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A Bis(azo−imine)palladium(II) System with 10 Ligand π Electrons. Synthesis, Structure, Serial Redox, and Relationship to Bis(azooximates) and Other Species

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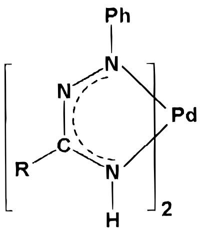
The first azo−imine chelate system, $Pd(N(H)C(R)NNPh)_2$ ($Pd(RA)_2$), has been isolated in the form of diamagnetic solids by the $6e^-−6H^+$ reduction of bis(phenylazooximato)palladium(II), $Pd(N(O)C(R)NNPh)_2$ (abbreviated $Pd(RB)_2$), with ascorbic acid in a mixed solvent (R = Ph, α-naphthyl). Selected spectral features are described. The X-ray structures of $Pd(PhA)_2$ and $Pd(PhB)_2$ have revealed trans-planar geometry consistent with metal oxidation state of +2. Bond length trends within the chelate rings are rationalized in terms of steric and electronic factors. In $Pd(PhA)_2$ a total of 10 ligand π electrons are present, each formally monoanionic ligand contributing five. Model EHMO studies have revealed that the filled HOMO (a_u) in $Pd(RA)_2$ is a bonding combination of two ligand π^* orbitals with large azo contributions. The LUMO (b_g) is roughly the corresponding antibonding combination. The outer π-electron configuration of $Pd(RA)_2$ is $(a_u)^2(b_g)^0$. Four successive voltammetric responses, two oxidative and two reductive, are observed. The $E_{1/2}$ range is −1.3 to +0.8 V vs SCE for $Pd(PhA)_2$ in a 1:9 $MeCN−CH_2Cl_2$ mixture (Pt electrode). EPR and electronic spectra of the electrogenerated one-electron-oxidized complex $Pd(PhA)_2^+$ are described. The azo−imine system is compared with imine−imine and azo−azo systems. Crystal data for the complexes are as follows. $Pd(PhA)_2$: crystal system monoclinic; space group $C2/c$; a = 18.167(5) Å, b = 7.420(3) Å, c = 16.527(6) Å; β = 92.70(3)°; V = 2225(1) Å^3; Z = 4; R = 2.61%, R_w = 3.58%. $Pd(PhB)_2$: crystal system monoclinic; space group $P2_1/n$; a = 5.735(5) Å, b = 10.797(6) Å, c = 18.022(11) Å; β = 97.73(6) Å; V = 1105(1) Å^3; Z = 2; R = 3.37%; R_w = 3.40%.

Introduction

Metal chelates of conjugated ligands are of abiding interest in inorganic research, especially those bearing one or more π^* orbitals lying low enough to promote properties like successive electron transfer, intense color, and oxidation state ambivalence. The dithiolenes,[1] dioxolenes,[2] diimines,[3−8] and tetraazenides[9] constitute good examples.[10] In the present work, we introduce the azo−imine system in the form of electroneutral diamagnetic bis chelates of palladium. The synthetic method is described along with X-ray structures of one complex and its azooxime precursor. The electronic structure, spectra, and electroactivity of the species are scrutinized.

Results and Discussion

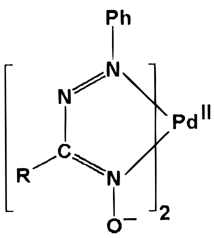
A. Synthesis and Spectral Characterization. The two azo−imine complexes reported here belong to the type **1** structure and are generally abbreviated as $Pd(RA)_2$, the R substituent being Ph or α-naphthyl (Np). In **1**, the dotted semicircle represents π electrons in the NNCN frame. The synthetic precursor to **1** is the bis(arylazooximate) $Pd(RB)_2$, **2**.[11,12] Attempted isolation of $1e^-−1H^+$ reduction products of $Pd(RB)_2$ in a manner similar to that recently described[13] for $Pt(RB)_2$ did not succeed, but the search led us to $Pd(RA)_2$.



Pd(RA)$_2$

R = Ph , Np

1



Pd(RB)$_2$

R = Ph , Np

2

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(1) (a) Burns, R. P.; McAuliffe, C. A. *Adv. Inorg. Chem. Radiochem.* **1979**, *22*, 303. (b) McCleverty, J. A. *Prog. Inorg. Chem.* **1968**, *10*, 49.

(2) (a) Lange, C. W.; Conklin, B. J.; Pierpont, C. G. *Inorg. Chem.* **1994**, *33*, 1276. (b) Bhattacharya, S.; Pierpont, C. G. *Inorg. Chem.* **1992**, *31*, 35 and references therein. (c) Masui, H.; Lever, A. B. P.; Auburn, P. R. *Inorg. Chem.* **1991**, *30*, 2402. (d) Bag, N.; Pramanik, A.; Lahiri, G. K.; Chakravorty, A. *Inorg. Chem.* **1992**, *31*, 40.

(3) Stufkens, D. J. *Coord. Chem. Rev.* **1990**, *104*, 39.

(4) van Koten, G.; Vrieze, K. *Adv. Organomet. Chem.* **1982**, *21*, 151.

(5) (a) DeArmond, M. K.; Hanck, K. W.; Wertz, D. W. *Coord. Chem. Rev.* **1985**, *64*, 65. (b) Vlcek, A. A. *Coord. Chem. Rev.* **1982**, *43*, 39.

(6) (a) Ghosh, P.; Chakravorty, A. *Inorg. Chem.* **1984**, *23*, 2242. (b) Dodsworth, E. S.; Lever, A. B. P. *Chem. Phys. Lett.* **1986**, *124*, 152.

