.55 (m, 4 H), 7.44–7.36 (m, 3 H), 7.28–7.22 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ 164.1, 150.3, 135.2, 134.0, 131.1, 129.5, 127.9, 123.1, −4.8.

[Bis(2-pyridyl)methylphenylsilane]palladium(II) Dichloride (3). To a solution of 1c (1.0 g, 3.6 mmol) in CH_2Cl_2 (20 mL) was added $(CH_3CN)_2PdCl_2$ (0.70 g, 2.7 mmol). The solution was stirred for an additional 1 h. The palladium complex was precipitated with ether (60 mL), filtered, and washed with ether. The complex was dried under reduced pressure to yield 3 as a light yellow powder in quantitative yield. ^1H NMR ($CDCl_3$): δ 9.33 (dd, J = 6, 1 Hz, 2 H), 7.80–7.60 (m, 6 H), 7.35–7.40 (m, 3 H), 2.08, 1.17 (SiMe's for 3(a):3(e), 1:8 ratio, s's, 3 H). Anal. Calcd for $C_{17}H_{16}Cl_2N_2PdSi$: C, 44.9; H, 3.6; N, 6.2. Found: C, 44.7; H, 3.6; N, 6.0.

Cross-Coupling Reaction with Benzoyl Chloride. A Schlenk tube was charged with dichloromethane (5 mL), benzoyl chloride (5 mmol), 2 mol % of 2, and vinyltributylstannane, in that order. The mixture was stirred at ambient temperature for 12 h. The mixture was diluted with ether (50 mL), combined with a 50% saturated KF(aq) solution, and stirred vigorously for 2 h. The mixture was filtered through a glass wool plug, and the layers were separated. The organic layer was washed with water (50 mL) and brine (50 mL) and then dried over K_2CO_3. Removal of the solvents and flash chromatography of the product gave spectroscopically pure vinyl phenyl ketone (0.56 g, 85%).

Cross-Coupling Reactions of Aryl Halides with Vinyltributylstannane or Trimethyl(phenylethynyl)stannane. A Schlenk tube was charged with DMF (5 mL), aryl halide (5 mmol), organostannane reagent (5 mmol), naphthalene (15–20 mg), and, if used, LiCl (20 mmol). The Schlenk tube was immersed in an oil bath at 60 °C for ~5 min, and then the appropriate precatalyst (2 mol %) was added. Aliquots were withdrawn and analyzed by gas chromatography at t = 0 (before catalyst addition) and then at 15-min intervals. Reactant loss and product formation were measured against the naphthalene internal standard. Response factors were obtained for naphthalene versus each reactant and product through averaging at least four separate runs of purified compounds. The GC yields of styrene varied between 85 and 90% for all catalysts studied except for 2 *without* the addition of salt, which then afforded a 60–70% GC yield of styrene. Homocoupling was measured indirectly from the monitoring of the disappearance of organostannane reagent and the iodobenzene. For reactions involving 5 the homocoupling byproduct 6 was measured directly by GC analysis.

In the cases of 2-chloropyridine and (η^6-C_6H_5Cl)$Cr(CO)_3$ the cross-coupling products were isolated (<90%) by flash column chromatography on alumina. Homocoupling was measured from GC analysis of the reaction mixture and found to be nonexistent.

Preparation of 4. A THF or dichloromethane (5 mL) solution containing 2 (100 mg, 0.24 mmol), vinyltributylstannane (~200 mg), and iodobenzene (~200 mg) was stirred at ambient temperature for 12 h. The mixture was diluted with ether (10 mL), and the red precipitate was collected on a glass frit and washed

---

(24) Reaction of (*E*)-1,2-diiodoethene with $Fe_2(CO)_9$ has been reported to generate $Fe_2(CO)_8I_2$, although no mechanistic details were given: Grevels, F.-W.; Schulz, D.; Gustorf, E. K.; Bunbury, D. St. P. *J. Organomet. Chem.* **1975**, *91*, 341.

(25) Polarography of the (*E*)-1,2-dihaloethene series showed the diiodo compound to undergo facile reduction, over 1.1 V more positive than the dibromo analogue: Markova, I. G.; Feoktistov, L. G. *Zh. Obschch. Khim.* **1970**, *40*, 740. Single-electron transfer (SET) has been presented as a possible first step in the oxidative addition of metal species to aryl halides. See: Kochi, J. K. *Acc. Chem. Res.* **1974**, *7*, 351. See also refs 6 and 19b and references cited therein.

(26) Gordon, A. J.; Ford, R. A. *The Chemists Companion*; Wiley: New York, 1972.

(27) Doyle, J. R.; Slade, P. E.; Jonassen, H. B. *Inorg. Synth.* **1960**, *6*, 216.

(28) King, A. O.; Negishi, E.; Villani, F. J., Jr.; Silveira, A., Jr. *J. Org. Chem.* **1978**, *43*, 358.

(29) Mitchell, T. N. *J. Organomet. Chem.* **1977**, *141*, 353. Cetinkya, B.; Lappert, M. F.; McMeeking, J.; Palmer, D. E. *J. Chem. Soc., Dalton Trans.* **1973**, 1202.

(30) Seyferth, D.; Stone, F. G. A. *J. Am. Chem. Soc.* **1957**, *79*, 515.

