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# $(\overset{\frown}{C\,N})$-Chelate, N,N′-Bridged Dimeric Palladium Complexes Derived from Hydrazones Ph—C(R)=N—N′HPh. X-ray Structure of $[\mathrm{Pd}(o\text{-}C_6H_4\text{—}C(R)\text{=}N\text{—}NPh)L]_2$ (R = Me, L = $P(OMe)_3$)

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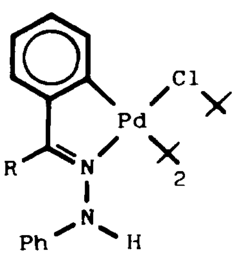
The lone pair on the amine nitrogen of the complexes $[\mathrm{PdCl}(o\text{-}C_6H_4\text{—}C(R)\text{=}N\text{—}NHPh)L]$ shows little tendency to coordinate, and removal of $Cl^-$ with $Tl[ClO_4]$ does not afford dimers but monomers with coordinated $FBF_3^-$ or $OClO_3^-$ in place of $Cl^-$. Removal of HCl with NaOMe renders the deprotonated nitrogen very coordinating, and deeply colored C,N-chelate, N,N′-bridged dimers $[\mathrm{Pd}(o\text{-}C_6H_4\text{—}C(R)\text{=}N\text{—}NPh)L]_2$ (R = Me, Ph; L = $P(OMe)_3$, 4-methylpyridine) are produced. The structure of one of them (R = Me; L = $P(OMe)_3$) was determined [crystal data: monoclinic, space group $P2_1/n$, $a = 13.477\ (2)$ Å, $b = 19.546\ (3)$ Å, $c = 14.231\ (3)$ Å, $\beta = 97.43\ (2)°$, $Z = 4$, $R = 0.057$, $R_w = 0.069$ based on 7081 independent reflections]. The dipalladacycle $Pd_2N_4$ has a butterfly shape with a hinge along the deprotonated nitrogen atoms and a Pd–Pd nonbonding distance of 3.788 (1) Å.

## Introduction

Cyclometalated complexes are a common and important type in palladium chemistry.[1] The dinuclear complexes $[\mathrm{Pd}(\overset{\frown}{C\,N})(\mu\text{-}X)]_2$ ($\overset{\frown}{C\,N}$ = orthopalladated ligand, X = bridging halide or carboxylate) are ubiquitous and so are the mononuclear complexes derived from them by bridge-splitting reactions. Some complexes have been described in which the nitrogen atom bears a substituent that is able to coordinate to the same palladium atom, thus blocking three coordination sites of the mononuclear unit.[2-8] We have focused our attention on orthometalated complexes of aryl ketone phenylhydrazones **1** and **2**, in which the N atom bears a N′ sustituent that is unable to coordinate to the same palladium atom but could perhaps be forced to coordinate to a second palladium atom to obtain C,N-chelate, N,N′-bridged complexes; in this case the resulting complexes should provide an interesting variation of the complexes $\{\mathrm{Pd}[\eta\text{-}(\overset{\frown}{C\,N})\text{-}\mu\text{-}C(C_6F_4PPh_2)\text{=}NMe]Br\}_2$[9] and $\{\mathrm{Pd}[\eta\text{-}(\overset{\frown}{C\,N})\text{-}\mu\text{-}C(C_6H_4CH_2SMe)\text{=}N\text{-}t\text{-}Bu]Br\}_2$,[10] which also contain ligands that are Pd-chelating and Pd,Pd′-bridging.



1, R = Me
2, R = Ph

## Experimental Section

**General Data.** All preparations were performed under argon by using standard Schlenk techniques. IR spectra were obtained on a Perkin-Elmer 577 instrument as KBr disks or Nujol mulls, and VUV spectra, on a Perkin-Elmer 554 instrument. $^1H$ NMR spectra were recorded on a Perkin-Elmer Hitachi R-24 B instrument at 60 MHz. Optical activity measurements were made in toluene solutions with a Perkin-Elmer Model 241 polarimeter. Molecular weight determinations were carried out in benzene (ca. 0.01 *m*) solutions on a Knauer vapor pressure osmometer. Elemental analyses were made on a Perkin-Elmer 240B instrument.

**Syntheses.** Starting dimers **1** and **2** were prepared as previously reported.[11] Sodium methoxide was prepared in methanol solution by careful treatment of a small piece of sodium with methanol and further titration with hydrochloric acid (1 N). Other reagents were from commercial sources.

**$\{Pd[C_6H_4C(Me)\text{=}NNH(Ph)](\mu\text{-}OOCMe)\}_2$ (3).** To a suspension of **1** (0.52 g, 0.755 mmol) in acetone (40 mL) was added thallium acetate (0.5 g, 1.9 mmol). After 30 min of stirring, the mixture was filtered and the solution evaporated to dryness. The residue was treated with dichloromethane (20 mL) and the mixture filtered. Addition of hexane and concentration afforded complex **3** as an orange powder (0.4 g, 75%).

**$\{PdCl[C_6H_4C(Me)\text{=}NNH(Ph)][P(OMe)_3]\}$ (9).** To a suspension of **1** (0.5 g, 0.712 mmol) in dichloromethane (10 mL) was added trimethyl phosphite (0.09 g, 0.72 mmol). Stirring for 5 min, filtration, addition of hexane, and concentration led to a yellow solid in nearly quantitative yield.