(7) (a) Hitoshi, M.; Lever, A. B. P.; Dodsworth, E. S. *Inorg. Chem.* **1993**, *32*, 258 and references therein. (b) Braterman, P. S.; Song, J.-I.; Wimmer, F. M.; Wimmer, S.; Kaim, W.; Klein, A.; Peacock, R. D. *Inorg. Chem.* **1992**, *31*, 5084.

(8) (a) Cloke, F. G. N.; Dalby, C. I.; Daff, P. J.; Green, J. C. *J. Chem. Soc., Dalton Trans.* **1991**, 181. (b) Gardiner, M. G.; Hanson, G. R.; Henderson, M. J.; Lee, F. C.; Raston, C. L. *Inorg. Chem.* **1994**, *33*, 2456.

(9) (a) Trogler, W. C. *Acc. Chem. Res.* **1990**, *23*, 426. (b) Lee, S. W.; Miller, G. A.; Campana, C. F.; Trogler, W. C. *Inorg. Chem.* **1988**, *27*, 1215.

(10) Ghosh, B. K.; Chakravorty, A. *Coord. Chem. Rev.* **1989**, *95*, 129.

(11) Bandyopadhyay, P.; Mascharak, P. K.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1981**, 623.

(12) Bandyopadhyay, D.; Bandyopadhyay, P.; Chakravorty, A.; Cotton, F. A.; Falvello, L. R. *Inorg. Chem.* **1984**, *23*, 1785.

(13) Pal, C. K.; Chattopadhyay, S.; Sinha, C.; Chakravorty, A. *Inorg. Chem.* **1994**, *33*, 6140.

0020-1669/96/1335-2442$12.00/0

Table 1. Spectral Data

complex	UV−vis:[a] λ_{max}, nm (ϵ, M^{-1} cm^{-1})	IR ν_{N-H}, cm^{-1}	^1H NMR[b] δ(N−H), ppm
$Pd(PhA)_2$	740 (17 900), 465^{sh} (3200), 350 (16 400)	3370^c 3365^d	6.766
$Pd(NpA)_2$	730 (16 500), 465^{sh} (4000), 380 (10 400)	3340^c 3347^d	6.822

[a] In dichloromethane. Superscript sh = shoulder. [b] In $CDCl_3$; multiplets in the region δ 7.2−8.6, aromatic protons. [c] In KBr disk. [d] In CCl_4 solution.

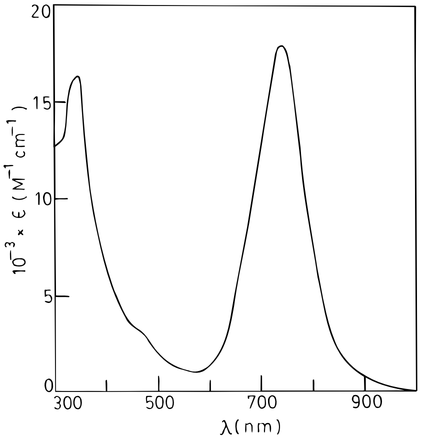


Figure 1. Electronic spectrum of $Pd(PhA)_2$ in dichloromethane solution.

The synthetic procedure consists of heating $Pd(RB)_2$ with excess ascorbic acid in a mixed-solvent medium. Chromatographic workup of the reaction mixture afforded $Pd(RA)_2$ as a dark solid in good yield. The synthetic reaction, eq 1, consumes

$$Pd(RB)_2 + 6e^- + 6H^+ \rightarrow Pd(RA)_2 + 2H_2O \qquad (1)$$

$$2(=N-O^-) + 4e^- + 6H^+ \rightarrow 2(=NH) + 2H_2O \qquad (2)$$

$6e^-$ and $6H^+$, of which $4e^-$ and $6H^+$ are used in the oximato → imine conversion, eq 2. The remaining $2e^-$ go to the azo−imine frame in $Pd(RA)_2$; *vide infra*. The free azo−imine ligand PhN=NC(R)=NH is not known, and we have not succeeded in isolating it either by demetalation of $Pd(RA)_2$ or by reduction of free arylazooximes, PhN=NC(R)=NOH. The azo−imine system reported here is apparently formed and stabilized only in the chelated state.

We have tried to synthesize R = alkyl species. Upon ascorbic acid reduction of $Pd(MeB)_2$, a violet solution was obtained, displaying electronic spectra very similar to that of $Pd(PhA)_2$. The complex however decomposes progressively in solution, and we have not succeeded in isolating it.

The $Pd(RA)_2$ complexes are diamagnetic both in the solid state and in solution. Selected spectral data are given in Table 1. The yellow-green solutions of $Pd(RA)_2$ in dichloromethane absorb strongly in the visible region (Figure 1). The N−H stretch occurs as a sharp feature of moderate intensity in the range 3340−3370 cm^{-1} in both the solid and solution phases. The strong N−O stretch near 1240 cm^{-1} characteristic of $Pd(RB)_2$[11] (no ν_{N-H}) is absent for $Pd(RA)_2$. In ^1H NMR ($CDCl_3$) the aromatic protons of $Pd(RA)_2$ afford sharp multiplets. The N−H signal is observed as a relatively broad (^{14}N quadrupole moment) singlet near δ 6.8 (width at half-height 0.06 ppm).

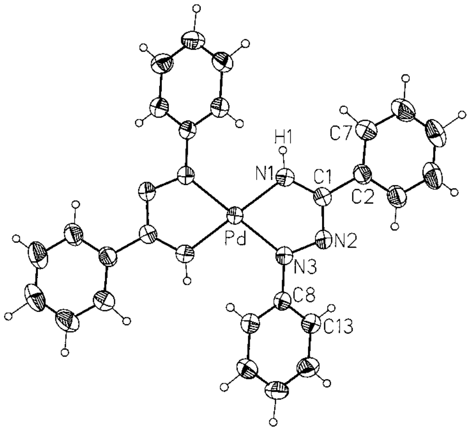


Figure 2. ORTEP plot and atom-labeling scheme for $Pd(PhA)_2$. All non-hydrogen atoms are represented by their 50% probability ellipsoids.

