Table V. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for 3

Bond Distances			
Ru(1)–Ru(2)	2.793 (1)	Ru(2)–C(14)	2.132 (6)
Ru(1)–Ru(3)	2.7248 (8)	Ru(3)–P(2)	2.360 (2)
Ru(1)–P(1)	2.266 (2)	Ru(3)–C(15)	2.117 (6)
Ru(1)–C(5)	2.696 (8)	C(14)–C(15)	1.420 (8)
Ru(1)–C(14)	2.319 (6)	C(14)–C(19)	1.413 (8)
Ru(1)–C(15)	2.327 (6)	C(15)C(16)	1.405 (8)
Ru(2)–Ru(3)	2.9227 (8)	C(16)–C(17)	1.37 (1)
Ru(2)–P(1)	2.340 (2)	C(17)–C(18)	1.39 (1)
Ru(2)–P(2)	2.311 (2)	C(18)–C(19)	1.366 (9)
Bond Angles			
Ru(2)–Ru(1)–Ru(3)	63.96 (2)	Ru(1)–Ru(3)–Ru(2)	59.14 (2)
Ru(2)–Ru(1)–C(14)	48.2 (1)	Ru(1)–Ru(3)–C(15)	55.7 (2)
Ru(2)–Ru(1)–C(15)	69.6 (2)	Ru(2)–Ru(3)–C(15)	69.5 (2)
Ru(3)–Ru(1)–C(14)	70.8 (1)	Ru(1)–C(14)–Ru(2)	77.6 (2)
Ru(3)–Ru(1)–C(15)	48.8 (1)	Ru(1)–C(14)–C(15)	72.5 (3)
C(14)–Ru(1)–C(15)	35.6 (2)	Ru(2)–C(14)–C(15)	110.5 (4)
Ru(1)–Ru(2)–Ru(3)	56.89 (2)	Ru(1)–C(15)–Ru(3)	75.5 (2)
Ru(1)–Ru(2)–C(14)	54.2 (2)	Ru(1)–C(15)–C(14)	71.9 (3)
Ru(3)–Ru(2)–C(14)	69.1 (1)		

(d, *J*(PP) = 201 Hz); ^{1}H (300 MHz, $CDCl_3$) δ 4.55 (m, 1), 4.7 (m, 1) 4.8 (m, 1), 5.0 (m, 1), 5.15 (m, 1), 5.25 (m, 1), 5.3–5.4 (m, 2), 5.5 (m, 1), 5.75 (m, 1), 6.4–6.5 (m, 2), 6.5–6.7 (m, 1), 7.08–7.18 (m, 1), 7.42–7.6 (m, 6), 7.6–7.75 (m, 2), 7.88–8.0 (m, 2). IR (FT, CH_2Cl_2): ν(CO) 2062 (s), 2010 (s), 1975 (s), 1904 (s) cm^{-1}. Mass spectrum (FAB): m/z 1216 (P$^+$). Anal. Calcd for $Ru_3CrP_2O_{13}C_{43}H_{24}\cdot CH_2Cl_2$: C, 40.56; H, 2.02. Found: C, 40.52; H, 2.02.

X-ray Crystallographic Analyses. Crystallographic data for $\{\mu_3\text{-}[P(\eta^6\text{-}C_6H_5)Cr(CO)_3]\}\{\mu_3\text{-}\eta^3\text{-}(\eta^6\text{-}C_6H_4)Cr(CO)_3]\}Ru_3(CO)_9$-(*2Ru–Ru*) (**2**) and $\{\mu_2\text{-}[PhP(\eta^6\text{-}C_6H_5)Cr(CO)_3]\}_2(\mu_3\text{-}\eta^2\text{-}C_6H_4)Ru_3$-$(CO)_7$(*3Ru–Ru*)$\cdot CH_2Cl_2$ (**3**$\cdot CH_2Cl_2$) appear in Table I. The final unit cell parameters were obtained by least squares on the setting angles for 25 reflections with 2θ = 29.8–33.7° for **2** and 27.2–33.4° for **3**. The intensities of three standard reflections, measured every 200 reflections throughout the data collections, decayed uniformly by 2.2 and 7.5%, respectively, for **2** and **3**. The data were processed[9] and corrected for Lorentz and polarization effects, decay, and absorption (empirical, based on azimuthal scans for four reflections).

