available to learn how to evaluate these kind of parameters.

The overall symmetry of the **D** tensor is compatible with C_s, the plane passing for the copper atoms, or, including the crystal C_i symmetry, with the C_{2h} point group. Indeed xy is antisymmetric referred to the plane and yz and $x^2 - y^2$ are symmetric, so that $J_{xy,yz,x^2-y^2,xy}$ is totally symmetric as required. The question still to be answered is why D_{yz} becomes so important for the pyridine *N*-oxide complexes, while for all the other members of the series its effect is much less evident. The best explanation we can find is that $J_{xy,yz,x^2-y^2,xy}$ does not vary much as the metal-metal distances decrease, so that D_{yz} does not vary appreciably. Since its value is determined essentially from the rotation of the principal D axes from the g_{zz} direction, keeping D_{yz} constant and increasing $|D_{xz}|$ and $|D_{yy}|$ yield progressively smaller angles, which eventually fall within experimental indetermination. Beyond the bis(μ-oxo)-bridged series, relevant deviations of the D_{xz} axis from the g_{zz} direction were determined also for 1,3-bis(μ-azido)bis(1,1,4,7,7-pentamethyldiethylenetriamine)copper(II) bis(tetraphenylborate), where the diagonal values were slightly smaller than in the present case (D = 0.0854 cm^{-1}).

Registry No. [Cu(pyO)Cl$_2$(Me$_2$SO)]$_2$, 57063-89-5; Mn, 7439-96-5.

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Palladated Azobenzenes and Regiospecific Aromatic Metaloxylation

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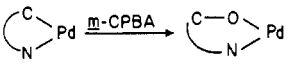
Three groups of ortho-palladated azobenzenes (**4**, **8**, and **9**) and their high-yield regiospecific oxidation (called aromatic metaoxylation, Ar–Pd → Ar–OPd) by *m*-chloroperbenzoic acid (*m*-CPBA) in acetonitrile solution are described. Schematically, the metaloxylation reaction is



the product being an azophenol chelate (**5**, **6**, **10**, **11**). Several modes of binding—bidentate N,O and C,N and tridentate C,N,O—of *o*-hydroxyazobenzenes to palladium(II) are characterized. The C,N,O mode occurs in **8**. The Pd–O bond in **8** can be reversibly cleaved by acids, resulting in sharp color changes that are useful for indicator action in acid–base titrations in acetonitrile. The tridentate binding of the organic ligands in **8** and **9** (C,N,S mode) is unequivocally revealed by their ^{1}H NMR spectra. The oxidation of **4** by *m*-CPBA is complicated by the formation of two products: **5** and **6**. The oxidation of **8b** furnishes **11** while **9** yields **10**. A notable feature is that the metaloxylation reaction is very much faster than the possible oxidation of other centers (e.g. pyridine in **8b** or SR″ in **9**). In all cases the identity of the metaloxylated product has been established by its independent synthesis from preformed (by nonoxidative routes) hydroxyazobenzenes and palladium(II) salts. The reaction **9c** → **10c** has been kinetically characterized (295.8 K), affording the rate law $d[\mathbf{10c}]/dt = k[\mathbf{9c}]^2[m\text{-CPBA}]$ with $k = 3.02 \times 10^4$ M^{-2} s^{-1}. It is proposed that an adduct (**13**) consisting of two **9c** molecules bridged (at palladium(II) centers) by a peroxo oxygen of *m*-CPBA is formed as a reactive intermediate, which decomposes in the rate-determining step to afford **10c**. The key step is the heterolytic dissociation of the O–O bond, allowing insertion of oxygen into the Pd–C bond of one **9c** molecule.

Introduction

The regiospecific oxidation of the aromatic C–H function to the C–OH function, reaction 1, is of considerable import in chemistry.[1,2] In Nature this reaction is a useful tool for imparting

$$\text{Ar–H} \rightarrow \text{Ar–OH} \quad (1)$$

$$\text{Ar–M} \rightarrow \text{Ar–OM} \quad (2)$$

desirable properties such as biological activity and water solubility to organic compounds.[3] The associated enzymes (monooxygenases) often have a metal (usually copper or iron) at the active site for binding and activating[4-11] dioxygen, the natural oxidant. This work stems from our interest[12] in reaction 2, which can be considered as the organometallic analogue of the aromatic

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(2) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidation of Organic Compounds*; Academic: New York, 1981.