Complexes **4–8** and **10** were prepared in the same way. Yields were almost quantitative.

**$\{Pd(FBF_3)[C_6H_4C(Me)\text{=}NNH(Ph)][P(OMe)_3]\}$ (11).** To a solution of **9** (0.3 g, 0.63 mmol) in acetone (20 mL) was added $TlBF_4$ (0.2 g, 0.68 mmol). After 15 min of stirring, the mixture was filtered and the solvent pumped off. Addition of dichloromethane (15 mL), filtration, and evaporation to dryness under vacuum led to **11** as a yellow solid (0.3 g, 91%). Complex **12** was prepared in the same way (90%).

**Safety Note.** Perchlorate complexes are potentially shock-sensitive and may explode or ignite on contact with organic material. They should be handled with care and prepared only on a small scale.

**$\{Pd[C_6H_4C(Me)\text{=}NNH(Ph)][P(OMe)_3]_2\}(BF_4)$ (14).** To a solution of **9** (0.3 g, 0.63 mmol) in acetone (20 mL) were added trimethyl phosphite (0.08 g, 0.65 mmol) and $TlBF_4$ (0.2 g, 0.69 mmol). After 15 min of stirring, the suspension was filtered and the solution evaporated to dryness. The residue was treated with dichloromethane (15 mL) and the mixture filtered again. Addition of hexane and concentration af-

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forded complex **14** as a yellow solid (0.35 g, 85%). The same procedure was used for the preparation of complex **13** (80%).

**$\{Pd[C_6H_4C(Me){=}NNPh][P(OMe)_3]\}_2$ (17).** To a solution of **9** (1 g, 2.1 mmol) in dichloromethane (20 mL) was added a solution of $NaOCH_3$ (2.1 mmol) in methanol (20 mL). Concentration under vacuum afforded complex **17** as a black crystalline solid (0.74 g, 80%).

Complexes **15**, **16**, and **18** were prepared in the same way in 60–80% yields.

**$\{Pd(OOCMe)[C_6H_4C(Me){=}NNH(Ph)][P(OMe)_3]\}$ (19). Method A.** The procedure used in the synthesis of complex **9** was employed. The starting compound was **3** (0.2 g, 0.27 mmol). Yield: 0.25 g, 94%.

**Method B.** To a solution of **17** (0.2 g, 0.23 mmol) in dichloromethane was added acetic acid (0.028 g, 0.46 mmol). After 5 min of stirring, hexane (10 mL) was added and concentration afforded a yellow solid (0.2 g, 88%).

**X-ray Data Collection and Solution and Refinement of 17.** Dark blue crystals were obtained from dichloromethane/hexane diffusion. A parallelepipedic crystal of dimensions 0.55 × 0.40 × 0.35 mm was used for intensity data collection; further details are given in Table I. A CAD4 Enraf Nonius diffractometer was used ($\omega/2\theta$ mode with scan width $(1.1 + 0.34 \tan \theta)°$, graphite monochromator, Mo K$\alpha$ radiation, $\theta$ range 1–25°, $-16 \le h \le 16$, $0 \le k \le 23$, $0 \le l \le 16$). A total of 7081 independent reflections measured with 5021 $F \ge 3\sigma(F)$ were used for refinements. Two standard reflections were measured every 2 h, no deviation being observed. An empirical absorption correction using $\psi$ scans of two reflections was applied.

Both independent palladium atoms were found on a Patterson map, and all other atoms, in subsequent Fourier maps. Hydrogen atoms were geometrically positioned. A disorder occurs for the phosphite group P(2); a difference map revealed two possible positions for O(5), O(6), C(54), and C(55), with about the same electron density values. Nevertheless only one peak was found for O(4) and C(56). The population parameters for disordered atoms converged to values in the range 47–53% when considered as free parameters. They were then fixed at 50%. Although the phosphite group P(1) is not disordered, its thermal motion is significantly high and the methyl H atoms were not included in the calculation. All heavy atoms but oxygen and carbon of the disordered ligand were anisotropically refined. Least-squares refinements in four blocks with CRYSTALS[12] were carried out. The weighting scheme is $w = w\{1 - [(F_o - F_c)/6\sigma(F_o)]^2\}^2$ where $w' = 1/\sum_{r=1,3} A_r T_r(X)$ with three coefficients $A$ = 7.56, 1.05, 4.62 for the Chebyshev polynomial $T_r(X)$ with $X = F_c/F_c(\max)$.[12,13] The atomic scattering factors with anomalous dispersion corrections were taken from CRYSTALS.

Final $R$ was 5.7%, and final $R_w$ was 6.9%. Maximum shift/esd was 0.04. The largest peaks in the last difference map (0.7 e Å$^{-3}$) were in the vicinity of the disordered phosphite. Atomic and thermal parameters are listed in Table II.