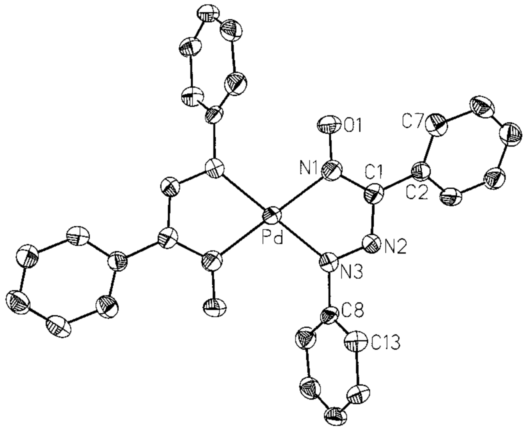


Figure 3. ORTEP plot and atom-labeling scheme for $Pd(PhB)_2$. All non-hydrogen atoms are represented by their 50% probability ellipsoids.

Table 2. Selected Bond distances (Å) and Angles (deg) and Their Estimated Standard Deviations for $Pd(PhA)_2$ and $Pd(PhB)_2$

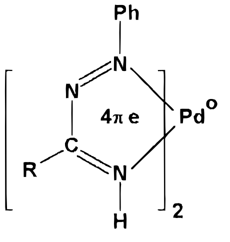
	$Pd(PhA)_2$	$Pd(PhB)_2$
	Distances	
Pd−N(1)	1.967(2)	2.039(4)
Pd−N(3)	1.973(2)	2.018(5)
N(3)−N(2)	1.332(3)	1.276(6)
N(2)−C(1)	1.342(3)	1.375(7)
C(1)−N(1)	1.320(3)	1.329(8)
N(1)−H(1)	0.89(2)	
N(1)−O(1)		1.258(7)
	Angles	
N(3)−Pd−N(1)	77.1(1)	76.6(2)
N(3)−Pd−N(1A)	103.0(1)	103.4(2)
Pd−N(1)−C(1)	114.9(2)	114.3(4)
N(2)−C(1)−N(1)	118.4(2)	115.9(5)
N(3)−N(2)−C(1)	111.3(2)	116.0(4)
Pd−N(3)−N(2)	118.1(1)	117.2(3)
N(1)−Pd−N(1A)	171.2(1)	180.0(1)
N(3)−Pd−N(3A)	179.6(1)	180.0(1)
N(1)−Pd−N(3A)	103.0(1)	103.4(2)
N(3)−Pd−N(1A)	103.0(1)	103.4(2)
Pd−N(1)−H(1)	123.4(8)	
Pd−N(1)−O(1)		124.0(4)

B. Structure. a. Trans-Planar Geometry and Metal Oxidation State. The X-ray structure of $Pd(PhA)_2$ and for comparison that of $Pd(PhB)_2$ have been determined. Molecular views are shown in Figures 2 and 3, and selected bond parameters are listed in Table 2. Both complexes have trans-planar geometry.

In $Pd(RA)_2$ (Figure 2), the metal atom lies on a crystallographic 2-fold axis of symmetry making the halves of the molecule equivalent. The chelate ring is excellently planar (mean deviation 0.02 Å), and the dihedral angle between the two of them is 11.6°. The PdN_4 coordination sphere is approximately planar (mean deviation 0.07 Å), the dihedral angle between the planes of Pd, N(1), N(3) and Pd, N(1A), N(3A) being 9.1°. The phenyl rings attached to C(1) and N(3) are inclined to the plane of the chelate ring by 16.2 and 32.0°, respectively. All hydrogen atoms in the structure including the N−H hydrogen were observed directly in difference Fourier maps.

In $Pd(PhB)_2$, the metal atom lies on a crystallographic center of symmetry making the PdN_4 coordination sphere exactly planar. The chelate ring is an excellent plane (mean deviation 0.01 Å) and the oximato oxygen atom also lies on this plane. The phenyl rings pendent from C(1) and N(3) are inclined to the chelate plane by 28.5 and 66.3°, respectively.

In its electroneutral form, the azo−imine ligand frame N═N−C═N is expected to have four bonding π electrons corresponding to the two double bonds. Structure **3** depicts this case. Since the complex has no net charge, the metal oxidation state in **3** is zero and the total number of azo−imine electrons is 8 (two ligands). Here the coordination geometry would be pseudotetrahedral.



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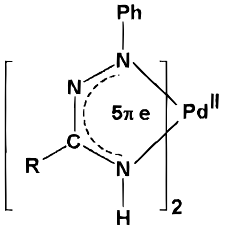


4

In practice however $Pd(PhA)_2$ and by inference $Pd(NpA)_2$ are very nearly planar. This, coupled with the observed diamagnetism, shows that the formal metal oxidation state in $Pd(RA)_2$ is +2. This requires each ligand to be in the formally monoanionic radical form, $RA^{\bullet -}$, corresponding to the population of the lowest azo−imine π^* orbital. This is indicated in structure **4** where the dotted semicircle represents five ligand π electrons. Diamagnetism is the result of trans-metal $\pi^*-\pi^*$ interaction; *vide infra*. In $Pd(RB)_2$, **2**, the ligand is simply the nonradical oximato monoanion $PhN{=}NC(R){=}N{-}O^-$ and the metal is bivalent. There is no question of oxidation state ambiguity here.