Both structures were solved by heavy-atom methods; the coordinates of the Ru and Cr atoms were determined from subsequent difference Fourier syntheses. All non-hydrogen atoms of both complexes were refined with anisotropic thermal parameters. Hydrogen atoms were fixed in idealized positions (C–H = 0.98 Å, $B_H = 1.2B_{\text{bonded atom}}$). A correction for secondary extinction was applied for **2**, the final value of the extinction coefficient being 1.31×10^{-6}. Neutral-atom scattering factors and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref 10. Final atomic coordinates and equivalent isotropic thermal parameters, selected bond lengths, and bond angles appear in Tables II–V.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Supplementary Material Available: Stereo ORTEP diagrams and listings of interatomic distances and angles, torsion angles, intermolecular contacts, and least-squares planes for **2** and **3**$\cdot CH_2Cl_2$ (65 pages); listings for measured and calculated structure-factor amplitudes (222 pages). Ordering information is given on any current masthead page.

---

(9) TEXSAN/TEXRAY structure analysis package, which includes versions of the following: DIRDIF, direct methods for difference structure, by P. T. Beurskens; ORFLS, full-matrix least squares, and ORFFE, function and errors, by W. R. Busing, K. O. Martin, and H. A. Levy; ORTEP II, illustrations, by C. K. Johnson.

(10) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K. (present distributor Kluwer Academic Publishers, Dordrecht, The Netherlands), 1974; Vol. IV, pp 99–102 and 149.

Synthesis and Characterization of *trans*-$(Me_3P)_2Pd(C_6H_4C(H){=}NPr^i)(NHPh)$. X-ray Crystal Structure Analysis of $[(Me_3P)_3Pd(C_6H_4C(H){=}NPr^i)][BF_4]$

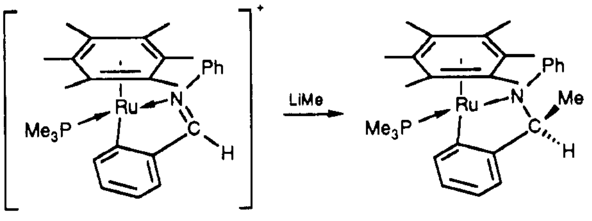
Lawrence A. Villanueva, Khalil Abboud, and James M. Boncella*

Department of Chemistry, University of Florida, Gainesville, Florida 32611

Received January 31, 1991

Summary: The reaction of $[Pd(C_6H_4CH{=}NPr^i)(CH_3CN)_2][BF_4]$ (**1**) with 3 equiv of PMe_3 produces $[(Me_3P)_3Pd(C_6H_4C(H){=}NPr^i)][BF_4]$ (**2**), which was characterized by a single-crystal X-ray diffraction study. Compound **2** was allowed to react with KNHPh in THF at −60 °C to produce *trans*-$Pd(C_6H_4CH{=}NPr^i)(NHPh)(PMe_3)_2$ (**4**), which was characterized by ^{1}H and ^{31}P NMR spectroscopy.

There has been an increasing interest in the potential use of late-transition-metal (groups 8–10) amide complexes to facilitate the formation of carbon–nitrogen bonds.[1] Consequently, there has been intensified interest in developing new synthetic routes to such compounds. Our attempts to develop new synthetic approaches to late-transition-metal amide complexes have focused on the addition of nucleophiles to cationic, ortho-metalated imine complexes as shown in eq 1.[2]



(1)

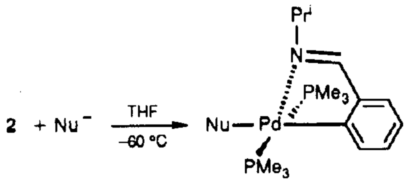
Attempts to extend the reaction in eq 1 to ortho-metalated benzaldimine complexes of palladium resulted in displacement of PMe_3 from the five-coordinate complex **2**, with preferential attack at the metal center (eq 2). While this unusual displacement of PMe_3 by an anionic nucleophile prevents the synthesis of ortho-metalated complexes of palladium analogous to the Ru complexes in

---

(1) (a) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163. (b) Fryzuk, M. D.; Montgomery, D. C. *Coord. Chem. Rev.* **1989**, *95*, 1–40. (c) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastrava, R. C. *Metal and Metalloid Amides*; Halsted Press: Chatham, Kent, England, 1980; pp 488–533.

