Cyclopalladated Complexes of 2-Acetylpyridine Phenylhydrazone: A Terdentate C,N,N′ Donor Ligand

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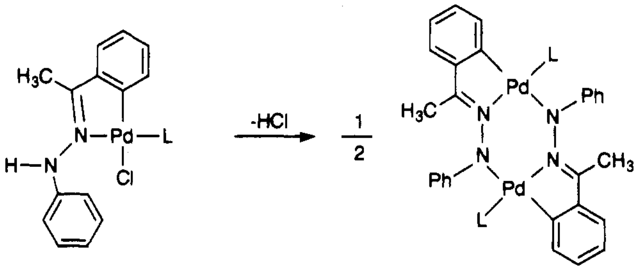
Cyclopalladated complexes of 2-acetylpyridine phenylhydrazone [$Pd(C_6H_4N(H)N{=}C(CH_3)C_5H_4N)Cl$] (**2**) and [$Pd(C_6H_4N(H)N{=}C(CH_3)C_5H_4N)L]BF_4$ (L = PPh_3 (**3a**), $P(OMe)_3$ (**3b**), $P(OPh)_3$ (**3c**), $CH_3C_5H_4N$ (**3d**), C_4H_8S (**3e**)) containing readily deprotonable N—H bonds have been prepared. Blue zwitterionic species, obtained after deprotonation of the cationic complexes, are characterized by their reactivity as nucleophiles toward H^+ or CH_3I; *e.g.* deprotonated (**3a**) reacts with CH_3I to give [$Pd(C_6H_4N(CH_3)N{=}C(CH_3)C_5H_4N)I$] (**5**). Some aspects of the *ortho*metalation reaction mechanism of phenylhydrazones are discussed. The crystal and molecular structure of the *face to face* complex {[$Pd(C_6H_4N(H)N{=}C(CH_3)C_5H_4N)]_2(\mu\text{-}Ph_2PCH_2PPh_2)\}[BF_4]_2{\cdot}OEt_2{\cdot}NCMe$ (**4**) [monoclinic, space group $P2_1/n$, $a = 15.911(4)$ Å, $b = 18.902(6)$ Å, $c = 18.563(4)$ Å, $\beta = 95.43(2)°$, $Z = 4$, $R = 0.032$, and $R_w = 0.034$ for 7038 observed reflections] shows a nonbonding Pd—Pd distance of 3.114(1) Å.

Introduction

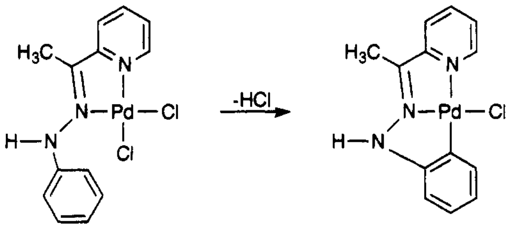
In a recent paper we described the synthesis of binuclear amido complexes of palladium containing two Pd-N amido bonds, obtained by deprotonation of mononuclear complexes of orthopalladated acetophenone phenylhydrazone (APPH) according to Scheme 1.[1] Amidocomplexes of the platinum group metals show reactivity patterns distinctly different from those of the early transition metal complexes.[2] For instance, phenylamido complexes of palladium and platinum undergo oxidative coupling leading to dimerization through carbon-carbon bond formation on the para position of the phenyl ring.[3-6] Further interest in complexes of palladium with phenylhydrazones and related ligands comes from their observed photochemical and photophysical activity.[7,8]

Following our interest in amido complexes, we decided to explore the behavior of other phenylhydrazone ligands and focused our attention on 2-acetylpyridine phenylhydrazone (2-APyPH, L¹). We expected this ligand to coordinate to a metal center in a chelate mode (resembling the well-known 2,2′-bipyridine) to give **1a**; subsequent deprotonation of the N-H bond might afford M-N amido bonds, providing binuclear complexes similar to those depicted in Scheme 1. The results described in this paper show that, whereas the synthesis of [$Pd(L^1)Cl_2$] **1a** is readily achieved according to our expectations, hydrogen chloride elimination occurs on a C-H rather than on a N-H bond, leading to a mononuclear orthopalladated complex [$Pd(L^1\text{-}H)Cl$] **2** containing a terdentate N,N,C-ligand. Complexes derived from **2** by replacement of Cl with different ligands, and blue zwitterionic species resulting from deprotonation of the cationic orthopalladated complexes are also described.

Scheme 1



Scheme 2



1a **2**

Results and Discussion

Unless otherwise stated, all complexes here presented have been characterized by ¹H NMR measurements and solid IR spectra (see Table 1) and elemental C, H, N analysis.

Preparation of Neutral Orthometalated Complexes. Treatment of $Li_2[PdCl_4]$ in methanol with 2-APyPH

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(1) Espinet, P.; García, G.; Herrero, F. J.; Jeannin, Y.; Philoche-Levisalles, M. *Inorg. Chem.* **1989**, *28*, 4207.

(2) Fryzuk, M. D.; Montgomery, C. D. *Coord. Chem. Rev.* **1989**, *95*, 1.

(3) Alcock, N. W.; O'Sullivan, R. D.; Parkins, A. W. *J. Chem. Soc., Chem. Commun.* **1980**, 1286.

(4) Espinet, P.; García-Herbosa, G.; Ramos, J. M. *J. Chem. Soc., Dalton Trans.* **1990**, 2931.

(5) Espinet, P.; Alonso, M. Y.; García-Herbosa, G.; Ramos, J. M.; Jeannin, Y.; Philoche-Levisalles, M. *Inorg. Chem.* **1992**, *31*, 2502.

(6) O'Sullivan, R. D.; Parkins, A. W.; Alcock, N. W. *J. Chem. Soc., Dalton Trans.* **1986**, 571.

(7) Giannetto, A.; Guglielmo, G.; Ricevuto, V.; Giuffrida, A.; Campagna, S. *J. Photochem. Photobiol., A: Chem.* **1990**, *53*, 23.