b. Bond Length Trends. The average Pd−N length in $Pd(PhA)_2$ is shorter than that in $Pd(PhB)_2$ by 0.06 Å (Table 2). The nonbonded O(1)···C(8A) distance in $Pd(PhB)_2$ is 3.130(8) Å, which equals the sum (3.1 Å) of van der Waals radii of O and C.[14] A closer approach (required for shorter Pd−N bonds) of the two chelate rings in $Pd(PhB)_2$ can occur only at the expense of considerable steric repulsion. In $Pd(PhA)_2$, however, the rings can come closer since the radii sum of C and H is 2.7 Å.[14] In $Pd(PhA)_2$, the existing N(1)H···C(8A) distance is much larger, 3.05(2) Å. We also note that the HOMO (*vide infra*) of $Pd(RA)_2$ involves a bonding interaction between chelate π frames and the ligand anionic charge lies in the chelate ring, while in $Pd(RB)_2$ the pendent oximato oxygen atoms hold at least a considerable part of the charge. These electronic factors could also contribute toward the relative shortness of Pd−N bonds in $Pd(PhA)_2$, but the steric factor is no doubt far more important.

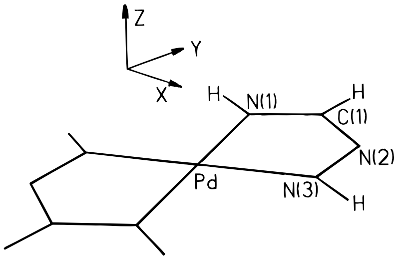
Table 3. Relative Percent Atomic Contributions[a] to the MO's of **5**

MO	Pd	2N(3)	2N(2)	2N(1)	2C(1)	largest contributor
HOMO (a_u) −11.79 eV	1	47	29	13	9	azo-π^*
LUMO (b_g) −11.18 eV	31	36	16	12	4	azo-π^*

[a] These do not add up to 100% since <1% contributions are not listed.

The bond lengths within the chelate rings will now be examined. Between $Pd(PhB)_2$ and $Pd(PhA)_2$ the N(2)−N(3) length *increases* by 0.05 Å, N(2)−C(1) *decreases* by 0.03 Å, and N(1)−C(1) remains virtually *unaffected* (Table 2). In the HOMO of $Pd(RA)_2$ (in $Pd(RB)_2$ the corresponding orbital is the LUMO), the pairwise π interactions between adjacent bonded atoms within each chelate ring are antibonding in N(2)−N(3) and N(1)−C(1) but bonding in N(2)−C(1); *vide infra*. Also, the relative weightage of these interactions are in the order N(2)−N(3) > N(2)−C(1) > N(1)−C(1). This is in qualitative agreement with the observed trend.

C. Molecular Orbitals. In order to gain insight into the frontier orbitals of $Pd(RA)_2$, extended Hückel calculations were performed on the simplified model **5** assumed to have (i) exact planarity (C_{2h} symmetry) and (ii) H atoms in place of the R and Ph substituents at C(1) and N(3). Relative percent atomic contributions of the HOMO and the LUMO are given in Table 3.



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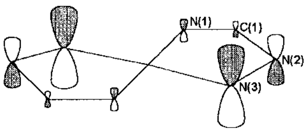
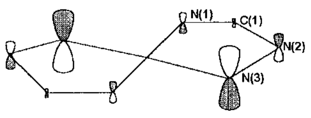
The HOMO **6** is constituted of the *bonding* combination of two groups of identical atomic orbitals, each chelate ring contributing one such group. The latter is essentially the lowest unoccupied π^* orbital of the electroneutral (4πe) azo−imine frame, N═N−C═N. The N(2)−N(3) interaction contributes 76% to the HOMO which may therefore be roughly described as a bonding combination of the azo-π^* pair. The HOMO has a_u symmetry. A metal d contribution is evidently absent, but there is a small p_z contribution (not shown in **6**). Qualitatively, the LUMO, **7**, is the antibonding counterpart of **6**. It has b_g representation, and the metal d_{xz} and d_{yz} orbitals (not shown in **7**) are significant contributors. The contribution of the azo-π^* pair is 52%.



HOMO (a_u)

6



LUMO (b_g)

7

The trans-metal interaction between the two chelate rings is appreciable, the HOMO−LUMO energy gap in the model being ~1 eV. Thus two antibonding electrons of the two $RA^{\bullet -}$ fragments pair up, occupying the HOMO in **5**. The intense Pd-

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(14) Huheey, J. E. *Inorganic Chemistry Principles of Structure and Reactivity*, 3rd ed.; Harper and Row: New York, 1983; p 258.

Table 4. Electrochemical Data

complex	cyclic voltammetric data:[a] $E_{1/2}$, V (ΔE_p, mV)[b]
$Pd(PhA)_2$	0.73 (190), 0.50 (220), −0.74 (180), −1.21 (240)
$Pd(NpA)_2$	0.66 (80), 0.51 (140), −0.72 (120), −1.18 (160)

[a] Conditions: solvent, 10% acetonitrile−90% dichloromethane; supporting electrolyte, TEAP (0.1 M); working electrode, platinum; reference electrode, SCE; solute concentration, $\sim 10^{-3}$ M. [b] $E_{1/2}$ is calculated as the average of anodic (E_{pa}) and cathodic (E_{pc}) peak potentials; $\Delta E_p = E_{pa} - E_{pc}$.