(2) Martin, G. C.; Boncella, J. M. *Organometallics* **1989**, *8*, 2968.

0276-7333/91/2310-2969$02.50/0 © 1991 American Chemical Society

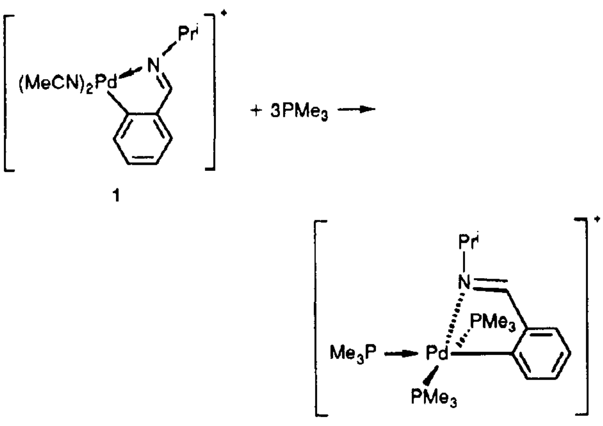


(2)

3: Nu = Me
4: Nu = N(H)Ph

eq 1, it does provide an efficient, high-yield synthesis of palladium amide complexes via direct reaction between 2 and alkali-metal amides. In this paper, we report the synthesis of the new palladium phenyl amide complex 4 and the X-ray crystal structure of 2.

Reaction of 3 equiv of PMe_3 with 1[3,4] in CH_2Cl_2 (eq 3) results in essentially quantitative conversion to the five-coordinate cation 2. Compound 2 is air-stable in both



1

2

(3)

solution and the solid state and is readily soluble in CH_2Cl_2. The compound has been characterized with use of ^1H, ^{13}C, and ^{31}P NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum shows a doublet and triplet in a 2:1 ratio ($^2J_{P-P}$ = 42 Hz) and is consistent with the pseudo-square-pyramidal structure 2. This structure was subsequently confirmed by a single-crystal X-ray diffraction study.

Slow diffusion of ether into a dichloromethane solution of 2 yielded white single crystals of X-ray quality. The crystal structure of 2 consists of well-separated anions and cations. An ORTEP drawing of one of the two independent cations of 2 is found in Figure 1, while selected bond lengths and angles can be found in Table III. The cations have a pseudo-square-pyramidal geometry with the PMe_3 groups and the phenyl group occupying sites in the basal plane and the imine nitrogen occupying the apical position. The Pd–N bond distance of 2.78 Å is extremely long and suggests a very weak Pd–N interaction. This distance is typical of Pd–N distances in related five-coordinate compounds.[5] The Pd–P distances show the strong trans influence of the phenyl group, which is in agreement with the observed chemistry (eq 2). The P1–Pd–P(2) angle is 165° and is bent toward the less sterically demanding phenyl group. The remaining bond lengths and angles fall within expected ranges.

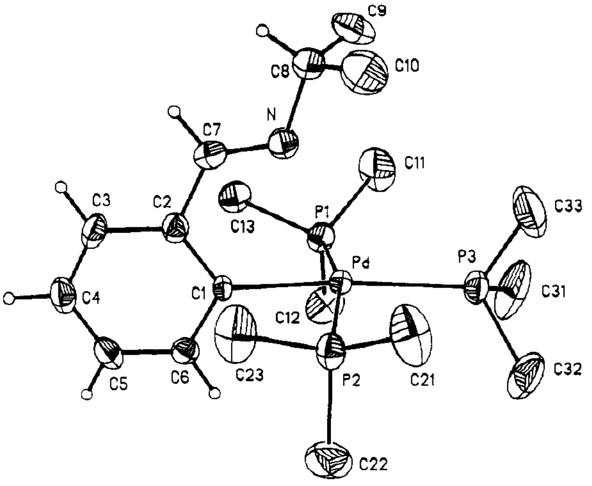


Figure 1. Structure of $[(Me_3P)_3Pd(C_6H_4C(H){=}NPr^i)][BF_4]$ (2), showing labeling scheme with 50% thermal ellipsoids. This drawing is of one of the two independent cations in the asymmetric unit.