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(4) In order to buttress this, a variety of synthetic metal-containing hydroxylating reagents[1,2] have been examined, such as those of Fenton (Fe^{2+}, H$_2$O$_2$),[5] Brackman and Havinga (Cu^{2+}, amine, H$_2$O$_2$),[6] Udenfriend (Fe^{2+}, edta, ascorbic acid, O$_2$),[7] and Hamilton (Fe^{3+}, catechol, H$_2$O$_2$).[1,8] Aromatic hydroxylation of copper(I) complexes of *m*-xylyl binucleating ligands by dioxygen is reported.[9] Macrocyclic polyamine complexes of nickel(II) can mediate aromatic hydroxylation:[10] Palladium(II) and platinum(II) complexes of azo ligands provide interesting cases of aromatic hydroxylation.[11]

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(9) Karlin, K. D.; Gultneh, Y.; Hayes, J. C.; Zubieta, Z. *Inorg. Chem.* **1984**, *23*, 519. Karlin, K. D.; Hayes, J. C.; Gultneh, Y.; Cruse, R. W.; McKown, J. W.; Hutchinson, J. P.; Zubieta, J. *J. Am. Chem. Soc.* **1984**, *106*, 2121. Karlin, K. D.; Cruse, R. W.; Gultneh, Y.; Hayes, J. C.; Zubieta, J. *J. Am. Chem. Soc.* **1984**, *106*, 3372.

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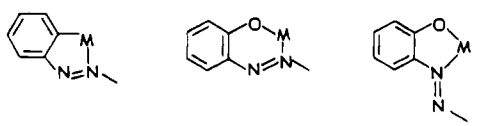
hydroxylation reaction 1. We call reaction 2 an aromatic *metaloxylation*. Here the metal center, which could be a potential site for oxidant binding, is part of the very bond that is oxygenated.

The system choice in the present study was guided by our familiarity[13,14] with platinum metal chemistry of azo ligands. The facile formation of the Cope metallacycle **1** (for brevity only an

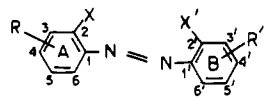


1 **2a** **2b**

unsubstituted aromatic ring is shown; the same applies to **2** below) via ortho metalation of azobenzenes is well documented.[15] On the other hand, *o*-hydroxyazobenzenes are known to afford[16,17] stable chelate rings of type **2a** or **2b**. Cyclometalated azobenzenes therefore represent model test substrates for exploring the feasibility of reaction 2 embodied in the conversion **1** → **2**. The synthesis and structure of a few systems incorporating the palladacycle **1** (M = Pd) were therefore explored. It is shown that the reactions of such systems with *m*-chloroperbenzoic acid indeed result in regiospecific aromatic metaloxylation (**1** → **2**) often proceeding in excellent yields.

Results and Discussion

A. Azobenzenes Used. In this paper we shall deal with a relatively large number of azobenzenes. To highlight their interrelationships, the ring designation, numbering scheme, and substituents used are shown in **3**. In **3**, the ring that does not

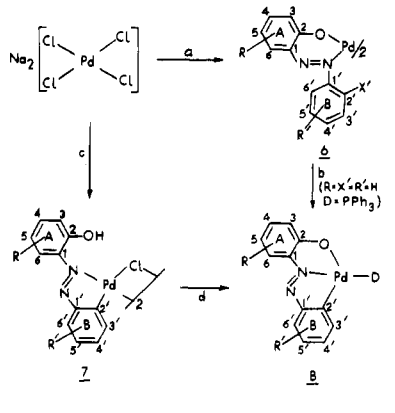


3

	R	X	R′	X′
3a	H	H	H	H
3b	6-Me	Me	5′-Me	H
3c	H	OH	H	H
3d	5-Me	OH	H	H
3e	5-Me	OH	4′-Me	H
3f	5-Me	OH	6′-Me	Me
3g	H	SMe	H	H
3h	H	SMe	5′-Me	H
3i	H	SMe	4′-Me	H
3j	H	SCH_2Ph	H	H
3k	H	SCH_2Ph	5′-Me	H
3l	H	SCH_2Ph	4′-Me	H
3m	H	OH	H	OH
3n	H	SMe	5′-Me	OH
3o	H	SCH_2Ph	5′-Me	OH

undergo ortho metalation is called the A ring with atom numbers 1–6. The ring that can be ortho metalated is the B ring—atoms 1′–6′ with the possible metalation site 2′. The substituents in A and B rings are respectively X, R and X′, R′.