(8) Campagna, S.; Cusumano, M.; Giuffrida, A.; Giglielmo, G.; Ricevuto, V. *Polyhedron* **1988**, *7*, 207.

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Table 1. IR (cm^{-1}) and ^{1}H NMR (ppm) Data

Compound	ν(N–H)	^{1}H NMR^a
L$^{1\,b}$	3205, 3170	2.36 (s, Me), 7.77 (m, H^5), 8.35 (m, H^3 + H^4), 8.68 (d, H^6), 10.26 (m, N–H)
1a, [PdCl$_2$L^1]^b	3249	2.36 (s, Me), 8.25 (m, H^4 + H^5), 8.72 (td, H^3), 9.03 (d, H^6)
1b, [PdCl$_2$L^2]^b		2.53 (s, Me), 3.37 (s, N–*Me*), 7.90 (m, H^5), 8.37(m, H^3 + H^4), 9.15 (d, H^6)
2, [Pd(L^1-H)Cl]^b	3230	2.32 (s, Me), 7.55 (m, H^4 + H^5), 8.00 (td, H^3), 8.30 (dd, H^6)
3a, [Pd(L^1-H)-PPh$_3$]BF$_4$^{c}	3277	2.56 (s, Me), ...^{d}
3b, [Pd(L^1-H)-P(OMe)$_3$]BF$_4$^{c}	3295	2.54 (s, Me), 3.95 (d, P(O*Me*)$_3$, $^3J_{P-H}$ = 13 Hz), 7.52 (m, H^4 + H^5), 8.18 (td, H^3), 8.79 (dt, H^6)
3c, [Pd(L^1-H)-P(OPh)$_3$]BF$_4$^{c}	3277	2.48 (s, Me), ..., 8.20 (td, H^3), 8.96 (dd, H^6)
3d, [Pd(L^1-H) 4-MeC$_6$H$_4$N]BF$_4$^{c}	3323	2.53 (s, Me), 2.58 (s, 4-*Me*C$_6$H$_4$N), ..., 8.91 (m, H^6)
3f, [Pd(L^1-H)-THT]BF$_4$^{c}	3290, 3226	2.25 (m, 4H, THT), 2.47 (s, Me), 3.40 (m, 4H, THT), 7.70 (m, H^4 + H^5), 8.11 (d, H^3), 8.30 (m, H^6)
4, {[Pd(L^1-H)]$_2$-dppm}[BF$_4$]$_2$^{c}	3288	2.54 (s, 6H, Me), 4.97 (t, Ph$_2$PC*H*$_2$PPh$_2$, $^2J_{P-H}$ = 13 Hz), ...^{d}
5, [Pd(L^2-H)I]^b		2.53 (s, Me), 3.35 (s, N–*Me*), ..., 8.13 (td, H^3), 8.79 (m, H^6)

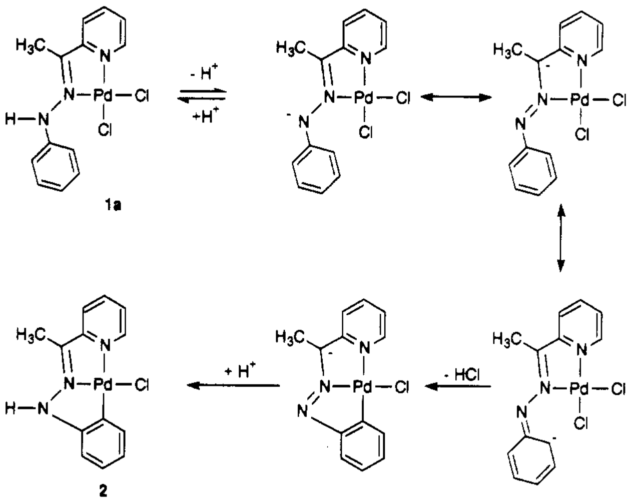
^{a} Resonances due to phenyl protons are not included. Proton numbering of pyridine ring. ^{b} In CD$_3$SOCD$_3$ solution. ^{c} In CD$_3$COCD$_3$ solution. ^{d} Precise assignment precluded by multiple overlapping phenyl resonances.

afforded a yellow solid **1a** which showed the common pattern for a "PdCl$_2$" *cis* arrangement with two ν(Pd—Cl) absorptions at 348 and 321 cm^{-1}. The hydrogen chloride elimination reaction of **1a** with bases (NaOMe or NEt$_3$) was attempted, in looking for binuclear amido complexes related to those previously described,[1] by following the reaction outlined in Scheme 1. However, the product of such a reaction was the *exo*-metallacycle[9] complex **2** (the C═N double bond is out of the orthometalated ring) according to Scheme 2. The deprotonated ligand L^1 in complex **2** may be regarded as a terdentate C,N,N′ donor analogue of 6-phenyl-2,2′-bipyridine and related ligands reported by Constable et al. and used to prepare cyclometalated complexes.[10–12]

Alternatively, complex **2** can also be prepared in high yield by treatment of **1a** with Tl[BF$_4$]. Chloride extraction on **1a** enhances electrophilic attack of the metal ion on the phenyl ring, leading to orthometalation, as observed in other cases.[13] Both synthetic ways (i.e. basic treatment or chloride extraction) are in agreement with the accepted mechanism of orthopalladation.[14]

Mechanism. In order to get further insight into the mechanism of orthometalation of hydrazones, we prepared the complex [Pd(C$_6$H$_5$N(CH$_3$)N═C(CH$_3$)C$_5$H$_4$N)Cl$_2$] (**1b**) by following the same scheme as indicated for **1a** but using 2-acetylpyridine *N*-methyl-*N*-phenylhydrazone (2-APyMePH, L^2). Treatment of **1b** with bases or Tl[BF$_4$], using the same conditions as for **1a**, did not lead to the expected complex analogous to **2**. However, as we will see below, an orthopalladated product of L^2-H (complex **5**) can be prepared by following a very different path. Thus, the presence of N—H or N—Me bonds seems to play an important role in the mechanism which is depicted in Scheme 3.