**Table I.** Crystallographic Data

$C_{34}H_{42}N_4O_6P_2Pd_2$
MW = 877.5
$a$ = 13.477 (2) Å
$b$ = 19.546 (3) Å
$c$ = 14.231 (3) Å
$\beta$ = 97.43 (2)°
$V$ = 3717 (2) Å$^3$
$Z$ = 4

space group $P2_1/n$
$T$ = 18 °C
$\lambda$ = 0.7107 Å
$\rho_{calc}$ = 1.57 g cm$^{-3}$
$\mu$ = 10.85 cm$^{-1}$
transm coeff = 1.00–0.89
$R$ = 0.057
$R_w$ = 0.069

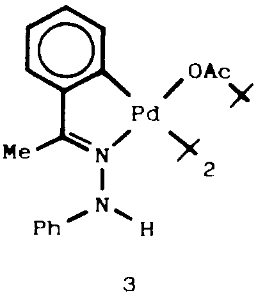
**Table II.** Atomic and Thermal Parameters

| atom | $x/a$ | $y/b$ | $z/c$ | $U$(equiv), Å$^2$ |
|---|---|---|---|---|
| Pd(1) | 0.01321 (4) | 0.31777 (3) | 0.03060 (4) | 0.0443 |
| Pd(2) | 0.23293 (4) | 0.33286 (3) | 0.10943 (4) | 0.0410 |
| N(1) | 0.1669 (5) | 0.3228 (3) | 0.0734 (4) | 0.0495 |
| N(2) | 0.0883 (4) | 0.2983 (3) | –0.1467 (4) | 0.0394 |
| N(3) | 0.0360 (4) | 0.2598 (3) | –0.0881 (4) | 0.0416 |
| N(4) | 0.2388 (4) | 0.2913 (3) | 0.0283 (4) | 0.0470 |
| C(1) | 0.1925 (7) | 0.3632 (4) | 0.1451 (5) | 0.0548 |
| C(2) | 0.0479 (5) | 0.3163 (4) | –0.2311 (5) | 0.0453 |
| C(11) | 0.1113 (7) | 0.3959 (4) | 0.1860 (5) | 0.0548 |
| C(12) | 0.0139 (7) | 0.3811 (4) | 0.1426 (5) | 0.0546 |
| C(13) | –0.0660 (9) | 0.4138 (5) | 0.1791 (7) | 0.0779 |
| C(14) | –0.047 (1) | 0.4583 (6) | 0.2582 (8) | 0.0835 |
| C(15) | 0.049 (1) | 0.4697 (5) | 0.2991 (6) | 0.0794 |
| C(16) | 0.1289 (9) | 0.4390 (5) | 0.2641 (6) | 0.0664 |
| C(17) | 0.3003 (8) | 0.3752 (5) | 0.1820 (7) | 0.0736 |
| C(21) | 0.1129 (6) | 0.3558 (4) | –0.2850 (5) | 0.0481 |
| C(22) | 0.2085 (6) | 0.3723 (4) | –0.2417 (5) | 0.0527 |
| C(23) | 0.2677 (8) | 0.4115 (5) | –0.2926 (7) | 0.0727 |
| C(24) | 0.237 (1) | 0.4313 (6) | –0.3849 (9) | 0.0902 |
| C(25) | 0.145 (1) | 0.4145 (6) | –0.4272 (7) | 0.0775 |
| C(26) | 0.0800 (8) | 0.3770 (5) | –0.3798 (6) | 0.0680 |
| C(27) | –0.0574 (6) | 0.2974 (6) | –0.2682 (6) | 0.0684 |
| C(31) | 0.0262 (5) | 0.1913 (3) | –0.1077 (5) | 0.0412 |
| C(32) | 0.0653 (6) | 0.1585 (4) | –0.1815 (5) | 0.0562 |
| C(33) | 0.0522 (8) | 0.0890 (5) | –0.1968 (7) | 0.0754 |
| C(34) | 0.0017 (9) | 0.0498 (4) | –0.1397 (8) | 0.0760 |
| C(35) | –0.0367 (7) | 0.0806 (4) | –0.0650 (7) | 0.0684 |
| C(36) | –0.0238 (5) | 0.1496 (4) | –0.0485 (6) | 0.0533 |
| C(41) | 0.2379 (6) | 0.2206 (4) | 0.0381 (5) | 0.0465 |
| C(42) | 0.1939 (7) | 0.1873 (4) | 0.1075 (6) | 0.0584 |
| C(43) | 0.2009 (9) | 0.1149 (5) | 0.1166 (7) | 0.0785 |
| C(44) | 0.252 (1) | 0.0782 (5) | 0.0569 (9) | 0.0833 |
| C(45) | 0.2983 (9) | 0.1107 (5) | –0.0099 (8) | 0.0830 |
| C(46) | 0.2914 (7) | 0.1804 (4) | –0.0210 (7) | 0.0625 |
| P(1) | –0.1505 (2) | 0.3211 (1) | –0.0089 (2) | 0.0614 |
| P(2) | 0.3881 (2) | 0.3711 (2) | –0.0853 (2) | 0.0793 |
| O(1) | –0.1875 (4) | 0.2640 (4) | –0.0838 (6) | 0.0843 |
| O(2) | –0.1968 (6) | 0.3909 (4) | –0.0476 (8) | 0.1067 |
| O(3) | –0.2239 (6) | 0.3134 (4) | 0.0690 (7) | 0.0915 |
| C(51) | –0.2882 (8) | 0.2459 (9) | –0.118 (1) | 0.1132 |
| C(52) | –0.144 (1) | 0.4383 (8) | –0.098 (1) | 0.1174 |
| C(53) | –0.204 (1) | 0.2594 (7) | 0.137 (1) | 0.1092 |
| O(4) | 0.4566 (7) | 0.3487 (4) | –0.1623 (6) | 0.131 (3)[a] |
| O(5a) | 0.4410 (9) | 0.3288 (6) | 0.0126 (7) | 0.085 (4)[a] |
| O(5b) | 0.4616 (8) | 0.3745 (6) | 0.0042 (7) | 0.086 (4)[a] |
| O(6a) | 0.419 (1) | 0.4471 (5) | –0.061 (1) | 0.161 (8)[a] |
| O(6b) | 0.391 (1) | 0.4522 (5) | –0.1095 (9) | 0.107 (5)[a] |
| C(54a) | 0.538 (1) | 0.390 (1) | –0.188 (2) | 0.108 (8)[a] |
| C(54b) | 0.466 (2) | 0.2765 (7) | –0.178 (2) | 0.15 (1)[a] |
| C(55a) | 0.543 (1) | 0.339 (1) | 0.056 (1) | 0.085 (6)[a] |
| C(55b) | 0.495 (2) | 0.3089 (9) | 0.038 (1) | 0.096 (7)[a] |
| C(56) | 0.340 (1) | 0.4976 (7) | –0.055 (1) | 0.186 (8)[a] |