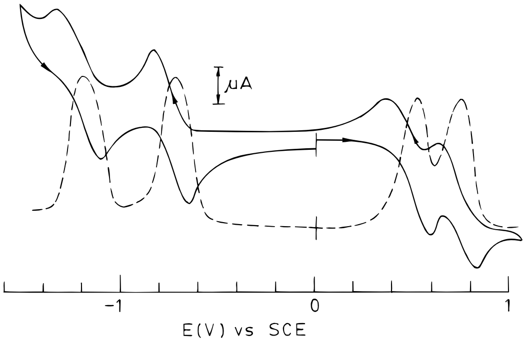

Figure 4. Cyclic (—) and differential pulse (- - -) voltammograms of a 10^{-3} M solution of $Pd(PhA)_2$ in 1:9 acetonitrile−dichloromethane (0.1 M TEAP) at a platinum electrode with scan rates of 50 mV s^{-1} (CV) and 10 mV s^{-1} (DPV). The marked current ranges are 10 μA (CV) and 20 μA (DPV).

$(RA)_2$ band in the visible region (Figure 1) can be assigned to the allowed HOMO (a_u) → LUMO (b_g) transition.

For comparison, EHMO computations were also performed on the precursor complex $Pd(RB)_2$ (R and Ph replaced by H).[15] Here the HOMO (a_g) is 90% metal (primarily d_{z^2}, d_{xy}) in character and the LUMO is similar in composition to the HOMO of **5**.

D. Voltammetry. a. Serial Redox. In mixed dichloromethane−acetonitrile solution, the $Pd(RA)_2$ complexes display four successive one-electron responses at a platinum electrode, the $E_{1/2}$ values lying in the range −1.3 to +0.8 V vs SCE (Table 4). The voltammograms of $Pd(PhA)_2$ are displayed in Figure 4. Two of the steps correspond to oxidation and two to reduction of $Pd(RA)_2$, eq 3. This is apparently consistent with

$$Pd(RA)_2^{2+} \underset{}{\overset{e^-}{\rightleftharpoons}} Pd(RA)_2^{+} \overset{e^-}{\rightleftharpoons} Pd(RA)_2 \overset{e^-}{\rightleftharpoons} Pd(RA)_2^{-} \overset{e^-}{\rightleftharpoons} Pd(RA)_2^{2-} \qquad (3)$$

the outermost π configuration $(a_u)^2(b_g)^0$ of $Pd(RA)_2$. However, it would be improper to assign electronic structures to the $Pd(RA)_2^z$ ($z = \pm1, \pm2$) species till these are individually characterized. Unfortunately bulk electrogeneration of the species by constant-potential coulometry has not succeeded so far due to instability, except in the case of $Pd(RA)_2^+$; see below.

The one-electron couple $Pd(PhB)_2-Pd(PhB)_2^-$ has a $E_{1/2}$ of −0.50 V vs SCE in dichloromethane.[11] Here the redox electron occupies an orbital like **6** which is the LUMO in $Pd(PhB)_2$. The above couple formally corresponds to the couple $Pd(PhA)_2^{2+}-Pd(PhA)_2^+$ ($E_{1/2} = 0.73$ V) in eq 3. The bischelated azo−imine function is thus far more easily reducible than the azo−oxime function so chelated. We can now look back at the synthetic reaction, eqs 1 and 2. Once the oximato function is reduced to the imine, $=N-O^- \rightarrow =NH$, the highly augmented reduction potential drives each azo−imine frame to accept an extra electron spontaneously: the result is electroneutral $Pd(RA)_2$.

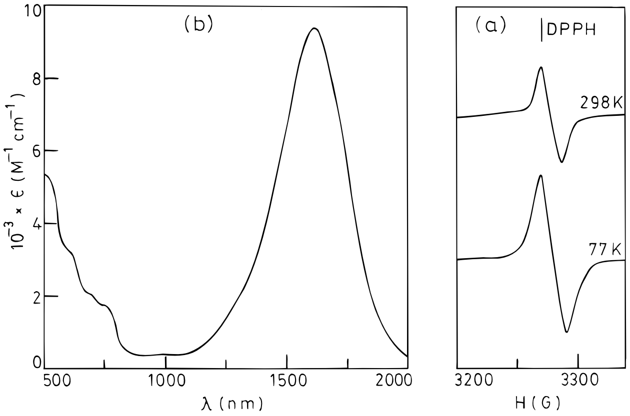

Figure 5. (a) X-band EPR spectra of electrogenerated $Pd(PhA_2)^+$ in 1:1 dichloromethane−toluene solution at 298 K (fluid) and at 77 K (glass). Instrument settings: power, 30 dB; modulation, 100 kHz; sweep center, 3200 G; sweep width, 1000 G; sweep time, 240 s; microwave frequency, 9.1 GHz. The apparent difference in the intensity of the signal at the two temperatures was due to the difference in receiver gain used (3.2×10^3 at 77 K and 1.6×10^3 at 298 K). (b) Electronic spectrum of electrogenerated $Pd(PhA_2)^+$ in 1:1 dichloromethane−acetonitrile solution.

b. $Pd(RA)_2^+$. One-electron coulometric oxidation at 0.6 V afforded a brown solution which displayed four voltammetric responses (three reductions and one oxidation), coinciding with those of $Pd(PhA)_2$. One-electron reduction of the oxidized solution at 0.3 V regenerated $Pd(PhA)_2$. Evidently $Pd(PhA)_2^+$ retains the gross structure of the parent complex.

It has not been possible to isolate $Pd(PhA)_2^+$ as a pure salt, but it has been spectrally studied in electrogenerated solutions. The complex is paramagnetic and displays (Figure 5a) a strong EPR signal both in fluid solution ($g = 2.001$) and in the glassy state at 77 K ($g = 1.998$). Extending the orbital description of $Pd(PhA)_2$, we propose that $Pd(PhA)_2^+$ has the π configuration $(a_u)^1(b_g)^0$. The HOMO (a_u) has large azo-π* character (*vide supra*), and this is consistent with the lack of resolvable hyperfine structure of the EPR signal. The azo ^{14}N coupling constant is small (4.8 G), and it is usually difficult to resolve it because of dominant anisotropic contributions, as has been repeatedly documented in literature.[13,16] The electronic spectrum of $Pd(PhA)_2^+$ in solution has a strong band at 1600 nm ($\epsilon = 9420$ M^{-1} cm^{-1}) (Figure 5b). There are only relatively weak absorptions near 740 nm, where the parent complex absorbs strongly (Figure 1). The origin of the 1600 nm band is unclear at present. It is tempting to assign it to $a_u \rightarrow b_g$ excitation strongly shifted to lower energy upon cation formation ($Pd(PhA)_2$ to $Pd(PhA)_2^+$). Significantly the intensity of the 1600 nm band in $Pd(PhA)_2^+$ is nearly half that of the 740 nm band in $Pd(PhA)_2$.