Scheme 3



The first step, deprotonation of the N–H bond, leads to a highly conjugated anion which can adopt the "azobenzene-like" resonance structure that is prone to orthometalation. Likewise, the resonance form with the negative charge in the *ortho* position is favorable to the electrophilic attack to the phenyl ring. Thus, chloride extraction can assist the reaction but the limiting step in our case seems to be the loss of the proton of the N–H bond. The importance of the deprotonation step can be further emphasized by considering the reaction times reported for orthopalladation of substituted arylhydrazones.[9] These reactions are faster when substituents on the phenyl ring have an electron withdrawing effect, which increases the acidic character of the N–H bond. Furthermore, methylphenylhydrazone of pinacolone reacts with Pd(II) in different conditions, always leading to cyclopalladated complexes with Pd–C(aliphatic) bonds, stressing the importance of the N–H bond in the orthometalation reaction of the phenyl ring in phenylhydrazones.[15] In contrast, reactions of osazones of phenylhydrazone with Pd(II) do not afford orthometalated compounds, which, however, can be prepared, not readily, with diacetyl bis(*N*-methyl-*N*-phenyl)osazone.[16]

Preparation of Cationic Complexes. The chloro ligand in complex **2** can be easily removed with different neutral P, N, or S donor ligands, giving cationic complexes which were isolated as [BF$_4$]$^-$ salts according to Scheme 4.

Formation of complexes **3b** and **3c** contrasts with the reaction described for the related complex [Pd(thbpy)-Cl]—where thbpy is the terdentate orthometalated C,N,N′ ligand 6-(2-thienyl)-2,2′-bipyridine—with P(OMe)$_3$, giving an Arbuzov-type of reaction leading to [Pd(thbpy)-

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[9] Granell, J.; Moragas, R.; Sales, J.; Font-Bardía, M.; Solans, X. *J. Chem. Soc., Dalton Trans.* **1993**, 1237.

[10] Constable, E. C.; Henney, R. P. G.; Leese, T. A.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1990**, 443.

[11] Constable, E. C.; Henney, R. P. G.; Raithby, P. R.; Sousa, L. R. *J. Chem. Soc., Dalton Trans.* **1992**, 2251.

[12] Constable, E. C.; Henney, R. P. G.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1992**, 2467.

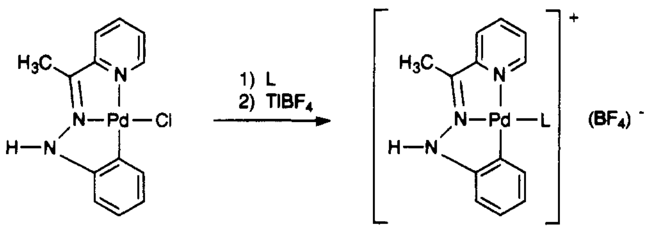
[13] Avshu, A.; O'Sullivan, R. D.; Parkins, A. W.; Alcock, N. W.; Countryman, R. M. *J. Chem. Soc., Dalton Trans.* **1983**, 1619.

[14] Ryabov, A. D. *Chem. Rev.* **1990**, 403.

[15] Galli, B.; Gasparini, F.; Maresca, L.; Natile, G.; Palmieri, G. *J. Chem. Soc., Dalton Trans.* **1983**, 1483.

[16] (a) Caglioti, L.; Cattalini, L.; Ghedini, M.; Gasparrini, F.; Vigato, P. A. *J. Chem. Soc., Dalton Trans.* **1972**, 514. (b) Bombieri, G.; Caglioti, L.; Cattalini, L.; Forsellini, E.; Gasparini, F.; Graziani, R.; Vigato, P. A. *J. Chem. Soc., Chem. Commun.* **1971**, 1415.

Scheme 4



2

3a L= PPh3
3b L= P(OMe)3
3c L= P(OPh)3
3d L= 4-methylpyridine
3e L= THT(tetrahydrothiophene)

{P(O)(OMe)$_2$}].[11] When L is the bidentate ligand dppm (bis(diphenylphosphino)methane), a stable binuclear dicationic complex **4** can be prepared, where dppm acts as a bridging ligand leading to a *face to face* structure (see Figure 1 and discussion below). This can be considered as a model for the recently described binuclear adenine bridged cyclopalladated nucleases used in DNA nicking.[17]

Crystal Structure of {[Pd(L^1-H)]$_2$(μ-dppm)}[BF$_4$]$_2$ (4). The molecular structure of **4** was determined by a single-crystal X-ray diffraction study. Structural and refinement details are given in Table 2, fractional atomic coordinates are in Table 3, and selected bond distances and angles are in Table 4. A perspective view with the atomic numbering scheme of the molecular structure is presented in Figure 1. The structure consists of two tetracoordinated Pd atoms in a square-planar configuration placed face to face with a Pd–Pd distance of 3.114(1) Å, which is outside the range (2.546–2.848 Å) found for dipalladium complexes having strong Pd–Pd bonding interactions.[18] The square-planar configuration around each Pd atom involves not only those atoms directly bonded to Pd but also the remaining atoms of the C,N,N′ ligand. Thus, from the best least-squares plane calculated through Pd(1), P(1), and the sixteen non-H atoms of the C,N,N′ ligand, the maximum deviation is 0.321(5) Å, affecting atom C(10). From the corresponding plane around Pd(2) the maximum deviation affects C(29), which lies 0.132(5) Å out of the plane. The two coordination planes are nearly parallel [angle between planes 6.57(3)°]. This should allow favorable intermolecular stacking interactions which, however, have not been found in the lattice. Most probably, the steric requirements of the dppm phenyl rings avoid the approximation of the molecules, thus precluding the formation of a stacked array.[17] The C,N,N′ ligands are in a head to tail arrangement that is not completely eclipsed, as shown by the values of the torsion angle P(1)–Pd(1)–Pd(2)–P(2) of 9.16(7)°. The geometries of the amine nitrogen atoms N(13) and N(23) are both distorted from pyramidal (sp^3) to planar (sp^2) with nearly planar five-membered metallacycles. This suggests a high degree of conjugation and accounts for the observed acidity of the N–H bond, which will be discussed below. Other palladium–ligand and intraligand distances and angles are similar to those reported for related complexes.[9,16,19]