[a] Isotropic $U$.

## Results

Orthopalladation of acetophenone $N$-phenylhydrazone (APPH) and benzophenone $N$-phenylhydrazone (BPPH) to the starting complexes **1** and **2** is achieved conveniently in both cases by Cope's procedure,[14] as described for complex **2**.[11] Complex **1** has been prepared previously by an alternative method.[15] In order to try different approaches to obtain N,N′-bridged dimers, some derivatives of **1** were prepared by trivial procedures; for **2** only those derivatives which had proved successful were made. Thus, complex **3** was prepared from **1** and thallium acetate, whereas bridge-splitting reactions with several monodentate ligands afforded complexes **4–10** (Analytical, IR, and $^1$H NMR data are given



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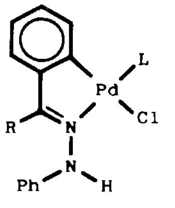

4 R = Me, L = piperidine
5 R = Me, L = morpholine
6 R = Me, L = 3-methylpyridine
7 R = Me, L = 4-methylpyridine
8 R = Ph, L = 4-methylpyridine
9 R = Me, L = $P(OMe)_3$
10 R = Ph, L = $P(OMe)_3$

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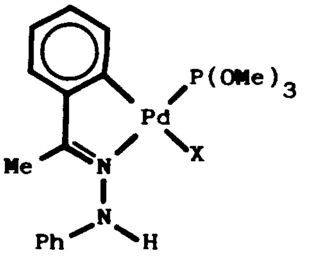
**Table III.** Analytical (%; Calculated in Parentheses), IR ($cm^{-1}$), and $^1H$ NMR ($\delta$, $CDCl_3$, Reference TMS) Data

| complex | C | H | N | $\nu$(N—H), $\nu$(C=N) | $^1H$ NMR[a] |
|---|---|---|---|---|---|
| **3** | 51.05 (51.26) | 3.98 (4.31) | 7.23 (7.48) | 3280, 1599 | 2.00 (s, Me); 1.80 (s, OAc) |
| **4** | 51.81 (52.19) | 5.51 (5.53) | 9.34 (9.61) | 3180, 1595 | 2.20 (s, Me); 1.60 (br m, 6 H, piperidine; 3.30 (br m, 5 H, $HN(CH_2)_2$ of piperidine) |
| **5** | 48.95 (49.33) | 4.99 (5.06) | 9.48 (9.59) | 3170, 1595 | 2.20 (s, Me); 3.50 (br m, 9 H, morpholine) |
| **6** | 53.75 (54.05) | 4.43 (4.54) | 9.09 (9.46) | 3190, 1592 | 2.23 (s, Me); 2.33 (s, 3-$MeC_5H_4N$) |
| **7** | 53.86 (54.05) | 4.41 (4.54) | 9.29 (9.46) | 3200, 1599 | 2.27 (s, Me); 2.42 (s, 4-$MeC_5H_4N$) |
| **8** | 58.95 (59.28) | 4.01 (4.38) | 8.15 (8.30) | 3222, 1598 | ...; 2.20 (s, 4-$MeC_5H_4N$) |
| **9** | 43.21 (42.97) | 4.69 (4.67) | 6.04 (5.88) | 3205, 1592 | 2.25 (s, Me); 3.77 (d, $P(OMe)_3$, $^3J_{P-H}$ = 12 Hz) |
| **10** | 49.41 (49.16) | 4.58 (4.50) | 5.58 (5.22) | 3245, 1598 | ...; 3.80 (d, $P(OMe)_3$, $^3J_{P-H}$ = 12 Hz) |
| **11** | 39.00 (38.78) | 4.15 (4.21) | 5.40 (5.32) | 3300, 1592 | 2.45 (s, Me); 3.71 (d, $P(OMe)_3$, $^3J_{P-H}$ = 12 Hz) |
| **12** | 38.03 (37.87) | 4.20 (4.11) | 5.35 (5.20) | 3310, 1598 | 2.38 (s, Me); 3.73 (d, $P(OMe)_3$, $^3J_{P-H}$ = 12 Hz) |
| **13** | 52.90 (53.04) | 4.54 (4.62) | 9.35 (9.52) | 3300, 1599 | 2.20 (s, Me); 2.40 (s, 4-$MeC_5H_4N$); 2.50 (s, 4-$MeC_5H_4N$) |
| **14** | 38.50 (38.75) | 5.26 (5.04) | 4.38 (4.52) | 3210, 1595 | 2.60 (s, Me); 3.60 (d, $P(OMe)_3$)[b] |
| **15** | 58.36 (58.08) | 4.26 (4.11) | 10.35 (10.70) | ..., 1585 | 2.35 (s, Me); 1.65 (s, 4-$MeC_5H_4N$) |
| **16** | 63.55 (63.89) | 4.45 (4.51) | 8.90 (8.95) | ..., 1590 | ...; 2.30 (s, 4-$MeC_5H_4N$) |
| **17** | 46.55 (46.52) | 4.78 (4.83) | 6.26 (6.39) | ..., 1588 | 2.23 (s, Me); 3.70 (d, $P(OMe)_3$, $^3J_{P-H}$ = 12 Hz) |
| **18** | 52.43 (52.74) | 4.65 (4.63) | 5.42 (5.59) | ...; 1593 | ...; 3.40 (d, $P(OMe)_3$, $^3J_{P-H}$ = 12 Hz) |
| **19** | 46.15 (45.73) | 5.35 (5.05) | 5.32 (5.62) | 3185, 1595 | 2.35 (s, Me); 1.85 (s, OAc); 3.80 (d, $P(OMe)_3$, $^3J_{P-H}$ = 12 Hz) |