E. Isoelectronic Systems. The azo-imine frame, **8**, introduced in this work is isoelectronic with the known imine−imine,[3,4] **9**, and azo−azo,[9] **10**, frames—all three being aza-substituted butadienes. However unlike **8**, neither **9** nor **10** is known to afford electroneutral bis chelates of palladium (or platinum).[17] The reported systems are of the types such as (i)

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[15] Pal, C. K.; Chakravorty, A. Unpublished.

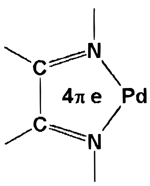
[16] (a) Krejcik, M.; Zails, S.; Klima, J.; Sykora, D.; Matcheis, W.; Klein, A.; Kaim, W. *Inorg. Chem.* **1993**, *32*, 3362. (b) Kaim, W.; Kohlmann, S. *Inorg. Chem.* **1986**, *25*, 3442. (c) Johnson, C. S.; Chang, R. *J. Chem. Phys.* **1965**, *43*, 3183.

[17] Such chelates (pseudotetrahedral) exist for nickel(0): (a) Servaas, P. C.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.* **1989**, *28*, 1774. (b) van Koten, G.; Overbosch, P.; Overbeek, O. *Inorg. Chem.* **1982**, *21*, 2373.

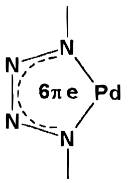
$-N{=}X{-}Y{=}N-$

	X	Y
8	N	-C
9	-C	-C
10	N	N

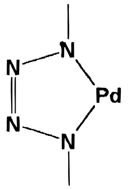
Pd^0(ligand)(olefin)[18] and Pd^{II}(ligand)Cl_2[19] in the case of **9** and (ii) Pd^{II}(ligand)$(PR_3)_2$[9] in the case of **10**. In (i) the ligand is present in the electroneutral 4πe form **11** while in (ii) it is formally dianionic, occurring in the 6πe form **12a**, for which a simplified valence-bond description is **12b**.



11



12a



12b

It seems that the larger the number of aza atoms, the larger are the number of π electrons and the associated anionic charge that can be easily sustained: **11** (diaza), 4πe (charge 0); **4** (triaza), 5πe (1−); **12** (tetraaza), 6πe (2−). Last, we note that the azo−imine system has a formal similarity to the dioxolene system, the state of the ligand in $Pd(RA)_2$ corresponding to the semiquinone ($sq^{\bullet -}$) stage. The diamagnetic planar bis chelates[20] of the type $Pd^{II}(sq)_2$ are then distant relatives of $Pd(RA)_2$.

F. Concluding Remarks. The main findings of this work will now be recapitulated. The first isolation of chelated azo imines has been achieved in the form of the spin-paired $Pd(RA)_2$, **4**, incorporating 10 ligand π electrons (R = Ph, α-naphthyl). The synthetic precursor is the bis(azooximate) $Pd(RB)_2$, **2**. The oximate to imine reduction $=N-O^- \rightarrow =N-H$ is associated with a large shift of reduction potentials to higher values, causing spontaneous addition of one electron to each chelated azo−imine frame.

The Pd−N lengths in $Pd(PhA)_2$ are significantly shorter than those in $Pd(PhB)_2$ owing to steric interaction between an oximato oxygen and a pendent Ph carbon in the latter complex. The trend of C−N and N−N lengths within the chelate rings are consistent with the nature of the HOMO's of the two complexes.

In $Pd(RA)_2$, both the HOMO (fully occupied) and the LUMO are constituted primarily of azo-π* orbitals. Observed serial redox and low-energy electronic transitions may be associated with these orbitals. In EPR-active $Pd(PhA)_2^+$, electrogenerated in solution, the HOMO is singly occupied.

The azo−imine frame can be looked upon as the intermediate member in the azo−azo, azo−imine, imine−imine sequence. The known palladium chemistry, including the first azo−imine results of this work, suggests that the chelate frame can sustain more ligand π electrons and anionic charge as the number of nitrogen atoms increases: imine−imine < azo−imine < azo−azo. Ongoing work concerns synthesis and characterization of azo-imine chelates of other transition metals.

Experimental Section

Materials. Sodium tetrachloropalladate and (phenylazo)benzaldoxime and (phenylazo)-1-naphthaldoxime were prepared by reported methods.[21,22] Solvents and chemicals used for syntheses were of analytical grade. Supporting electrolyte (tetraethylammonium perchlorate, TEAP) and solvents for electrochemical work were obtained as before.[23]

Physical Measurements. A Hitachi 330 spectrophotometer was used to record UV−vis−near-IR spectra. IR spectra were recorded with a Perkin-Elmer 783 IR spectrophotometer. A Varian E-109C spectrometer fitted with a quartz dewar was used for EPR studies. DPPH ($g = 2.0037$) was used to calibrate the spectra. ^1H NMR spectra in $CDCl_3$ were recorded with a Varian VXR 300S spectrometer. TMS was used as internal standard. A Perkin-Elmer 240C elemental analyzer was used to collect microanalytical data (CHN). Electrochemical measurements were performed under nitrogen atmosphere on a PAR Model 370-4 electrochemistry system as reported earlier.[24] All potentials reported in this work are referenced to the saturated calomel electrode (SCE) and are uncorrected for junction contribution.