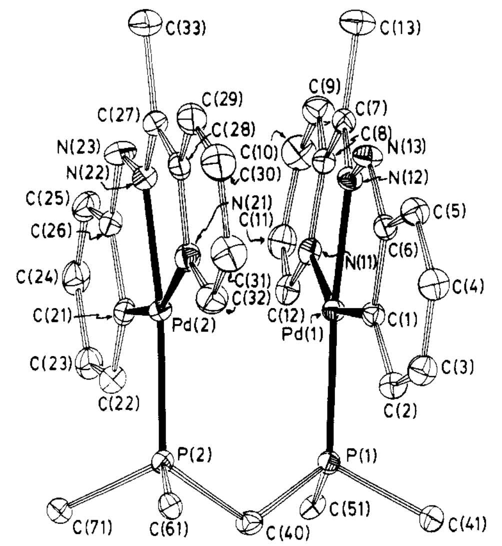


Figure 1. Perspective view of the cation in {[Pd(C$_6$H$_4$N(H)N=C(CH$_3$)C$_5$H$_4$N)]$_2$(μ-dppm)}[BF$_4$]$_2$·OEt$_2$·NCMe (**4**), showing the numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. All hydrogen atoms, and the C2–C6 atoms of the phenyl rings of the dppm ligand have been omitted for clarity.

Table 2. Crystal and Intensity Data for [{Pd(C$_6$H$_4$NHN=C(CH$_3$)C$_5$H$_4$N)}$_2$(μ-dppm)][BF$_4$]$_2$·OEt$_2$·NCMe (4)

empirical formula	$C_{57}H_{59}B_2F_8N_7O_1P_2Pd_2$
M	1306.49
cryst syst, space group	monoclinic, $P2_1/n$
a/Å	15.911(4)
b/Å	18.902(6)
c/Å	18.563(4)
β/deg	95.34(2)
V/Å^3	1588(1)
Z	4
T, K	293
D_c/g cm^{-3}	1.56
F(000)	2648
λ(Mo Kα)/Å	0.710 73
μ/cm^{-1}	7.67
cryst size/mm; color	0.23 × 0.23 × 0.20; red
method of collcn	$\omega/2\theta$ scan
scan range/deg	$1 \le \theta \le 25$
collcn limits	$0 \le h \le 18, 0 \le k \le 22, -22 \le l \le 21$
no. of reflns collcd	9754
no. of reflns obsd	7038 [$I \ge 3\sigma(I)$]
no. of params	721
data of param ratio	9.76
weighting scheme	$w = [\sigma^2(F) + 0.0001F^2]^{-1}$
final residuals: R, R_w	0.032, 0.034

Acidic Character of Complexes 2–4. Treatment of complexes **2**, **3**, or **4** with NaOMe in MeOH showed dramatic changes from orange to dark blue colors, and bluish-black solids were isolated. However we were unable to get satisfactory elemental analysis and ^{1}H NMR spectra for these products. In spite of that, the reactivity pattern displayed by complex **2** strongly suggests that blue colors are due to the deprotonated N–H bond. Thus, reaction of complex **2** in dimethyl sulfoxide solution with a stoichiometric amount of NaOMe in MeOH afforded a dark blue solution which, after stirring 2 h at room temperature, was treated with an equimolar amount of aqueous HCl, yielding unaltered complex **2** quantiatively. This behavior is consistent with a classic description for a protic acid, as depicted in Scheme 5.

When L is a neutral ligand, the blue species can be regarded as zwitterions with a dipolar distribution of charge (negative on the deprotonated nitrogen and positive on

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(17) Suggs, J. W.; Dube, M. J.; Nichols, M. *J. Chem. Soc., Chem. Commun.* **1993**, 307.

(18) (a) Yap, G. P. A.; Jensen, C. M. *Inorg. Chem.* **1992**, *31*, 4823 and references therein. (b) Cotton, F. A.; Matusz, M.; Poli, R.; Feng, X. *J. Am. Chem. Soc.* **1988**, *110*, 1144.

(19) Bolger, J. A.; Ferguson, G.; James, J. P.; Long, C.; McArdle, P.; Vos, J. G. *J. Chem. Soc., Dalton Trans.* **1993**, 1577.