Table I. Crystallographic Data

Crystal Data	
a, Å	30.594 (9)
b, Å	9.586 (2)
c, Å	19.279 (5)
β, deg	99.24 (2)
V, Å^3	5581 (3)
d_{calc}, g cm^{-3} (298 K)	1.35
empirical formula	$[C_{19}H_{39}NP_3Pd]BF_4$
cryst syst	monoclinic
space group	Cc
Z	8
$F(000)$, e	2336
cryst size	0.19 × 0.30 × 0.40
Data Collection	
scan range (ω, deg)	1.2
scan rate, deg min^{-1}	3.0–6.0
2θ range, deg	3.0–50.0
range of hkl[a]	$0 \le h \le 37$, $0 \le k \le 11$, $-23 \le l \le 23$
mode	ω scan
bkgd measurement	stationary cryst and stationary counter at beginning and end of scan, each for 50% of total scan time
total no. of rflns measd	5940
no. of unique rflns	5585
no. of obsd rflns $[I_o \ge 3\sigma(I_o)]$	4504
Structure Refinement	
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0004F^2$
S,[b] goodness of fit	1.14
no. of variables	553
R, R_w	5.01, 4.86
R, R_w (all data),[b] %	6.83, 4.87
$R_{int}(I)$, %	0.88
max shift/esd	0.005
min peak in diff Fourier map, e Å^{-3}	−0.51
max peak in diff Fourier map, e Å^{-3}	0.72

[a] Reflections with $h + k = 2n + 1$ were not collected. [b] Relevant expressions are as follows, where F_0 and F_c represent respectively the observed and calculated structure factor amplitudes. The function minimized was $\sum w(|F_o| - |F_c|)^2$. $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$. $S = [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$.

---

(3) (a) Onoue, H.; Moritani, I. *J. Organomet. Chem.* **1972**, *43*, 431. (b) Pregosin, P. S.; Rüedi, R. *J. Organomet. Chem.* **1984**, *273*, 401. (c) Clark, P. W.; Dyke, S. F. *J. Organomet. Chem.* **1984**, *276*, 421. (d) Brisdon, B. J.; Nair, P.; Dyke, S. F. *Tetrahedron* **1981**, *37*, 173. (e) Barr, N.; Dyke, S. F. *J. Organomet. Chem.* **1983**, *243*, 223. (f) Dehand, J.; Jordanov, J.; Pfeffer, M. *J. Chem. Soc., Dalton Trans.* **1976**, 1553.

(4) Dupont, J.; Pfeffer, M.; Rotteveel, M. A.; De Cian, A.; Fischer, J. *Organometallics* **1989**, *8*, 1116.

(5) (a) Granell, J.; Sainz, D.; Sales, J.; Solans, X.; Font-Altaba, M. *J. Chem. Soc., Dalton Trans.* **1986**, 1785. (b) Weaver, D. L. *Inorg. Chem.* **1970**, *9*, 2250. (c) Taira, Z.; Yamazaki, S. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 395. (d) Bushnell, G. W.; Dixon, K. R.; Khan, M. A. *Can. J. Chem.* **1974**, *52*, 1367. (e) Wernberg, O.; Hazell, A. *J. Chem. Soc., Dalton Trans.* **1980**, 973. (f) Louw, W. J.; deWaal, D. J. A.; Kruger, G. J. *J. Chem. Soc., Dalton Trans.* **1976**, 2364. (g) Favez, R.; Roulet, R.; Pinkerton, A. A.; Schwarzenbach, D. *Inorg. Chem.* **1980**, *19*, 1356. (h) Okeya, S.; Miyamato, T.; Ooi, S.; Nakamura, Y.; Kawaguchi, S. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 395.

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3)