[a] Other than aryl protons. These appeared at 6.0–7.5 ppm. [b] The two expected doublets overlap in two broad signals, and $^3J_{P-H}$ cannot be measured.

in Table III.) Tertiary amines such as $NEt_3$ or N-*n*-$Bu_3$ led to complications, and no further efforts to isolate their corresponding complexes were made.

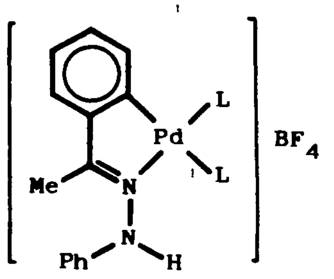
In a first approach to prepare N,N′-bridged dinuclear complexes simply by removing the $Cl^-$ ligand in **9** with $TlBF_4$ or $TlClO_4$, the lone pair on the uncoordinated nitrogen proved to be very unreactive and complexes **11** and **12** with the poorly coordinating



11 X = $FBF_3^-$

12 X = $OClO_3^-$

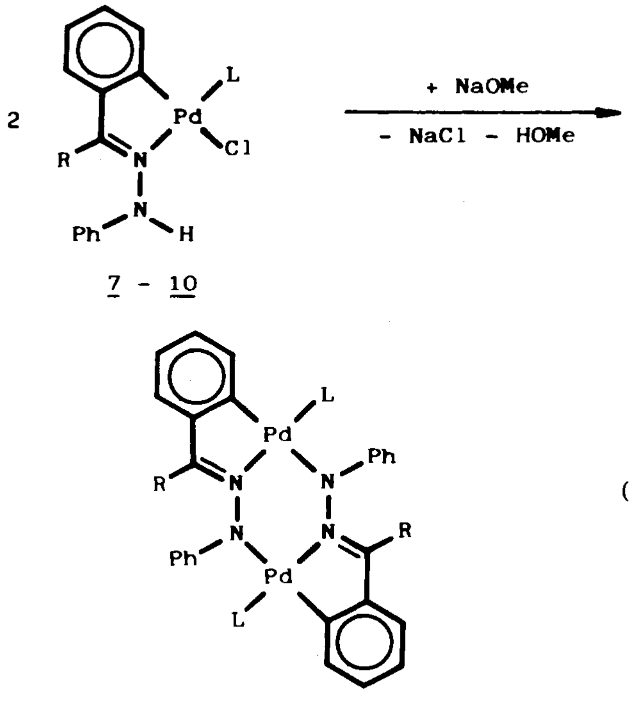
ligands $FBF_3^-$ or $OClO_3^-$ occupying the vacant position were isolated. Their IR spectra show characteristic absorptions of the anions acting as monodentate ligands ($C_{3v}$) rather than as counterions ($T_d$). In addition, the complexes are nonconducting in benzene solution. In contrast, these complexes are 1:1 electrolytes in acetone, where the cationic species $[Pd(\widehat{CN})L(OCMe_2)]X$ ($X^- = BF_4^-$, $ClO_4^-$; L = $P(OMe)_3$) are probably formed; although these species were not isolated, the reaction of **7** or **9** with $TlBF_4$ and L (L = 4-methylpyridine, $P(OMe)_3$) leads to the formation of complexes **13** and **14**, $[Pd(\widehat{CN})L_2][BF_4]$.