Synthesis of Parent Complexes. *trans*-Bis[(phenylazo)benzaldoximato]palladium(II), $Pd(PhB)_2$. The complexes were prepared by following the reported procedures.[11] Bis[(phenylazo)-1-naphthaldoximato]palladium(II), $Pd(NpB)_2$, was prepared by reaction of Na_2PdCl_4 with the ligand (phenylazo)-1-naphthaldoxime in a similar way. The complex, hitherto unreported, was synthesized in 60% yield. Anal. Calcd for $C_{34}H_{24}N_6O_2Pd$: C, 62.34; H, 3.69; N, 12.83. Found: C, 62.21; H, 3.78; N, 12.96. UV−vis (CH_2Cl_2), λ_{max} in nm (ϵ in M^{-1} cm^{-1}): 625 (2528), 580 (sh) (2325), 418 (5351). Sharp ν_{NO} in IR (KBr disk) at 1240 cm^{-1}.

Synthesis of Azo−Imine Complexes. The azo−imine complexes were prepared by the same general procedure from the respective precursors. Details are given below for $Pd(PhA)_2$.

***trans*-Bis[(phenylazo)benzaldiminato]palladium(II), $Pd(PhA)_2$.** To a 1:1 dichloromethane−acetonitrile solution (20 mL) of $Pd(PhB)_2$ (0.140 g, 0.25 mmol) was added ascorbic acid (0.130 g, 0.75 mmol) in 2 mL of water, and the resultant solution was refluxed for 2.5 h. The deep violet solution containing the product was evaporated in vacuo. The dark residue was washed thoroughly with water and dried. The brown mass thus obtained was chromatographed over a silica gel (60−120 mesh) column. The yellowish-green band containing the product was eluted with petroleum ether (boiling range 40−60 °C) and benzene (1:4). Evaporation of solvent afforded pure product which was dried over anhydrous $CaCl_2$. Yield: 80 mg, 60%. Anal. Calcd for $C_{26}H_{22}N_6Pd$: C, 59.49; H, 4.19; N, 16.03. Found: C, 59.64; H, 4.27; N, 15.96. Anal. Calcd for $Pd(NpA)_2$, $C_{34}H_{26}N_6Pd$: C, 65.33; H, 4.18; N, 13.45. Found: C, 65.18; H, 4.26; N, 13.52.

$Pd(PhA)_2^+$. A 20 mL 1:1 dichloromethane−acetonitrile (0.1 M TEAP) solution of $Pd(PhA)_2$ (7.29 mg, 0.014 mmol) was oxidized coulometrically at a constant potential of +0.64 V vs SCE under a dinitrogen atmosphere. Electrolysis was stopped when 1.34 C (corresponding to the transfer of one electron) had passed. The initial yellow-green color of the solution changed to dark brown after electrolysis. This solution was subjected to spectral characterization by UV−vis−near-IR and EPR spectroscopy. The oxidized solution was reduced at +0.30 V vs SCE under nitrogen atmosphere. This regenerated the parent complex, $Pd(PhA)_2$.

Molecular Orbital Calculations. Extended Hückel calculations were performed on an IBM PC AT using the ICON software package originally developed by Hoffmann.[25] The orthogonal coordinate system chosen for calculations is defined in structure **5**. The averaged experimental bond distances and angles were used in our calculations.

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(18) Cavell, K. J.; Stufkens, D. J.; Vrieze, K. *Inorg. Chim. Acta* **1980**, *47*, 67.

(19) (a) van der Poel, H.; van Koten, G.; Vrieze, K. *Inorg. Chem.* **1980**, *19*, 1145. (b) van der Poel, H.; van Koten, G.; Vrieze, K.; Kokkes, M.; Stam, C. H. *J. Organomet. Chem.* **1979**, *175*, C21.

(20) Fox, G. A.; Pierpont, C. G. *Inorg. Chem.* **1992**, *31*, 3718.

(21) Mahapatra, A. K.; Bandyopadhyay, D.; Bandyopadhyay, P.; Chakravorty, A. *Inorg. Chem.* **1986**, *25*, 2214 and references therein.

(22) Kalia, K. C.; Chakravorty, A. *J. Org. Chem.* **1970**, *35*, 2231.

(23) (a) Goswami, S.; Chakravarty, A. R.; Chakravorty, A. *Inorg. Chem.* **1981**, *20*, 2246. (b) Datta, D.; Mascharak, P. K.; Chakravorty, A. *Inorg. Chem.* **1981**, *20*, 1673.

(24) Chandra, S. K.; Basu, P.; Ray, D.; Pal, S.; Chakravorty, A. *Inorg. Chem.* **1990**, *29*, 2423.

(25) (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. (b) Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.

Table 5. Crystallographic Data for Pd(PhA)$_2$ and Pd(PhB)$_2$

	Pd(PhA)$_2$	Pd(PhB)$_2$
empirical formula	$C_{26}H_{22}N_6Pd$	$C_{26}H_{20}N_6O_2Pd$
fw	524.9	554.9
space group	*C*2/*c*	*P*2$_1$/*n*
a, Å	18.167(5)	5.735(5)
b, Å	7.420(3)	10.797(6)
c, Å	16.527(6)	18.022(11)
β, deg	92.70(3)	97.73(6)
V, Å^3	2225.4(13)	1105.4(13)
Z	4	2
T, K	296	296
λ, Å	0.710 73	0.710 73
ρ_{calcd}, g cm^{-3}	1.567	1.667
μ, cm^{-1}	8.61	8.78
transm coeff[a]	0.8801/1	0.9468/1
R,[b] %	2.61	3.37
R_w,[c] %	3.58	3.40
GOF[d]	1.72	1.24

[a] Maximum value normalized to 1. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w^{-1} = \sigma^2(|F_o|) + g|F_o|^2$; $g = 0.0002$ for *trans*-Pd(PhA)$_2$ and $g = 0.0001$ for *trans*-Pd(PhB)$_2$. [d] The goodness of fit is defined as $[w(|F_o| - |F_c|)^2/(n_o - n_v)]^{1/2}$ where n_o and n_v denote the numbers of data and variables, respectively.