	x	y	z	U^a
Pd	3174 (1)	8866 (1)	856 (1)	47 (1)
P(1)	2758 (1)	7028 (3)	1189 (1)	68 (1)
P(2)	3491 (1)	10565 (3)	234 (1)	69 (1)
P(3)	3194 (1)	10179 (3)	1896 (2)	75 (1)
N	3914 (3)	7181 (10)	859 (4)	88 (4)
C(1)	3098 (3)	7808 (8)	−79 (3)	45 (3)
C(2)	3415 (3)	6859 (9)	−231 (4)	59 (3)
C(3)	3351 (4)	6092 (10)	−859 (5)	71 (4)
C(4)	2977 (4)	6324 (10)	−1340 (5)	82 (4)
C(5)	2664 (4)	7260 (12)	−1210 (5)	75 (4)
C(6)	2730 (3)	8022 (9)	−603 (5)	58 (4)
C(7)	3815 (4)	6585 (11)	285 (6)	82 (5)
C(8)	4327 (4)	6764 (15)	1293 (7)	137 (7)
C(9)	4222 (7)	6146 (26)	1945 (9)	250 (16)
C(10)	4602 (5)	8024 (18)	1464 (8)	210 (11)
C(11)	2886 (6)	6369 (14)	2072 (6)	145 (9)
C(12)	2190 (3)	7438 (13)	1058 (7)	109 (6)
C(13)	2769 (4)	5387 (10)	713 (5)	88 (5)
C(21)	3938 (5)	11654 (15)	767 (7)	134 (7)
C(22)	3084 (5)	11747 (12)	−199 (7)	135 (7)
C(23)	3761 (5)	9967 (15)	−470 (7)	132 (7)
C(31)	2793 (6)	9923 (15)	2440 (8)	179 (10)
C(32)	3093 (5)	12035 (13)	1781 (7)	142 (8)
C(33)	3693 (5)	10109 (19)	2477 (7)	205 (11)
Pd′	5682 (5)	13371 (1)	3496 (1)	49 (1)
P(1′)	5185 (1)	11704 (3)	3750 (2)	78 (1)
P(2′)	6077 (1)	14985 (3)	2943 (1)	60 (1)
P(3′)	5821 (1)	14463 (3)	4605 (1)	81 (1)
N′	6279 (3)	11309 (8)	3262 (4)	79 (3)
C(1′)	5504 (3)	12675 (9)	2497 (4)	55 (3)
C(2′)	5743 (3)	11589 (10)	2222 (5)	68 (4)
C(3′)	5620 (4)	11163 (12)	1533 (6)	89 (5)
C(4′)	5265 (5)	11812 (14)	1101 (6)	102 (6)
C(5′)	5039 (4)	12806 (14)	1364 (5)	88 (5)
C(6′)	5153 (3)	13240 (10)	2048 (5)	63 (3)
C(7′)	6129 (4)	10929 (11)	2641 (5)	77 (4)
C(8′)	6680 (5)	10601 (15)	3602 (7)	109 (6)
C(9′)	6569 (5)	9866 (17)	4230 (9)	167 (10)
C(10′)	7054 (5)	11559 (16)	3794 (8)	151 (9)
C(11′)	5324 (6)	10765 (15)	4540 (7)	164 (9)
C(12′)	5060 (5)	10275 (13)	3144 (7)	119 (7)
C(13′)	4653 (5)	12392 (18)	3751 (7)	157 (9)
C(21′)	6574 (4)	15786 (12)	3419 (6)	99 (6)
C(22′)	6289 (4)	14405 (12)	2160 (5)	86 (5)
C(23′)	5731 (4)	16474 (11)	2618 (6)	101 (5)
C(31′)	5753 (5)	16356 (11)	4565 (7)	115 (6)
C(32′)	6377 (5)	14254 (15)	5058 (6)	123 (7)
C(33′)	5496 (5)	14076 (15)	5263 (6)	148 (8)
B	4438 (2)	6712 (7)	4056 (3)	98 (7)
F(1)	4029	6663	3685	152 (10)
F(2)	4453	5953	4642	153 (11)
F(3)	4544	8038	4227	237 (17)
F(4)	4727	6196	3668	152 (10)
F(5)	4714	7760	4286	149 (14)
F(6)	4039	7229	3798	226 (19)
F(7)	4599	6013	3549	350 (41)
F(8)	4403	5845	4589	390 (49)
B′	1830 (2)	6767 (8)	−3409 (4)	106 (8)
F(1′)	2027	7047	−3966	146 (10)
F(2′)	1925	7776	−2928	255 (16)
F(3′)	1391	6704	−3614	182 (12)
F(4′)	1976	5540	−3130	267 (19)
F(5′)	2092	6246	−2846	177 (12)
F(6′)	2015	7920	−3627	214 (15)
F(7′)	1434	7084	−3239	212 (18)
F(8′)	1778	5817	−3926	228 (17)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected Bond Lengths (Å) and Angles (deg) for 2[a]

Pd–P(1)	2.324 (3)	N–C(7)	1.238 (13)
Pd–P(2)	2.325 (3)	N–C(8)	1.457 (15)
Pd–P(3)	2.360 (3)	Pd–N	2.779 (3)
Pd–C(1)	2.048 (7)		
P(1)–Pd–P(2)	165.0 (1)	P(1)–Pd–C(1)	83.0 (2)
P(1)–Pd–P(3)	96.3 (1)	P(2)–Pd–C(1)	83.7 (2)
P(2)–Pd–P(3)	96.2 (1)	P(3)–Pd–C(1)	174.6 (2)

[a] These bond lengths are for one of the two independent molecules. The bond lengths in the other cation do not differ significantly.