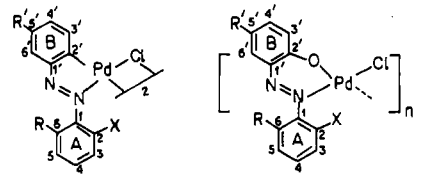
Scheme I



Complexes	R	R′	D
6a	H	H	—
6b	5-Me	6′-Me	—
7a	H	H	—
7b	5-Me	4′-Me	—
8a	H	H	PPh_3
8b	H	H	Py
8c	5-Me	H	PPh_3
8d	5-Me	H	γ-Pic
8e	5-Me	4′-Me	PPh_3
8f	5-Me	4′-Me	Py

[a] Add 2 mol of **3c**/**3f** in aqueous EtOH. [b] Silica gel, adsorb; ~345 K, 24 h; MeCN, extract, add D. [c] 1 mol of **3c**/**3d**/**3e** in EtOH, boil 6 h. [d] H_2O, stir 2 h; EtOH, add D.

B. Cope Dimers. The two compounds[18,19] **4a** and **4b** were studied in this work, and these were synthesized[13,15] by the reaction of Na_2PdCl_4 with the corresponding azobenzenes (**3a** and **3b**) in ethanol. The complex **4b** is new, and here cyclometalation ex-



4 **5**

	X	R	R′
4a, **5a**	H	H	H
4b, **5b**	Me	Me	Me

pectedly[13] occurs at the sterically unhindered carbon (position 2′ as opposed to 6′) only. The isomeric purity of the complex is established by the observation of only two ^1H NMR methyl signals:[20,21] 2,6-Me_2, 2.33 ppm; 5′-Me, 2.36 ppm. The metaloxylation **4** → **5** is considered later.

C. Cyclopalladation of *o*-Hydroxyazobenzenes (3c–e). a. Pd(N,O), Pd(C,N), and Pd(C,N,O) Coordination Spheres. The main synthetic reactions and complexes are summarized in Scheme I. The N,O bidentate coordination of *o*-hydroxyazobenzenes affording bis complexes[22] of type **6** occurs in aqueous ethanol. In anhydrous ethanol, ortho metalation (for ligands having X′ = H) is the preferred reaction, furnishing the brown C,N-coordinated complex **7**, which undergoes facile[23] chelative dehydrohalogenation in aqueous media to generate (after addition of donor D) the C,N,O adduct **8** in high yield.

These observations can be rationalized. The Pd–O bond is quite sensitive to cleavage by acids (see reaction 3) in nonaqueous media. In anhydrous ethanol, the phenolic OH function therefore remains unreactive toward palladium(II), allowing the ortho metalation reaction to take its own course—the Pd–C bond being unreactive[13]

(12) Mahapatra, A. K.; Bandyopadhyay, D.; Bandyopadhyay, P.; Chakravorty, A. *J. Chem. Soc., Chem. Commun.* **1984**, 999.
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(14) Ghosh, B. K.; Mukhopadhyay, A.; Goswami, S.; Ray, S.; Chakravorty, A. *Inorg. Chem.* **1984**, *23*, 4633 and references therein. Pal, S.; Melton, T.; Mukherjee, R.; Chakravarty, A. R.; Tomas, M.; Falvello, L. R.; Chakravorty, A. *Inorg. Chem.* **1985**, *24*, 1250 and references therein.
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(17) Pregosin, P. S.; Steiner, E. *Helv. Chim. Acta* **1979**, *62*, 62.
(18) The structure of the platinum analogue of **3** is accurately known.[19]
(19) Elder, R. C.; Cruea, R. D. P.; Morrison, R. F. *Inorg. Chem.* **1976**, *15*, 1623.
(20) Other signals: 6′-H, 7.74 ppm; remaining aromatic signals, 7.10 ppm (center of complex pattern). On bridge splitting of **4b** by triphenylphosphine, the adduct (PPh_3 located trans[21] to the coordinated azo nitrogen) has the following characteristic ^1H NMR features: 2,6-Me_2, 2.35 ppm; 5′-Me, 2.25 ppm; 3′-H, 6.33 ppm ($J_{3'4'}$ = 7.8 Hz); 4′-H, 6.58 ppm ($J_{4'3'}$ = 8.0 Hz; $J_{4'6'}$ = 2.0 Hz); 6′-H, 7.88 ppm. The shift of 5′-Me, 3′-H, and 4′-H signals to higher fields in the phosphine adduct arises from the shielding of the nearby PPh_3 phenyls.[13]
(21) Weaver, D. L. *Inorg. Chem.* **1970**, *9*, 2250. Crociani, B.; Boschi, T.; Pietropaolo, R.; Belluco, U. *J. Chem. Soc. A* **1970**, 531.
(22) Kalia, K. C. *Indian J. Chem.* **1970**, *8*, 1035.
(23) It is difficult to obtain pure samples of **7** due to partial dehydrohalogenation even in the presence of traces of moisture.