(31) Jackson, W. R.; Nicholls, B.; Whiting, M. C. *J. Chem. Soc.* **1960**, 469.

several times with ether. The red solid was dried under reduced pressure to afford complex 4 (140 mg, 95%). ^{1}H NMR ($CDCl_3$): δ 9.53 (m, 2 H), 7.77 (dt, J = 7.5, 1.5 Hz, 2 H), 7.66–7.62 (m, 2 H), 7.34–7.28 (m, 2 H), 1.63 (s, 3 H), 0.92 (s, 3 H). Anal. Calcd for $C_{12}H_{14}I_2N_2PdSi$: C, 25.08; H, 2.44; I, 44.2. Found: C, 24.98; H, 2.36; I, 43.8.

(*E*)-1,2-Diiodoethene (8a).[32] A petroluem ether (40 mL, 35–60 °C) mixture containing I_2 (7.40 g, 29.1 mmol) and alumina (25 g, Brockmann I, basic) had acetylene (dried by passing the gas through a −78 °C trap) bubbled through the solution for 90 min while vigorous stirring was maintained. The mixture was capped and stirred for an additional 12 h at ambient temperature. The mixture was diluted with chloroform (75 mL) and filtered and the alumina washed with with an additional 50 mL of chloroform. The organic layer was washed with metabisulfite (10% aqueous) and then brine. The organic layer was dried over K_2CO_3 (anhydrous) and the solvents removed to afford 2.7 g (33%) of **8a** as an off-white solid.

(*E*)-1,2-Diiodo-1,2-diphenylethene (8c). A petroluem ether (15 mL) mixture containing diphenylacetylene (1.00 g, 5.6 mmol), alumina (6 g), and I_2 (1.70 g, 6.7 mmol) was stirred at ambient temperature for 4 h. The mixture was diluted with chloroform (75 mL), heated with a "heat gun", and then filtered into a separatory funnel. The alumina was extracted with hot chloroform (5 × 50 mL), and the washes were combined in the separatory funnel. Workup as above and then recrystallization from hot chloroform gave pure **8c** (1.65 g, mp 192 °C dec, 68%). ^{1}H NMR ($CDCl_3$): δ 7.45–7.30 (m). Anal. Calcd for $C_{10}H_{14}I_2$: C, 38.92; H, 2.33. Found: C, 39.01; H, 2.37.

Structure Determination of 3(e). The material was crystallized by diffusion of ether into a chloroform solution enriched in 3(e). The crystals were orange diamond-shaped platelets, many with striations and twinning. The platelet face was {100} with edges $\{01\bar{1}\}$ and {011}. The crystals degenerated to a fine powder if left without protection from the ambient air. The third crystal examined, which was found to be a suitable single crystal, was coated with Devcon 5-min epoxy. Data were collected on a Nicolet R3 diffractometer at room temperature, 18 °C. Unit cell parameters were determined from 25 computer-centered reflections with 2θ values ranging from 10 to 25°. During data collection three check reflections (040), (−7,0,1), and (5,3,−4) were monitored every 93 reflections and were found to vary by less than 4%. Additional crystal data and experimental details are given in Table I. The intensity data were corrected for absorption numerically, as well as for Lorentz and polarization effects. All calculations were performed with SHELXTL[33] and with neutral atomic scattering factor coefficients for palladium.[34]

An initial phase solution based on Pd, Si, and one Cl was obtained from the SHELXTL Patterson interpretation program. The first structure-factor calculation and Fourier map based on these three atoms indicated the positions of the remaining Cl and all of the C and N atoms, except for the methyl carbon. After a few least-squares cycles, the methyl C, in addition to three significant peaks unconnected with the molecule, were observed on a difference Fourier map. The unconnected peaks were modeled initially as a partially occupied CCl_2 group. After a few more refinement cycles almost all of the hydrogen atoms were observed on a difference Fourier maps. Refinement was by least-squares minimization of $[\sum w(|F_0| - k|F_c|)^2]$ with $w = 1/[\sigma_F^2 + gF^2]$ for $g = 0.00065$ by use of SHELXTL's blocked-cascade algorithm with 103 parameter blocks (maximum). For the final refinement, all of the non-hydrogen atoms were refined anisotropically; all of the hydrogen atoms were geometrically constrained but had unconstrained thermal parameters except for the methyl hydrogens, which were refined without any constraints. The final model chosen for the solvent was as one disordered CCl_2 for formula unit. The Cl atoms were allowed to be 2-fold disordered, but the population parameters of the two sites totaled one for each Cl. The thermal parameters for the solvent atoms were refined without constraints. The final difference map had peaks and troughs ranging from +0.83 e/Å^3 to −0.48 e/Å^3. The three strongest difference peaks were +0.83, +0.69, and 0.60 e/Å^3 at 0.9–1.0 Å away from the Pd atom.

Acknowledgment. M.E.W. is grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for generously supporting this research. M.E.W. also thanks Myung-Jong Jin for technical assistance and Prof. Vernon D. Parker for partaking in many helpful discussions prior to publication. M.E.W. is indebted to Prof. P. J. Stang for supplying manuscripts prior to publication and helpful suggestions.

Supplementary Material Available: Listings of the best plane for atoms involved in the coordination sphere, anisotropic thermal parameters for non-hydrogen atoms, and fractional coordinates and thermal parameters for hydrogen atoms and solvent atoms (3 pages); a listing of structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

---

(32) Kaufmann, H. P. *Ber. Dtsch. Chem. Ges.* **1922**, *55*, 249.

(33) SHELXTL, Version 4.1; Nicolet XRD: Madison, WI, 1983.

(34) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974, Vol. 4.