13 L = 4-methylpyridine

14 L = $P(OMe)_3$

Our next approach was to treat complexes of the type **4**–**10** with a base in order to remove HCl, and this met with success. Thus treatment of a yellow solution of complex **9** in dichloromethane with the stoichiometric amount of NaOMe in methanol produced a dramatic change in color to red-violet, and complex **17** could be isolated in excellent yield from the solution (eq 1). Complexes



(1)

15 R = Me, L = 4-methylpyridine

16 R = Ph, L = 4-methylpyridine

17 R = Me, L = $P(OMe)_3$

18 R = Ph, L = $P(OMe)_3$

**7**, **8**, and **10** behaved similarly to give **15**, **16**, and **18**; in contrast, **4**, **5**, and **6** when treated with NaOMe produced orange solutions that were not further investigated. Hence, the reaction is quite influenced by the ancillary ligand, and it is worth noting that treatment of $[PdCl(\widehat{CN})(Ph_2PCH_2C(O)Ph)]$ ($\widehat{CN}$ = orthopalladated APPH) with NaH leads to $[Pd(\widehat{CN})(Ph_2PCHC(O)Ph)]$; i.e., deprotonation occurs in the methylene group of the coordinated (diphenylphosphino)acetophenone and not in the NH group of the orthopalladated APPH.[16]

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(16) Bouaoud, S. E.; Braunstein, P.; Grandjean, D.; Matt, D.; Nobel, D. *Inorg. Chem.* **1986**, *25*, 3765.

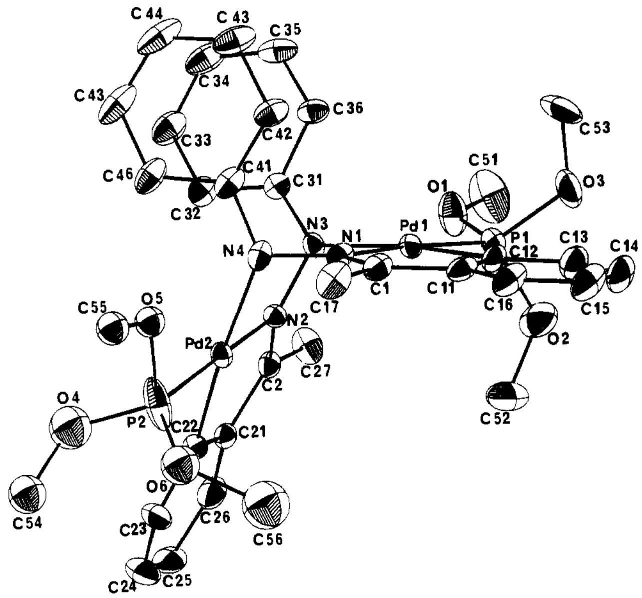
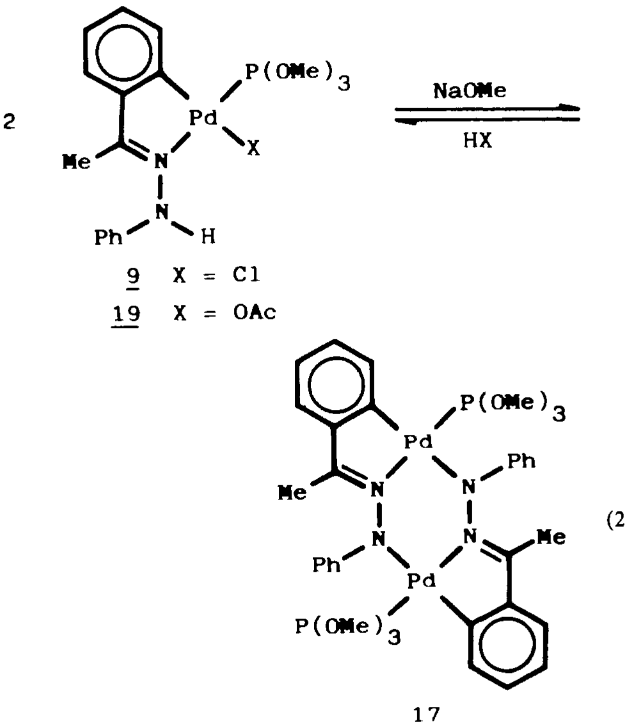


**Figure 1.** Molecular structure of 17 showing the atom numbering scheme.

The dinuclear nature of complexes **15**–**18** was confirmed by their molecular weights in benzene solution and by the X-ray diffraction study of complex **17**, which is described below. The molecule is chiral and is obtained as a racemic mixture of the two enantiomers; their solutions show no optical activity, and the crystal studied is also racemic.

The origin of the deep color was studied for complex **17**; it is associated with a charge-transfer band, as indicated by its high extinction coefficient ($\epsilon$ = 4400 mol$^{-1}$ cm$^{-1}$, $c = 0.7 \times 10^{-4}$ M) and by the dependence of its energy upon the polarity of the solvent,[17] as measured by $E_T$;[18] a linear dependence $\lambda$ (nm)/$E_T$ (kJ/mol) is found in the following solvents: benzene (508/144.3), dichloromethane (492/172.0), acetone (490/176.6), and acetonitrile (484/192.5).