The Pd–N bond length in this complex 2 suggests that the imine carbon is only weakly coordinated to the metal center. Examination of the ^{13}C NMR spectrum of 2 reveals the imine carbon resonance at 163 ppm, a value very close to that of the free ligand. This value differs by 15–20 ppm from that observed in other ortho-metalated benzaldimine complexes in which the N atom is definitely bound to the metal[6] and suggests that, in solution, the N atom in 2 may not be coordinated, making the metal center the most likely site of nucleophilic attack. Indeed, addition of CH_3Li to 2 in THF at −60 °C and subsequent warming to room temperature gives the palladium methyl complex 3 in high yield (eq 2), suggesting that attack at the metal occurs preferentially.

Complex 3 has been characterized spectroscopically as the four- or five-coordinate complex shown. The ease with which CH_3^- displaces PMe_3 from 2 suggested that reagents such as $M{-}NR_2$ might also be useful in similar reactions that would result in the formation of amide complexes.[7] When 2 was allowed to react with KNHPh in THF at −60 °C, yellow crystals of 4 were isolated in high yield. The $^{31}P\{^1H\}$ NMR spectrum of 4 has only one peak, suggesting the presence of trans phosphines and substitution trans to the phenyl group. Other amide reagents such as NaNH-*t*-Bu and $KN(SiMe_3)_2$ appear to react in a similar fashion but give products that are thermally unstable at room temperature.

The reaction of eq 2 offers an interesting alternative to nucleophilic displacement of halides or other anionic leaving groups for the synthesis of these compounds. Typically, phosphine ligands are not used as leaving groups for nucleophilic displacement reactions with anionic nucleophiles. When *trans*-$Pd(PhN{=}CHC_6H_4)Cl(PMe_3)_2$ was allowed to react with KNHPh in THF under the same reaction conditions, only intractable products were formed. It is possible that the strong electron-donating ability of PMe_3 stabilizes 2 to reduction by the amide reagent, thereby facilitating the formation of the metal amide complex.

In an NMR-tube experiment, compound 4 reacts with methyl iodide to give a palladium complex that appears to be *trans*-$(Me_3P)_2Pd(C_6H_4C(H){=}NPr^i)I$ (5) and *N*-methylaniline as observed by NMR spectroscopy,[8] suggesting that the lone pair of the amide has significant nucleophilic character.[9] Complex 4 also reacts with carbon monoxide, activated acetylenes, and olefins. These reac-

---

(6) Clark, P. W.; Dyke, S. F. *J. Organomet. Chem.* **1984**, *276*, 421.

(7) (a) Cowan, R. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1989**, *111*, 4750. (b) Cowan, R. L.; Trogler, W. C. *Organometallics* **1987**, *6*, 2451. (c) Bartlett, R. A.; Power, P. P. *J. Am. Chem. Soc.* **1987**, *109*, 7563. (d) Olmstead, M. M.; Power, P. P.; Siegel, G. *Inorg. Chem.* **1986**, *25*, 1027. (e) Bryndza, H. F.; Fultz, W. C.; Tam, W. *Organometallics* **1985**, *4*, 939.

(8) Spectroscopic characterization was consistent with the presence of 5. ^1H NMR (25 °C, C_6D_6): δ 0.97 (virtual t, J_{P-H} = 3 Hz, 18 H, $P\mathit{Me}_3$), 1.28 (d, J_{H-H} = 7.5 Hz, 6 H, $CH(\mathit{CH}_3)_2$, 3.47 (sept, J_{C-H} = 7.5 Hz, 1 H, $C\mathit{H}Me_2$), 6.95 (m, 2 H, ring), 7.46 (d, J_{H-H} = 9 Hz, 1 H, ring), 7.88 (d, J_{H-H} = 9 Hz, 1 H, ring), 8.71 (s, 1 H, $N{=}C(\mathit{H})-$). $^{31}P\{^1H\}$ NMR (25 °C, $CDCl_3$): δ −20.62 (s).