The C−H distance was taken as 0.96 Å. The atomic parameters and H_{ii} values for C, O, H, N, and Pd were taken from literature.[26]

X-ray Structure Determination. Single crystals of Pd(PhA)$_2$ and Pd(PhB)$_2$ were grown by slow diffusion of hexane into respective dichloromethane solutions of the complexes at 298 K (Pd(PhA)$_2$, brown, prismatic 0.32 × 0.34 × 0.45 mm^3; Pd(PhB)$_2$, dark, prismatic 0.08 × 0.06 × 0.20 mm^3). Cell parameters were obtained by least-squares fits of 30 machine-centered reflections obtained from rotation photograph. Systematic absences afforded the space group *C*2/*c* (or *Cc*; the structure was successfully solved in in *C*2/*c*) for Pd(PhA)$_2$ and *P*2$_1$/*n* for Pd(PhB)$_2$. Data were collected at 296 K by the ω-scan method over the 2θ range 2−50° on a Nicolet R3m/V diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Two check reflections measured after every 98 reflections showed no significant change in intensity over 25 h (Pd(PhA)$_2$) and 23 h (Pd(PhB)$_2$) of exposure to X-rays. Data were corrected for Lorentz−polarization effects and absorption (azimuthal scan).[27] Of the 2560 and 1938 unique reflections, 2233 and 1158 with $I > 3\sigma(I)$ were used for respective structure solution of Pd(PhA)$_2$ and Pd(PhB)$_2$ (heavy-atom method). All non-hydrogen atoms were made anisotropic. All hydrogen atoms in the structure were directly located from difference Fourier maps. Least-squares refinements were performed by full-matrix procedures. All calculations were done on a MicroVAX II computer with programs of SHELXTL-PLUS.[28] Significant crystal data are listed in Table 5, and atomic coordinates and isotropic thermal parameters are listed in Tables 6 and 7.

Table 6. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for Pd(PhA)$_2$

	x	*y*	*z*	*U*(eq)[a]
Pd	0	2888(1)	2500	34(1)
N(1)	36(1)	2685(3)	3688(1)	41(1)
N(2)	−1220(1)	2666(3)	3522(1)	40(1)
N(3)	−1051(1)	2897(3)	2753(1)	37(1)
C(1)	−612(1)	2556(3)	4012(1)	38(1)
C(2)	−701(1)	2250(3)	4882(1)	40(1)
C(3)	−1372(2)	1715(4)	5155(2)	51(1)
C(4)	−1452(2)	1326(5)	5967(2)	62(1)
C(5)	−870(2)	1504(5)	6510(2)	62(1)
C(6)	−205(2)	2089(5)	6254(2)	69(1)
C(7)	−116(2)	2482(5)	5447(2)	58(1)
C(8)	−1663(1)	2913(3)	2197(1)	35(1)
C(9)	−1622(1)	3905(4)	1484(1)	40(1)
C(10)	−2209(1)	3899(4)	927(1)	48(1)
C(11)	−2846(2)	2959(4)	1077(2)	52(1)
C(12)	−2889(2)	2006(4)	1790(2)	50(1)
C(13)	−2304(1)	1979(3)	2353(2)	43(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 7. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for Pd(PhB)$_2$

	x	*y*	*z*	*U*(eq)[a]
Pd	0	0	0	33(1)
O(1)	−3727(8)	−1095(4)	−1079(3)	51(2)
N(1)	−3017(8)	−118(6)	−739(2)	36(1)
N(2)	−3180(8)	1951(4)	−461(2)	34(2)
N(3)	−1237(8)	1752(4)	−45(2)	34(1)
C(1)	−4158(11)	949(6)	−862(3)	35(2)
C(2)	−6289(9)	1170(5)	−1401(3)	30(2)
C(3)	−6643(10)	2333(5)	−1719(3)	40(2)
C(4)	−8642(11)	2602(5)	−2223(3)	44(2)
C(5)	−10324(11)	1708(6)	−2410(3)	46(2)
C(7)	−7987(9)	257(5)	−1599(3)	37(2)
C(8)	−397(10)	2822(5)	400(3)	32(2)
C(6)	−9997(10)	542(6)	−2098(3)	45(2)
C(9)	1727(10)	3354(5)	278(3)	39(2)
C(10)	2417(10)	4445(5)	667(3)	39(2)
C(11)	1083(9)	4934(7)	1168(3)	39(2)
C(12)	−969(10)	4344(5)	1303(3)	40(2)
C(13)	−1739(10)	3289(5)	908(3)	38(2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

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Supporting Information Available: For Pd(PhA)$_2$ and Pd(PhB)$_2$, complete bond distances (Tables S1 and S5) and angles (Tables S2 and S6), anisotropic thermal parameters (Tables S3 and S7), and hydrogen atom positional parameters (Tables S4 and S8) (6 pages). Ordering information is given on any current masthead page.

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(26) (a) Tatsumi, K.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 3328. (b) Hoffmann, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858. (c) Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857.

(27) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.

(28) Sheldrick, G. M. *SHELXTL-PLUS 88: Structure Determination Software Programs*; Nicolet Instrument Corp.: Madison, WI, 1988.