Table I. UV–Vis Spectral Data of Selected Compounds

compd[a]	UV–vis λ_{max}, nm (ϵ, M^{-1} cm^{-1})
4a	436 (2500),[d] 380 (5000),[d] 328 (9500), 235 (14 000), 230 (7000)
4b	445 (1600),[d] 380 (4500),[d] 365 (5500), 302 (10 000), 240 (24 000)
6b	548 (7500), 330 (24 000), 290 (38 000), 252 (60 000)
7a	430 (3000),[d] 360 (5000),[d] 315 (8000), 240 (25 000)
8a	660 (6000),[d] 625 (6600), 350 (10 000)
8b	650 (4400),[d] 610 (6100), 670 (4700),[d] 380 (9600),[d] 360 (10 700), 325 (11 900), 380 (16 900), 260 (17 700)
5b	495 (7000), 302 (3500),[d] 272 (23 000)
5a	495 (6000), 320 (15 000),[d] 292 (17 000)
9a[b]	480 (2900), 405 (6400), 370 (10 700),[d] 355 (11 500), 325 (10 100), 240 (18 200),[d] 225 (25 500)
9b[b]	500 (2700), 410 (7300), 375 (11 100),[d] 355 (12 200), 325 (10 800), 250 (17 200),[d] 225 (28 700)
9c[b]	490 (2200), 410 (6700), 375 (9000),[d] 355 (10 200), 245 (17 200), 224 (31 200)
9d[b]	485 (4700), 405 (8600), 370 (11 600),[d] 355 (12 000), 330 (10 800),[d] 250 (16 100)
10a[b]	530 (7400), 370 (8700),[d] 338 (12 000), 230 (28 000)
10b[b]	545 (7300), 265 (9000),[d] 340 (11 900), 232 (29 500)
10c[b]	548 (8000), 365 (8000),[d] 340 (10 700)
11	510 (16 500), 480 (14 000),[d] 360 (5000),[d] 340 (8000),[d] 325 (8300), 302 (9000)
8c + $HClO_4$[b,c]	445 (6400), 350 (10 000)

[a] In dichloromethane unless otherwise noted. [b] In acetonitrile. [c] Protonated yellow species generated in situ. [d] Shoulder.

toward the liberated hydrogen chloride. In the formation of **6** and **8** water essentially acts as a base facilitating proton removal and formation of the Pd–O bond.

Reports on silica gel promoted ortho metalation reactions are sparse.[12,24] The conversion **6a** → **8a** (Scheme I) is therefore of interest. The acidic SiOH protons[25] of silica gel could conceivably provide the necessary electrophilic assistance[24] for the observed ortho metalation and the attendant rejection of 1 mol of ligand.

b. Spectra and Structure. The different types of species described in this paper, including those appearing in Scheme I, can be distinguished with the help of their characteristic UV–vis spectra. Selected data are in Table I. The six-membered chelated ring structure of **6** is based on an analogy with a nickel(II) congener of known structure.[16,26] The structure of complex **7** is primarily based on spectra (data for **7b**: IR ν_{OH}, 3100 cm^{-1}; NMR δ_{OH}, 12.75; UV–vis spectrum closely similar to those of **5** (Table I)).