(9) (a) Huang, L.; Ozawa, F.; Yamamoto, A. *Organometallics* **1990**, *9*, 2603. (b) Cowan, R. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1989**, *111*, 4750. (c) Dewey, M. A.; Bakke, J. M.; Gladysz, J. A. *Organometallics* **1990**, *9*, 1349.

tions are currently under study and will be reported separately.

In conclusion, nucleophilic attack at the imine carbon of a nitrogen-bound imine complex is possible but the metal–nitrogen interaction must be strong enough to make the imine the most electrophilic site in the molecule. The fact that the Pd atom in 2 is either five- or four-coordinate allows the nucleophile easy access to the Pd atom and offers a competing site for nucleophilic attack. Evidently, the coordination of the imine nitrogen in 2 is too weak and will not allow attack at the imine carbon to compete with nucleophilic attack at the metal center. The net result is the displacement of PMe_3 and the formation of 4. Finally, it is also possible that the weak coordination of the imine nitrogen may be an important factor in the success of reaction 2. This possibility is currently under active investigation.

Experimental Section

All procedures were carried out under an atmosphere of argon. The compounds $[(C_6H_4CH{=}NPr^i)PdCl]_2$ and $[(C_6H_4CH{=}NPr^i)Pd(NCCH_3)_2][BF_4]$ were prepared by using literature procedures.[3,4] Solvents and reagents were dried and deoxygenated by using standard methods prior to use. NMR spectra were obtained on either General Electric QE-300 or Varian VXR 300 spectrometers. Proton or carbon chemical shifts were referenced to residual signals in the solvent and are reported relative to TMS. ^{31}P chemical shifts are reported relative to H_3PO_4. Elemental analyses were performed by Atlantic Microlabs, Inc., or the analytical services of this department.

Preparation of $[(C_6H_4C(H){=}NPr^i)Pd(PMe_3)_3][BF_4]$ (2). To a solution of $[(C_6H_4CH{=}NPr^i)Pd(CH_3CN)_2][BF_4]$ (4.90 g, 12.18 mmol) in 150 mL of CH_2Cl_2 was added 3 equiv of PMe_3 (27.68 mL, 36.54 mmol; 1.32 M in toluene), and the suspension was stirred for 1 h. Solvent was removed under reduced pressure, and 6.32 g of 2 was isolated; yield 91.4%. Recrystallization from dichloromethane/diethyl ether gave yellow crystals. A single crystal suitable for X-ray diffraction was grown by layering a CH_2Cl_2 solution of 2 with diethyl ether. Anal. Calcd for $C_{19}H_{39}BF_4NP_3Pd$: C, 40.20; H, 6.88; N, 2.47. Found: C, 39.91; H, 6.97; N, 2.31. ^1H NMR (25 °C in $CDCl_3$): δ 1.03 (virtual t, J_{P-H} = 6 Hz, 18 H, trans PMe_3), 1.17 (d, J_{P-H} = 7.5 Hz, 9 H, cis PMe_3), 1.54 (d, J_{H-H} = 9 Hz, 6 H), 3.54 (m, 1 H), 7.08 (m, 2 H), 7.27 (d, J_{H-H} = 7.5 Hz, 1 H), 7.39 (t, J_{H-H} = 6 Hz, 1 H). $^{13}C\{^1H\}$ NMR (25 °C in $CDCl_3$): δ 15.78 (t, trans PMe_3), 17.74 (d, cis PMe_3), 24.74, 61.20, 124.15, 129.90, 133.06, 136.24, 141.84, 160.20, 161.95, 163.04. $^{31}P\{^1H\}$ NMR (25 °C in $CDCl_3$): δ −19.53 (d, J_{P-P} = 43 Hz, trans PMe_3), −28.06 (t, J_{P-P} = 42 Hz, cis PMe_3).