Table 3. Fractional Coordinates for $[\{Pd(C_6H_4NHN{=}C(CH_3)C_5H_4N)\}_2(\mu\text{-dppm})][BF_4]_2{\cdot}OEt_2{\cdot}NCMe$ (4)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Pd(1)	0.10957(2)	0.21029(2)	0.01518(2)	C(44)	0.3607(3)	–0.0064(3)	–0.0439(3)
Pd(2)	0.11024(2)	0.35691(2)	–0.06124(2)	C(45)	0.3209(3)	0.0211(2)	0.0131(3)
P(1)	0.14641(6)	0.15571(6)	–0.08669(5)	C(46)	0.2578(3)	0.0702(2)	0.0003(2)
P(2)	0.16865(6)	0.30972(6)	–0.15768(5)	C(51)	0.0671(2)	0.0969(2)	–0.1317(2)
N(11)	–0.0208(2)	0.1817(2)	0.0315(2)	C(52)	0.0234(3)	0.1089(2)	–0.1993(2)
N(12)	0.0902(2)	0.2560(2)	0.1104(2)	C(53)	–0.0390(3)	0.0627(3)	–0.2260(3)
N(13)	0.1566(2)	0.2946(2)	0.1408(2)	C(54)	–0.0585(3)	0.0038(3)	–0.1879(3)
N(21)	0.2057(2)	0.4217(2)	–0.0033(2)	C(55)	–0.0144(3)	–0.0096(3)	–0.1212(3)
N(22)	0.0470(2)	0.4028(2)	0.0157(2)	C(56)	0.0476(3)	0.0367(2)	–0.0931(3)
N(23)	–0.0362(2)	0.3850(2)	0.0140(2)	C(61)	0.2727(3)	0.3441(2)	–0.1736(2)
C(1)	0.2267(3)	0.2471(2)	0.0419(2)	C(62)	0.3482(3)	0.3089(2)	–0.1542(2)
C(2)	0.3026(3)	0.2395(2)	0.0096(2)	C(63)	0.4247(3)	0.3416(3)	–0.1629(2)
C(3)	0.3776(3)	0.2696(2)	0.0405(2)	C(64)	0.4271(3)	0.4076(3)	–0.1914(3)
C(4)	0.3789(3)	0.3069(3)	0.1047(2)	C(65)	0.3534(3)	0.4430(3)	–0.2104(3)
C(5)	0.3052(3)	0.3158(2)	0.1382(2)	C(66)	0.2758(3)	0.4118(3)	–0.2020(3)
C(6)	0.2305(2)	0.2861(2)	0.1069(2)	C(71)	0.1072(2)	0.3322(2)	–0.2425(2)
C(7)	0.0204(3)	0.2483(2)	0.1404(2)	C(72)	0.0526(3)	0.3890(2)	–0.2437(2)
C(8)	–0.0428(3)	0.2051(2)	0.0977(2)	C(73)	0.0044(3)	0.4091(3)	–0.3067(3)
C(9)	–0.1196(3)	0.1883(3)	0.1221(2)	C(74)	0.0115(3)	0.3709(3)	–0.3689(3)
C(10)	–0.1769(3)	0.1477(3)	0.0792(3)	C(75)	0.0678(3)	0.3149(3)	–0.3691(2)
C(11)	–0.1568(3)	0.1258(3)	0.0123(3)	C(76)	0.1168(3)	0.2959(2)	–0.3065(2)
C(12)	–0.0775(3)	0.1444(2)	–0.0099(2)	B(1)	0.7081(3)	0.0775(3)	0.7979(3)
C(13)	0.0075(3)	0.2806(3)	0.2116(2)	F(11)	0.6958(2)	0.1486(2)	0.7814(2)
C(21)	–0.0042(3)	0.3153(2)	–0.0895(2)	F(12)	0.7522(2)	0.0465(2)	0.7452(2)
C(22)	–0.0350(3)	0.2700(2)	–0.1445(2)	F(13)	0.7537(2)	0.0726(2)	0.8624(2)
C(23)	–0.1179(3)	0.2468(3)	–0.1523(2)	F(14)	0.6332(2)	0.0441(2)	0.8008(2)
C(24)	–0.1740(3)	0.2697(3)	–0.1043(3)	B(2)	0.3054(5)	0.1126(5)	0.6710(5)
C(25)	–0.1470(3)	0.3158(3)	–0.0492(3)	F(21)	0.3530(3)	0.0631(3)	0.7129(3)
C(26)	–0.0635(3)	0.3379(2)	–0.0416(2)	F(22)	0.3463(3)	0.1274(3)	0.6177(2)
C(27)	0.0843(3)	0.4460(2)	0.0620(2)	F(23)	0.3062(4)	0.1720(3)	0.7173(3)
C(28)	0.1739(3)	0.4584(2)	0.0520(2)	F(24)	0.2292(4)	0.0896(4)	0.6693(4)
C(29)	0.2244(3)	0.5042(3)	0.0953(2)	N(80)	0.1531(4)	0.1511(3)	0.2756(3)
C(30)	0.3090(4)	0.5112(3)	0.0853(3)	C(81)	0.2135(4)	0.1425(3)	0.2492(3)
C(31)	0.3414(3)	0.4732(3)	0.0308(3)	C(82)	0.2907(4)	0.1296(3)	0.2146(3)
C(32)	0.2873(3)	0.4295(3)	–0.0125(2)	O(90)	0.0585(2)	0.2492(2)	0.4612(2)
C(33)	0.0416(3)	0.4809(3)	0.1211(3)	C(91)	0.1245(3)	0.1994(3)	0.4808(3)
C(40)	0.1819(3)	0.2126(2)	–0.1592(2)	C(92)	0.0892(4)	0.1417(3)	0.5253(4)
C(41)	0.2330(3)	0.0930(2)	–0.0699(2)	C(93)	0.0862(4)	0.3079(3)	0.4228(3)
C(42)	0.2719(3)	0.0646(2)	–0.1268(2)	C(94)	0.0122(4)	0.3554(3)	0.4047(3)
C(43)	0.3366(3)	0.0154(3)	–0.1144(3)				

palladium). Likely, deprotonation induces high conjugation, making possible resonance structures containing the azo group, the base of many industrial dyes. Acid–base pH dependent equilibria of these complexes are readily followed by UV/vis spectrophotometry. For instance, complex **3c** showed a pK_a value of 7.19 in dimethyl sulfoxide (10%)/water (90%) solutions. This value corresponds to a weak acid and can be compared with the first dissociation constants of hydrogen sulfide (pK_{a1} = 7.04) or boric acid (pK_{a1} = 9.14). Complete thermodynamic data for these "protic organometallic acids" will be published elsewhere. Further support of the proposed formula for the blue species comes from the reaction of deprotonated **3a** with the electrophile CH_3I to give complex **5** (see Scheme 6).

In spite of the high conjugation expected for deprotonated **3a**, electrophilic addition occurs only at the amido nitrogen, and PPh_3 is substituted by iodide. Methyl addition to the iminic carbon would avoid conjugation through the N,N′ chelate moiety. On the other hand, addition to carbon atoms at the pyridine or phenyl rings is unfavorable, as it would involve loss of aromatic character.

Experimental Section

Instrumentation. The ^1H NMR spectra were obtained on a Bruker AF80 Fourier-transform spectrometer and are referenced to internal $SiMe_4$. Infrared spectra were recorded as KBr disks on a Perkin-Elmer 843 machine. Elemental analyses were made on a Perkin-Elmer 240B instrument. Acid–base pH dependent equilibria were recorded on a UV/vis spectrophotometer Milton Roy Spectronic 3000 Array using dimethyl sulfoxide (10%)/water (90%) solutions. Different values of pH were adjusted with NaOH aqueous solution.