The complexes of type **8** are of particular interest for the metaloxylation studies described later. High-resolution ^1H NMR spectra of the complexes in the aromatic region are in complete agreement with the tridentate coordination pattern of the *o*-hydroxyazobenzene ligands in **8**. A representative spectrum is given in Figure 1. The spin–spin structure due to ortho coupling is clearly revealed in all cases. Finer structure due to meta and para couplings can also be seen in some cases. A schematic correlation of the observed spectra (aromatic region with ortho coupling only) of several complexes is shown in Figure 2, and chemical shift and spin–spin splitting data are collected in Table II. Unambiguous assignment of aromatic signals is based on their (i) spin–spin structure and changes therein on substitution, (ii) high-field shift of signals of methylated rings (e.g. **8a** vs. **8c**), and (iii) large high-field shifts of signals close to PPh_3 due to phosphine phenyl shielding[13] (e.g. **8c** vs. **8d**).

c. Acid Cleavage of Pd–O Bond of 8. Solutions of **8** absorb strongly in the visible region (Table I). On addition of perchloric acid (**8**:$HClO_4$ = 1:1) to a dilute acetonitrile solution of **8** the color changes sharply to yellow. The original color is quantitatively regenerated upon acid neutralization by triethylamine ($HClO_4$:NEt_3 = 1:1). The dramatic spectral changes can be seen in Figure 3 for the case of **8c**. The associated reversible chemical reaction is believed to be as shown schematically in eq 3. Here

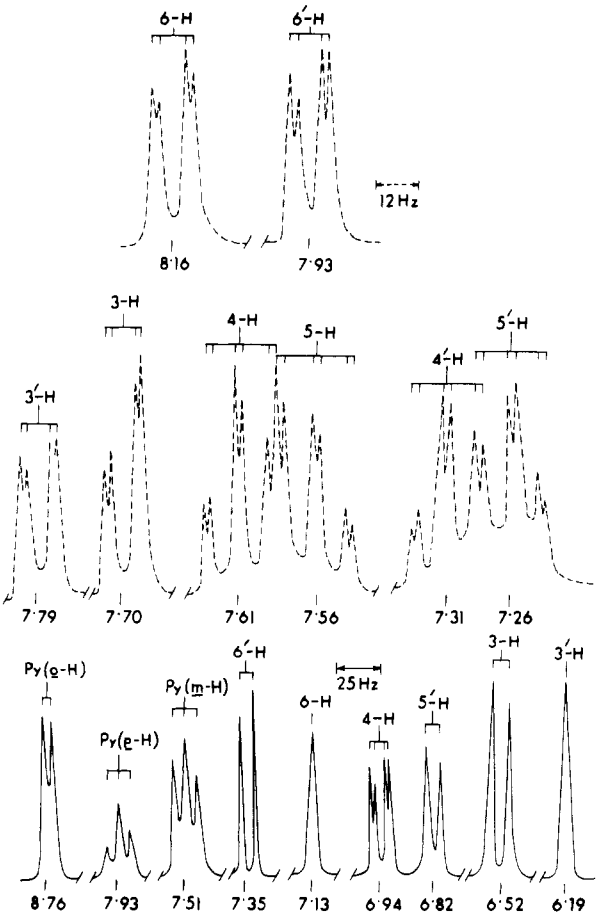
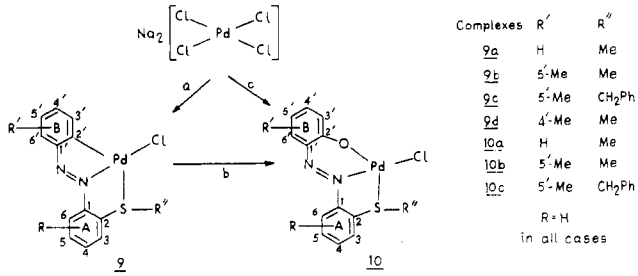
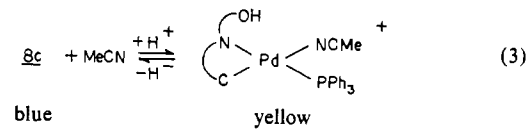


Figure 1. ^1H NMR spectra of **8f** (solid line) and **9a** (dotted line) in the aromatic region. The solvent and internal standard are $CDCl_3$ and tetramethylsilane, respectively.

Scheme II



[a] 1 mol of **3g**/**3h**/**3i**/**3k** in 95% EtOH, warm 2 h. [b] 1 mol of *m*-CPBA in MeCN, stir 2 h. [c] 1 mol of **3n**/**3o** in 95% EtOH.



(3)

protonation cleaves the Pd–O bond, freeing the phenolic OH group—the vacant coordination site presumably occupied by a solvent molecule. The process is reversed on removal of the phenolic proton by base. Attempted isolation of the yellow species as pure crystalline salts has not been successful so far.