The reversibility of the deprotonation reaction was studied for complex **17** (eq 2). Complex **17** is protonated with HCl to regenerate **9** or with HOAc to produce complex **19**, which can be independently obtained by bridge splitting of **3** with P(OMe)$_3$ and contains an acetate ligand acting as monodentate. Complex **17** is not protonated by acetylacetone (Hacac); on the contrary, complex **9** is deprotonated to **17** when treated with Tl(acac), although this method is not an improvement on that using NaOMe.



9 X = Cl
19 X = OAc

17

(2)

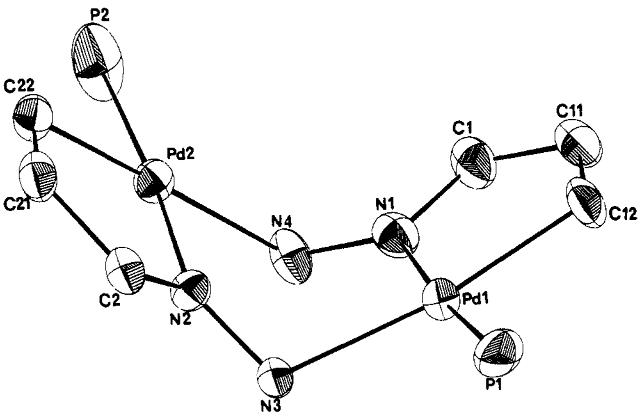


**Figure 2.** Alternative view of the basic skeleton of **17**.

**Table IV.** Selected Interatomic Distances (Å) and Angles (deg)

| | | | |
|---|---|---|---|
| Palladium Coordination | | | |
| Pd(1)–N(1) | 2.084 (7) | Pd(2)–N(2) | 2.067 (5) |
| Pd(1)–N(3) | 2.089 (5) | Pd(2)–N(4) | 2.115 (6) |
| Pd(1)–C(12) | 2.019 (7) | Pd(2)–C(22) | 2.021 (7) |
| Pd(1)–P(1) | 2.207 (2) | Pd(2)–P(2) | 2.206 (2) |
| N(3)–Pd(1)–N(1) | 91.0 (2) | N(4)–Pd(2)–N(2) | 91.9 (2) |
| C(12)–Pd(1)–N(1) | 81.0 (3) | C(22)–Pd(2)–N(2) | 81.4 (3) |
| C(12)–Pd(1)–N(3) | 170.6 (3) | C(22)–Pd(2)–N(4) | 172.9 (3) |
| P(1)–Pd(1)–N(1) | 175.1 (2) | P(2)–Pd(2)–N(2) | 174.1 (2) |
| P(1)–Pd(1)–N(3) | 93.3 (2) | P(2)–Pd(2)–N(4) | 93.7 (2) |
| P(1)–Pd(1)–C(12) | 94.5 (3) | P(2)–Pd(2)–C(22) | 93.0 (3) |
| Ligand | | | |
| N(1)–N(4) | 1.375 (8) | N(2)–N(3) | 1.382 (7) |
| N(1)–C(1) | 1.300 (9) | N(2)–C(2) | 1.301 (8) |
| N(3)–C(31) | 1.371 (8) | N(4)–C(41) | 1.388 (9) |
| C(1)–C(11) | 1.45 (1) | C(2)–C(21) | 1.46 (1) |
| C(1)–C(17) | 1.50 (1) | C(2)–C(27) | 1.50 (1) |
| av phenyl C–C | 1.39 (2) | | |
| N(4)–N(1)–Pd(1) | 125.3 (4) | N(3)–N(2)–Pd(2) | 124.0 (4) |
| C(1)–N(1)–Pd(1) | 114.3 (5) | C(2)–N(2)–Pd(2) | 114.8 (4) |
| C(1)–N(1)–N(4) | 120.3 (7) | C(2)–N(2)–N(3) | 121.2 (6) |
| N(2)–N(3)–Pd(1) | 109.4 (4) | N(1)–N(4)–Pd(2) | 108.4 (4) |
| C(31)–N(3)–Pd(1) | 132.5 (5) | C(41)–N(4)–Pd(2) | 118.4 (5) |
| C(31)–N(3)–N(2) | 116.8 (5) | C(41)–N(4)–N(1) | 112.6 (6) |
| C(11)–C(1)–N(1) | 116.2 (8) | C(21)–C(2)–N(2) | 114.7 (6) |
| C(17)–C(1)–N(1) | 121.4 (8) | C(27)–C(2)–N(2) | 121.7 (7) |
| C(17)–C(1)–C(11) | 122.4 (7) | C(27)–C(2)–C(21) | 123.6 (7) |
| C(12)–C(11)–C(1) | 116.5 (7) | C(22)–C(21)–C(2) | 118.4 (6) |
| C(11)–C(12)–Pd(1) | 111.9 (5) | C(21)–C(22)–Pd(2) | 110.8 (5) |
| av phenyl C–C–C | 120 (1) | | |

**Discussion of the X-ray Structure of Complex 17.** The molecular structure of complex **17** and the atom numbering scheme are shown in Figure 1. An alternative view of the basic skeleton of the dimer is shown in Figure 2. Selected bond lengths and bond angles are given in Table IV.

The structure consists of a dimer and the geometry around the palladium atoms is approximately square planar. Each palladium atom is ligated to a trimethyl phosphite ligand, to the imine nitrogen of a first APPH molecule, to the ortho carbon of the phenyl ring to which this imine group is attached, and to the deprotonated amine nitrogen of a second APPH molecule.