Reagents and Materials. $PdCl_2$, acetylpyridine, phenylhydrazone, and methylphenylhydrazone were obtained from Aldrich Químíca SA. Hydrazones L^1 and L^2 were prepared by simple condensation of 2-acetylpyridine with phenylhydrazine or *N*-methyl-*N*-phenylhydrazine.[20]

$PdCl_2(L^1)$ (1a). $PdCl_2$ (0.82 g, 4.62 mmol) was suspended in methanol (100 mL), and LiCl (0.39 g, 9.24 mmol) was added. After stirring for 0.5 h at 60 °C, the solution was filtered. Addition of 2-APyPH (0.975 g, 4.62 mmol), dissolved in MeOH (15 mL) and 35% HCl (1 mL), afforded a bright yellow precipitate. The mixture was stirred for 24 h and the solid collected by filtration, washed with methanol (2 × 10 mL) and diethyl ether (1 × 10 mL), and dried *in vacuo*. Yield: 1.56 g (86%). Anal. Calcd for $C_{13}H_{13}Cl_2N_3Pd$: C, 40.18; H, 3.37; N, 10.81. Found: C, 40.30; H, 3.20; N, 10.76.

$PdCl_2(L^2)$ (1b). Experimental conditions were carried out as for **1a** but using 2-APyMePH (1.045 g, 4.62 mmol). Yield: 1.118 g (60%). Anal. Calcd for $C_{14}H_{16}Cl_2N_3Pd$: C, 41.66; H, 3.99; N, 10.41. Found: C, 41.84; H, 3.65; N, 10.44.

$Pd(L^1\text{-}H)Cl$ (2). Method 1. To a suspension of **1a** (1 g, 2.57 mmol) in CH_2Cl_2 (100 mL) was added NEt_3 (0.35 mL, 2.57 mmol). After stirring for 24 h the solid was collected by filtration. Recrystallization from dimethyl sulfoxide/ethanol afforded an orange crystalline solid. Yield: 0.75 g (83%).

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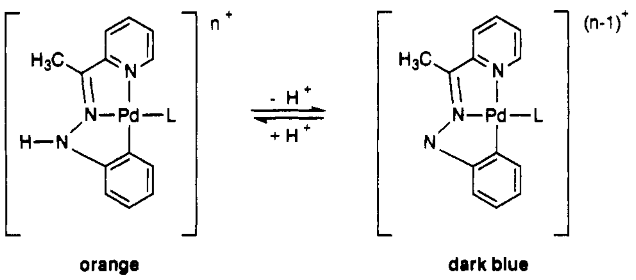
[20] Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*; Longman Scientific & Technical: Essex, U.K., 1989.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $[\{Pd(C_6H_4NHN{=}C(CH_3)C_5H_4N)\}_2(\mu\text{-dppm})][BF_4]_2{\cdot}OEt_2{\cdot}NCMe$ (4)

Pd(1)–Pd(2)	3.114(1)	Pd(1)–P(1)	2.278(1)
Pd(1)–N(11)	2.192(3)	Pd(1)–N(12)	2.017(3)
Pd(1)–C(1)	2.008(4)	Pd(2)–P(2)	2.275(1)
Pd(2)–N(21)	2.159(4)	Pd(2)–N(22)	2.018(3)
Pd(2)–C(21)	2.007(4)	P(1)–C(40)	1.850(4)
P(1)–C(41)	1.822(4)	P(1)–C(51)	1.825(4)
P(2)–C(40)	1.849(4)	P(2)–C(61)	1.829(4)
P(2)–C(71)	1.824(4)	N(11)–C(8)	1.381(5)
N(11)–C(12)	1.332(5)	N(12)–N(13)	1.363(5)
N(12)–C(7)	1.296(5)	N(13)–C(6)	1.394(5)
N(21)–C(28)	1.373(5)	N(21)–C(32)	1.334(6)
N(22)–N(23)	1.363(5)	N(22)–C(27)	1.290(5)
N(23)–C(26)	1.401(6)	C(1)–C(2)	1.405(6)
C(1)–C(6)	1.411(5)	C(2)–C(3)	1.395(6)
C(3)–C(4)	1.383(6)	C(4)–C(5)	1.386(6)
C(5)–C(6)	1.392(6)	C(7)–C(8)	1.469(6)
C(7)–C(13)	1.487(6)	C(8)–C(9)	1.379(6)
C(9)–C(10)	1.386(7)	C(10)–C(11)	1.375(6)
C(11)–C(12)	1.407(6)	C(21)–C(22)	1.387(6)
C(21)–C(26)	1.421(6)	C(22)–C(23)	1.385(6)
C(23)–C(24)	1.387(6)	C(24)–C(25)	1.382(7)
C(25)–C(26)	1.388(6)	C(27)–C(28)	1.473(6)
C(27)–C(33)	1.496(6)	C(28)–C(29)	1.387(6)
C(29)–C(30)	1.382(7)	C(30)–C(31)	1.379(7)
C(31)–C(32)	1.392(6)		