The **8** (D = PPh_3) complexes can be used as sensitive indicators in quantitative acid–base titration in acetonitrile media. The color

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(25) Yermakov, Yu. L.; Kuznetsov, B. N.; Zakharov, V. A. *Catalysis by Supported Complex*; Elsevier: New York, 1981; p 59.
(26) Admittedly, a five-membered chelate ring structure of type **2b** cannot be excluded simply on these grounds. However, the exact structure of the bis complexes is not an important concern in the present work.

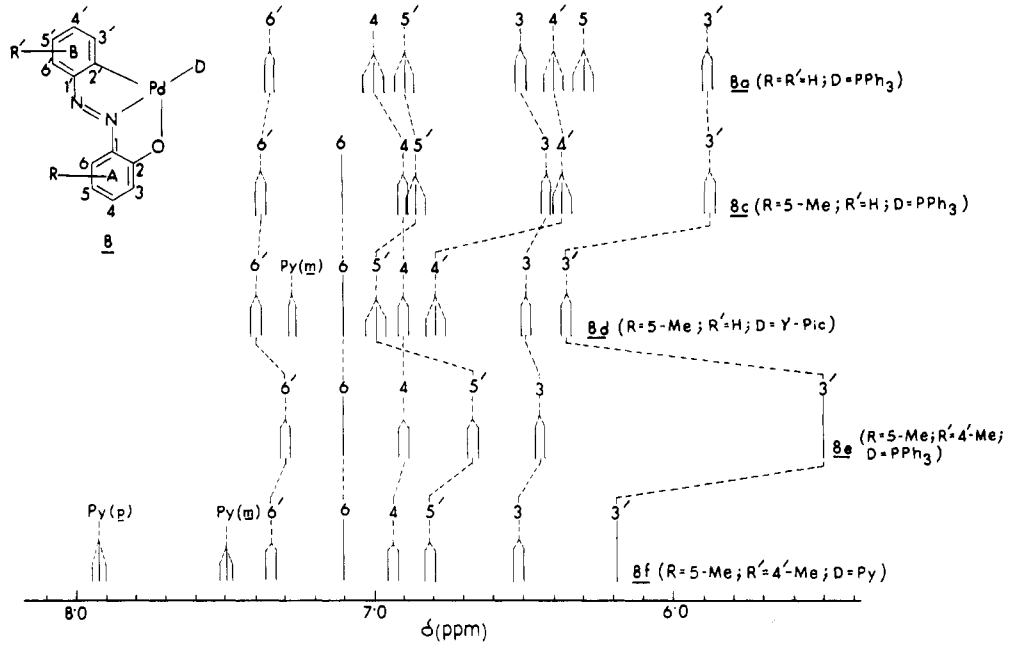


Figure 2. Schematic ^{1}H NMR spectra of complexes of type **8**.

Table II. ^{1}H NMR Spectral Data in $CDCl_3$

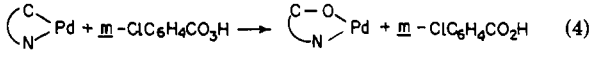
	δ (J)[a]							
compd	6-H	6'-H	4-H	5'-H	3-H[i]	4'-H	5-H[j]	3'-H
8a	?[g]	7.35 (7.2)[i]	7.05 (7.2)[j]	6.90 (7.2)[j]	6.51 (8.5)	6.40 (7.2)[j]	6.31 (7.2)	5.88 (8.0)[i]
8c[b]	7.11[h]	7.38 (8.4)[i]	6.90 (8.4)[i]	6.88 (8.4)[j]	6.42 (8.4)	6.37 (8.4)[j]		5.86 (8.4)[i]
8d[b,d]	7.11[h]	7.40 (8.0)[i]	6.90 (8.0)[i]	6.99 (8.0)[j]	6.49 (8.0)	6.79 (8.0)[j]		6.36 (8.0)[i]
8e[b,c]	7.12[h]	7.30 (7.0)[i]	6.89 (8.6)[i]	6.67 (8.0)[i]	6.45 (8.6)			5.50[h]
8f[b,c]	7.13[h]	7.35 (8.7)[i]	6.94 (8.7)[i]	6.82 (8.7)[i]	6.52 (8.7)			6.19[h]
9a[e]	8.16 (9.0)[i]	7.93 (9.0)[i]	7.61 (9.0)[j]	7.26 (9.0)[j]	7.70 (9.0)	7.31 (9.0)[j]	7.56 (9.0)	7.79 (9.0)[i]
9b[e,f]	8.16 (9.0)[i]	7.76[h]	7.61 (9.0)[j]		7.71 (9.0)	7.12 (8.4)[i]	7.54 (9.0)	7.66 (9.0)[i]
9d[c,e]	8.19 (8.2)[i]	7.87 (9.5)[i]	7.56 (9.0)[j]	7.12 (9.0)[i]	7.70 (9.0)		7.53 (9.0)	7.60[h]
10b[e,f]	7.38 (9.5)[i]	7.56[h]	7.57 (9.5)[j]		7.71 (8.0)	7.20 (9.5)[i]	7.49 (9.0)	7.37 (9.5)[i]