The two five-membered orthopalladacycles are very similar to that found in the related[19] [Pd($\overset{\frown}{C\ N}$)ClBr]$^-$ anion; small angles

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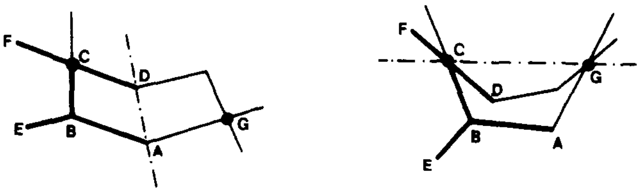
[17] See, for example: Chaudhury, N.; Puddephatt, R. J. *J. Organomet. Chem.* **1975**, *84*, 105. Espinet, P.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1979**, 1542.

[18] Reichart, C. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 29.

[19] Dehand, J.; Fischer, J.; Pfeffer, M.; Mitschler, A.; Zinsius, M. *Inorg. Chem.* **1976**, *15*, 2675.



3a 3b

**Figure 3.** Schematic representation of the two types of dipalladacycle discussed in the text.

of 81.0 and 81.3° are subtended by the chelating atoms N(1)–C(12) for Pd(1) and N(2)–C(22) for Pd(2), which are comparable to the angle of 80.02 (0.23)° reported in ref 19.

The six-membered dipalladacycle Pd(1)–N(1)–N(4)–Pd(2)–N(2)–N(3) has a butterfly shape with a dihedral angle of 118.5° around its N(3)–N(4) hinge. The nonbonding Pd(1)–Pd(2) distance is 3.788 (1) Å. This nonbonding Pd–Pd distance is much larger than the nonbonding Pd–Pd distances found in the related six-membered dipalladacycles with imidoyl bridges,[9,10,20–22] which are close to 2.9 Å. This huge difference is mainly due to the planarity of the five-membered orthopalladacycles, which, with an $sp^2$ hybridization in the N(1) and N(2) atoms, forces dihedral angles N(4)–N(1)–Pd(1)–N(3) and N(3)–N(2)–Pd(2)–N(4) very close to 0°. This can be clearly seen for Pd(1) in Figure 1. The palladium planar surrounding includes the orthopalladated phenyl ring, and a mean-square-plane calculation including Pd(1), P(1), C(1), C(17), N(1), N(3), N(4) and the phenyl ring C(11) to C(16) shows that the largest deviation occurs at N(3), which deviates only by 0.1 Å. In the case of Pd(2) and equivalent atoms, the largest deviation is 0.07 Å at P(2).

Figure 3 shows schematically the relationship between the structure of complex **17**, **3a**, which is seen as a butterfly with a hinge through A,D (the amine N atoms) and that of imidoyl-bridged complexes, **3b**, which is better seen as a butterfly with a hinge through C,G (the Pd atoms). In order to move from **3a** to **3b**, thus bringing the two palladium atoms closer, it is necessary to open the AB–CD dihedral angle, which is 0° in **3a**. Due to the coplanarity of bonds imposed around C (the Pd atom) and around B (the $sp^2$ imine nitrogen in complex **17** or the $sp^2$ imidoyl carbon in the imidoyl-bridged systems), this means opening the EB–CF dihedral angle, and this is only possible if E and F are not involved in a rigid planar cycle. Hence, structure **3b** is forbidden for complex **17** whereas it is the one found for imidoyl-bridged complexes, where E and F are not involved in a cycle[20–22] or where the cycle is not planar.[9,10]

N(3) and N(4) should be approximately $sp^3$; however, their phenyl substituents could occupy neither the equatorial positions along the hinge of the butterfly because of steric hindrance with phosphite ligands nor axial positions under the butterfly because of mutual steric hindrance. Hence, a distortion toward an $sp^2$ hybridization might be expected. Such a distortion occurs, but unexpectedly, it turns out that angles around N(3) and N(4) are markedly different although both parts of the dimer are chemically identical. The sum of angles around N(3) is 358.7°, and that around N(4) is 339.4° (compare with 360° for $sp^2$ and 328.2° for $sp^3$ hybridization). Particularly, angles C(31)–N(3)–Pd(1) and C(41)–N(3)–N(2) are very different (132.5 and 118.4°, respectively) whereas angles Pd(1)–N(3)–N(2) and Pd(2)–N(4)–N(1), involved in both dipalladacycles, are very similar (109.4 and 108.4°) and close to the $sp^3$ value. We have no explanation for such a different behavior of N(3) and N(4). The overall result is that both phenylhydrazine phenyl rings C(31) to C(36) and C(41) to C(46) are nearly parallel (Figure 1), with an average distance between them of 3.5 Å (consistent with the accepted van der Waals coverage of a phenyl ring, 1.7 Å),[23] and an angle between them of 16.6°, with its vertex under the hinge.

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**Supplementary Material Available:** Tables of distances and angles, least-squares planes, complete experimental data for the crystallographic analysis, atomic parameters for hydrogen atoms, and anisotropic thermal parameters (5 pages); a listing of observed and calculated structure factors (36 pages). Ordering information is given on any current masthead page.

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