P(1)–Pd(1)–Pd(2)	90.70(1)	N(11)–Pd(1)–Pd(2)	109.0(1)
N(11)–Pd(1)–P(1)	108.9(1)	N(12)–Pd(1)–Pd(2)	91.4(1)
N(12)–Pd(1)–P(1)	173.5(1)	N(12)–Pd(1)–N(11)	76.1(1)
C(1)–Pd(1)–Pd(2)	76.2(1)	C(1)–Pd(1)–P(1)	93.3(1)
C(1)–Pd(1)–N(11)	156.9(1)	C(1)–Pd(1)–N(12)	81.3(1)
P(2)–Pd(2)–Pd(1)	91.60(1)	N(21)–Pd(2)–Pd(1)	108.1(1)
N(21)–Pd(2)–P(2)	107.2(1)	N(22)–Pd(2)–Pd(1)	92.1(1)
N(22)–Pd(2)–P(2)	173.1(1)	N(22)–Pd(2)–N(21)	77.1(1)
C(21)–Pd(2)–Pd(1)	74.3(1)	C(21)–Pd(2)–P(2)	93.9(1)
C(21)–Pd(2)–N(21)	158.6(2)	C(21)–Pd(2)–N(22)	81.6(2)
C(40)–P(1)–Pd(1)	117.4(1)	C(41)–P(1)–Pd(1)	113.6(1)
C(41)–P(1)–C(40)	103.0(2)	C(51)–P(1)–Pd(1)	115.8(1)
C(51)–P(1)–C(40)	105.4(2)	C(51)–P(1)–C(41)	99.3(2)
C(40)–P(2)–Pd(2)	117.2(1)	C(61)–P(2)–Pd(2)	115.5(1)
C(61)–P(2)–C(40)	104.2(1)	C(71)–P(2)–Pd(2)	111.2(1)
C(71)–P(2)–C(40)	105.8(2)	C(71)–P(2)–C(61)	101.4(2)
C(8)–N(11)–Pd(1)	111.4(3)	C(12)–N(11)–Pd(1)	130.5(3)
C(12)–N(11)–C(8)	118.0(4)	N(13)–N(12)–Pd(1)	114.6(2)
C(7)–N(12)–Pd(1)	122.4(3)	C(7)–N(12)–N(13)	123.0(3)
C(6)–N(13)–N(12)	113.9(3)	C(28)–N(21)–Pd(2)	111.6(3)
C(32)–N(21)–Pd(2)	130.3(3)	C(32)–N(21)–C(28)	118.1(4)
N(23)–N(22)–Pd(2)	115.2(3)	C(27)–N(22)–Pd(2)	121.0(3)
C(27)–N(22)–N(23)	123.9(4)	C(26)–N(23)–N(22)	114.0(3)
C(2)–C(1)–Pd(1)	132.4(3)	C(6)–C(1)–Pd(1)	111.0(3)
C(6)–C(1)–C(2)	116.6(4)	C(3)–C(2)–C(1)	121.3(4)
C(4)–C(3)–C(2)	120.4(4)	C(5)–C(4)–C(3)	120.2(4)
C(6)–C(5)–C(4)	119.2(4)	C(1)–C(6)–N(13)	118.4(4)
C(5)–C(6)–N(13)	119.3(4)	C(5)–C(6)–C(1)	122.3(4)
C(8)–C(7)–N(12)	113.7(4)	C(13)–C(7)–N(12)	122.0(4)
C(13)–C(7)–C(8)	124.3(4)	C(7)–C(8)–N(11)	116.2(3)
C(9)–C(8)–N(11)	121.6(4)	C(9)–C(8)–C(7)	122.2(4)
C(10)–C(9)–C(8)	119.7(4)	C(11)–C(10)–C(9)	119.3(4)
C(12)–C(11)–C(10)	118.7(4)	C(11)–C(12)–N(11)	122.7(4)
C(22)–C(21)–Pd(2)	133.2(3)	C(26)–C(21)–Pd(2)	110.9(3)
C(26)–C(21)–C(22)	115.9(4)	C(23)–C(22)–C(21)	122.7(4)
C(24)–C(23)–C(22)	119.9(4)	C(25)–C(24)–C(23)	119.8(4)
C(26)–C(25)–C(24)	119.7(4)	C(21)–C(26)–N(23)	118.3(4)
C(25)–C(26)–N(23)	119.6(4)	C(25)–C(26)–C(21)	122.1(4)
C(28)–C(27)–N(22)	114.1(4)	C(33)–C(27)–N(22)	123.8(4)
C(33)–C(27)–C(28)	122.2(4)	C(27)–C(28)–N(21)	116.2(4)
C(29)–C(28)–N(21)	121.0(4)	C(29)–C(28)–C(27)	122.8(4)
C(30)–C(29)–C(28)	120.0(5)	C(31)–C(30)–C(29)	119.0(5)
C(32)–C(31)–C(30)	118.6(5)	C(31)–C(32)–N(21)	123.3(4)
P(2)–C(40)–P(1)	121.6(2)		

Scheme 5



Method 2. To a suspension of **1a** (200 mg, 0.51 mmol) in acetone (20 mL) was added $TlBF_4$ (148 mg, 0.51 mmol). After stirring for 4 h at room temperature, the solid was collected by filtration, dried under a vacuum, and treated with hot dimethyl sulfoxide (5 mL). Filtration and addition of ethanol (20 mL) afforded the complex. Yield: 137 mg (78%). Anal. Calcd for $C_{13}H_{12}ClN_3Pd$: C, 44.34; H, 3.43; N, 11.93. Found: C, 44.47; H, 3.19; N, 11.98. Visible spectra for the blue conjugated base of **2**: λ_{max} = 571 nm.

$[Pd(L^1\text{-}H)L]BF_4$ (L = PPh_3 (3a), $P(OMe)_3$ (3b), $P(OPh)_3$ (3c), MePy (3d), THT (3e)). All these complexes were prepared in the same way. The procedure for **3a** (L = PPh_3) is described below.