[a] J in Hz. [b] 5-Me signals (δ): **8c**, 2.11; **8d**, 2.13; **8e**, 2.11; **8f**, 2.13. [c] 4'-Me signals (δ): **8e**, 1.71; **8f**, 2.18; **9d**, 2.39. [d] Me of γ-picoline of **8d**, δ 2.43. [e] S-Me signals (δ): **9a**, 2.91; **9b**, 2.90; **9d**, 2.89; **10b**, 3.01. [f] 5'-Me signals (δ): **9b**, 2.38; **10b**, 2.36. [g] 6-H of **8a** is not observable due to overlap with strong triphenylphosphine proton signals. [h] Singlet. [i] Doublet. [j] Triplet.

changes of eq 3 are applicable even when H^+ is replaced by a Lewis acid such as BF_3, and a quantitative titration is possible in this case also.

D. Tridentate Palladation of *o*-(Alkylthio)azobenzenes (3g–l): Pd(C,N,S) Coordination Sphere. The ligands are obtained by condensing nitroso aromatics with *o*-(alkylthio)aniline.[27] The orange complexes of type **9** are afforded in high yield by the reaction of Na_2PdCl_4 with the ligands in hot aqueous ethanol (Scheme II). The C,N,S bonding mode in **9** is fully supported by their high-resolution ^{1}H NMR spectra (Figures 1 and 4; Table II). The logic followed in assignment of ^{1}H signals is similar to that used in the case of **8**. The tridentate binding of the present ligands is also observed in ruthenium(II) complexes that have been structurally characterized by diffraction studies.[24] The UV–vis spectral data of **9** are in Table I.

E. Regiospecific Metaloxylation. The oxidation of the Pd–C bond to the Pd–OC bond was achieved in all the three types of species (**4**, **8**, and **9**) with use of *m*-chloroperbenzoic acid (*m*-CPBA) in acetonitrile solution at ambient temperature as the oxidant. The general reaction is schematically shown in eq 4. The authenticity of the Pd–OC fragment, on the right-hand side of eq 4, is established wherever possible by its independent synthesis



(4)

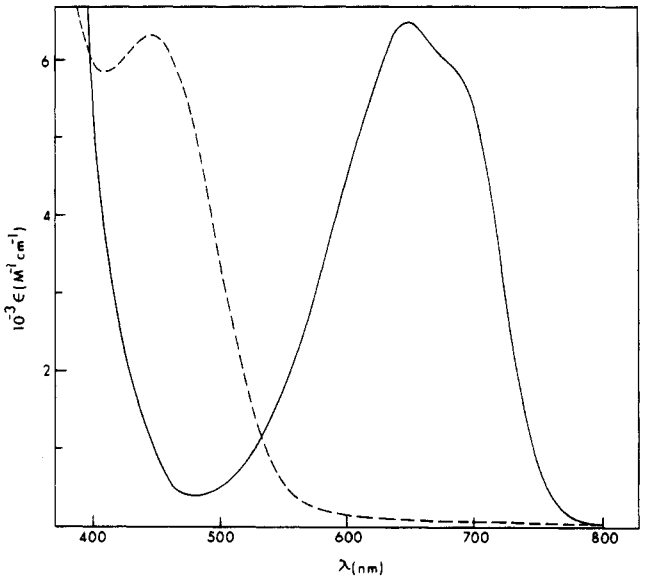


Figure 3. Electronic spectra of **8c** (solid line) and **8c** with 1 mol of $HClO_4$ added (dotted line) in acetonitrile.

from preformed hydroxyazo ligands (**3m–o**) and palladium(II) salts. For optimum yield in reaction 4, slightly larger than the stoichiometric amount of *m*-CPBA is usually used. The results obtained in the cases of **8** and **9** are more definitive than those in the case of **4**.