Preparation of *trans*-$(Me_3P)_2Pd(C_6H_4C(H){=}NPr^i)(NHPh)$ (4). A solution of 2 (2.00 g, 3.53 mmol) in 100 mL of THF was cooled to −60 °C. To this solution was added KNHPh (472.4 mg, 3.60 mmol) as a solution of THF. Once all the amide was added, the reaction mixture was warmed to room temperature and stirred for 12 h. The solution was a deep orange-red with a very fine suspended solid. The solvent was removed by reduced pressure, the residue was extracted with pentane (4 × 50 mL), and the extract was concentrated to ca. 10 mL and cooled to 0 °C. After two recrystallizations, bright yellow crystals of 4 were isolated (698 mg); yield 37.5%. Anal. Calcd for $C_{22}H_{35}N_2P_2Pd$: C, 50.06; H, 6.87; N, 5.31. Found: C, 49.93; H, 7.01; N, 5.29. ^1H NMR (25 °C in C_6D_6): δ 0.71 (Br, s, 18 H, trans PMe_3), 1.36 (d, J_{P-H} = 7 Hz, 6 H), 1.61 (s, 1 H, N–H), 3.62 (m, 1 H), 6.54 (t, J_{H-H} = 6 Hz, 1 H), 6.96 (d, J_{H-H} = 12 Hz, 2 H), 7.02 (m, 2 H), 7.29 (t, J_{H-H} = 9 Hz, 2 H), 7.47 (d, J_{H-H} = 12 Hz, 1 H), 8.06 (d, J_{H-H} = 9 Hz, 1 H), 8.99 (s, 1 H). $^{13}C\{^1H\}$ NMR (25 °C in $CDCl_3$): δ 13.48 (t, trans PMe_3), 24.59, 61.85, 108.78, 115.28, 122.44, 127.27, 127.59, 128.26, 129.12, 136.89, 162.17, 163.09. $^{31}P\{^1H\}$ NMR (25 °C in $CDCl_3$): δ −16.87 (s, trans PMe_3).

X-ray Crystallography. Data were collected at room temperature on a Siemens R3m/e diffractometer equipped with a graphite monochromator utilizing Mo Kα radiation (λ = 0.71069 Å). A total of 25 reflections with $20.00° \leq 2\theta \leq 22.00°$ were used to refine the cell parameters; 5940 reflections were collected with use of the ω-scan method. Four reflections (313, 222, $3\bar{1}3$, $13\bar{2}$) were measured every 96 reflections to monitor instrument and crystal stability (maximum correction on Λ was <1.01%). Absorption corrections were not applied due to the crystal size and the small value of the absorption coefficient (μ = 8.60 cm^{-1}).

The structure was solved by direct methods in SHELXTL,[10] from which the locations of both Pd atoms were obtained. The rest of the nonhydrogen atoms were obtained from a subsequent difference Fourier map. The structure was refined in SHELXTL with use of cascade-matrix least squares. The two BF_4^- anions were found to be disordered and could not be refined freely. Two partial BF_4^- units were refined as a rigid group for each of the anions in the asymmetric unit. The non-H atoms were treated anisotropically, whereas the hydrogen atom positions were calculated in ideal positions and their isotropic thermal parameters were fixed. A total of 553 parameters were refined, and $\sum w(|F_o| - |F_c|)^2$ was minimized; $w = 1/(\sigma|F_o|)^2$, $\sigma(F_o) = 0.5\,kI^{-1/2}\{[\sigma(I)]^2 + (0.02I)^2\}^{1/2}$, I(intensity) = $(I_{peak} - I_{background})$(scan rate), $\sigma(I) = (I_{peak} + I_{background})^{1/2}$(scan rate), k is the correction due to decay and Lp effects, and 0.02 is a factor used to downweight intense reflections and to account for instrument instability. The linear absorption coefficient was calculated from values from ref. 11. Scattering factors for nonhydrogen atoms were taken from Cromer and Mann[12] with anomalous dispersion corrections from Cromer and Liberman,[13] while those of hydrogen atoms were from Stewart, Davidson, and Simpson.[14]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

Supplementary Material Available: Listings of bond distances and angles and thermal parameters (6 pages); a table of observed and calculated structure factors (33 pages). Ordering information is given on any current masthead page.

---

(10) Sheldrick, G. M. SHELXTL; Nicolet XRD Corp.: Madison, WI, 1986.

(11) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, p 55 (present distributor D. Reidel, Dordrecht, The Netherlands).

(12) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321–324.

(13) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891–1898.

(14) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–3187.