To a suspension of **2** (100 mg, 0.28 mmol) in acetone (25 mL) was added PPh_3 (73 mg, 0.28 mmol). After stirring for 5 min at room temperature, $TlBF_4$ (81 mg, 0.28 mmol) was added. The mixture was kept under stirring for 1 h and then filtered and the solvent removed under vacuum. The residue was treated with CH_2Cl_2 (20 mL) and filtered again. Addition of hexane and concentration to induce precipitation afforded the complex which was washed with hexane (2 × 10 mL) and dried *in vacuo*. Yield of **3a**: 174 mg (92%). Anal. Calcd for $C_{31}H_{27}BF_4N_3PPd$: C, 55.92; H, 4.08; N, 6.31. Found: C, 55.71; H, 3.83; N, 6.53. Visible spectra for the blue conjugated base of **3a**: λ_{max} = 641 nm. Yield of **3b**: 124 mg (84%). Anal. Calcd for $C_{16}H_{21}BF_4N_3PPdO_3$: C, 36.42; H, 4.01; N, 7.96. Found: C, 36.64; H, 3.84; N, 8.30. Visible spectra for the blue conjugated base of **3b**: λ_{max} = 635 nm. Yield of **3c**: 157 mg (78%). Anal. Calcd for $C_{31}H_{27}BF_4N_3PPdO_3$: C, 52.16; H, 3.18; N, 5.88. Found: C, 51.85; H, 3.33; N, 5.99. Visible spectra for the blue conjugated base of **3c**: λ_{max} = 631 nm. Yield of **3d**: 90 mg (60%). Anal. Calcd for $C_{19}H_{27}BF_4N_4Pd$: C, 45.95; H, 3.85; N, 11.28. Found: C, 45.67; H, 3.54; N, 11.24. Yield of **3e**: 92 mg (67%). Anal. Calcd for $C_{17}H_{20}BF_4N_3PdS$: C, 41.53; H, 4.10; N, 8.55. Found: C, 41.25; H, 4.03; N, 8.47.

$\{[Pd(L^1\text{-}H)]_2(\mu\text{-dppm})\}[BF_4]_2$ (4). To a suspension of **2** (200 mg, 0.57 mmol) in acetone (25 mL) was added dppm (109 mg, 0.28 mmol). After stirring for 5 min at room temperature, $TlBF_4$ (164 mg, 0.57 mmol) was added. The mixture was kept under stirring for 1 h and then filtered and the solvent removed under vacuum. The residue was treated with CH_2Cl_2 (30 mL) and filtered again. Addition of hexane and concentration to induce precipitation afforded the complex which was washed with hexane (2 × 10 mL) and dried under vacuum. Yield: 316 mg (95%). Anal. Calcd for $C_{51}H_{46}B_2F_8N_6P_2Pd_2{\cdot}CH_2Cl_2$: C, 48.93; H, 3.79; N, 6.58. Found: C, 48.92; H, 3.86; N, 6.40. Visible spectra for the blue conjugated base of **4**: λ_{max} = 638 nm.

X-ray Crystal Structure Determination of 4. Crystals suitable for an X-ray analysis were grown by slow diffusion of diethyl ether into a concentrated solution of the complex in acetonitrile. Crystal and refinement data are collected in Table 2. Unit cell parameters were determined from the least-squares refinement of a set of 25 centered reflections. Three reflections were measured every 1 h as orientation and intensity controls. Significant decay was not observed. Heavy atoms were located from a Patterson synthesis, and the remaining non-hydrogen atoms by DIRDIF.[21] Full-matrix least-squares refinements were made with a local version of SHELX76.[22] After isotropic refinement, an empirical absorption correction was made with

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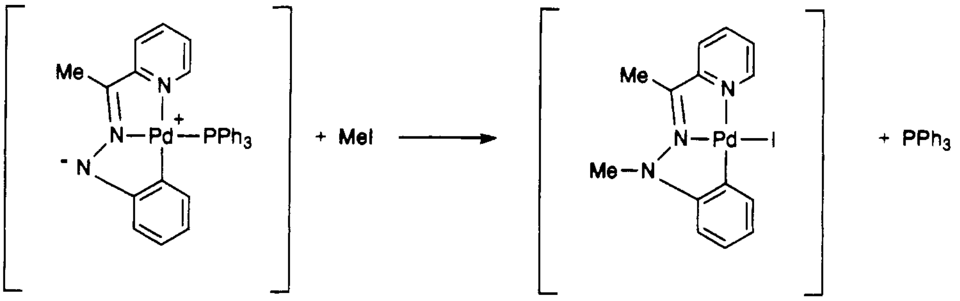
[21] Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; García-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *The DIRDIF Program System, Technical Report of the Crystallography Laboratory*; University of Nijmegen: The Netherlands, 1992.

[22] Sheldrick, G. M. *SHELX76, Program for Crystal Structure Determinations*; University of Cambridge: Cambridge, U.K., 1976. Local version: van der Maelen, F. J. Ph.D. Thesis, University of Oviedo, Oviedo, Spain, 1991.

Scheme 6



3a deprotonated

5

DIFABS.[23] All non-H atoms were refined anisotropically. H atoms of the amine nitrogens, H(130) and H(230) were found on a difference map, and their parameters (x, y, z, U_{iso}) were included in the refinements. The remaining hydrogen atoms were placed on calculated positions, and were given a common isotropic temperature factor which was refined. Torsion angles and least-squares planes were calculated with PARST.[24] The drawing of Figure 1 was made with EUCLID.[25]

Pd(L^2-H)I (5). To a mixture of **2** (100 mg, 0.28 mmol) and PPh$_3$ (73 mg, 0.28 mmol) in acetone (30 mL) was added a solution (0.27 M) of sodium methoxide (1.04 mL, 0.28 mmol) in MeOH. The mixture immediately turned dark blue. Addition of MeI and stirring for 1 h at room temperature led to a red precipitate. The solvent was removed by filtration, and the residue was washed with water (2 × 5 mL), ethanol (2 × 5 mL), and diethyl ether (5 mL) and dried under vacuum. Treatment of the solid with dimethyl sulfoxide (5 mL) and addition of ethanol (10 mL) to the solution afforded the complex as red crystals. Yield: 102 mg (80%). Anal. Calcd for $C_{14}H_{15}IN_3Pd$: C, 36.67; H, 3.29; N, 9.16. Found: C, 36.56; H, 2.96; N, 8.97.

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Supplementary Material Available: Complete tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, torsion angles, and least-squares planes for the structure of **4** (13 pages). Ordering information is given on any current masthead page. A list of structure factor amplitudes is available from the authors.

OM930788C

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[23] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.

[24] Nardelli, M. *Comput. Chem.* **1983**, *7*, 95.

[25] Spek, A. L. The EUCLID Package. In *Computational Crystallography*; Sayre, E., Ed.; Clarendon Press: Oxford, U.K., 1982; p 528.