(27) Burawoy, A.; Vellins, C. E. *J. Chem. Soc.* **1954**, 90. Livingstone, S. E. *J. Chem. Soc.* **1956**, 437. Shriner, R. L.; Struck, H. C.; Jorison, W. J. *J. Am. Chem. Soc.* **1930**, *52*, 2060.

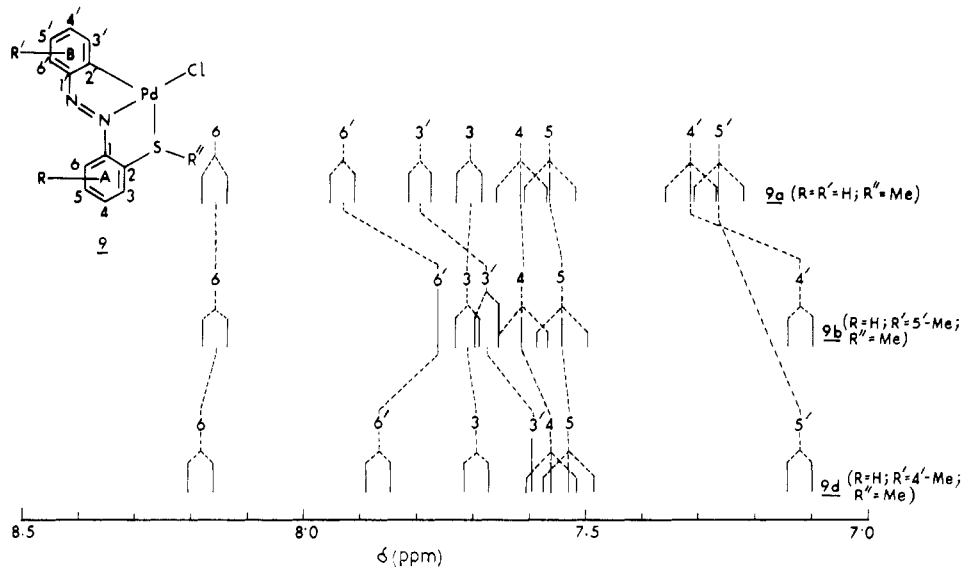
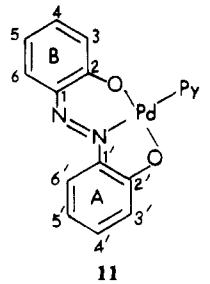


Figure 4. Schematic ^{1}H NMR spectra of complexes of type **9**.

a. The Case of 4. In this case the oxidation reaction is complicated in that two products (total yield ~60%) are formed: a red-brown to red-violet complex having the composition of **5** and the bis(*o*-hydroxyazobenzene) complex **6** (Scheme I). The separation of the two compounds is achieved chromatographically. Bis complex formation is more favorable in the case of **4a** (yields 30% for **5a** and 30% for **6a**) than in the case of **4b**, where yields are 50% for **5b** and 10% for **6b**.

An important observation is that the complex **5b** can be independently made by directly reacting 2,6,5-trimethyl-2′-hydroxyazobenzene with Na_2PdCl_4 in ethanol. Initially[12] we considered **5** to have a halogen-bridged dimeric structure similar to that of **4** (Pd–OC in place of Pd–C). However, its ^{1}H NMR spectrum is complex[28] and does not correspond to this proposal. The molecular weight of neither of the two complexes could be determined due to lack of sufficient solubility. The molecularity and structure of **5** remain uncertain at present. That the primary oxidation of **4** by *m*-CPBA is essentially regiospecific metalloxylation is however certain: complexes of *o*-hydroxyazobenzenes constitute the major oxidation products.

b. Oxidation of Pd(C,N,O) to Pd(O,N,O): 8b → 11. On addition of *m*-CPBA to **8** in acetonitrile, the solution color very rapidly changes from blue (D = PPh_3) or bluish green (D = py) to orange-yellow. Product (**11**, yield 80%) isolation was done in



11

the case of **8b** only.[29] The identity of **11** was firmly established by its direct synthesis from *o,o′*-dihydroxyazobenzene (**3m**) and Na_2PdCl_4. The NMR characterization of the structure of **11** is already reported in the literature.[17]

Free pyridine is readily oxidized[30] by perbenzoic acid to the *N*-oxide, but no such oxidation of the coordinated pyridine in **8b** was observed in the present study.

c. Oxidation of Pd(C,N,S) to Pd(O,N,S): 9 → 10. This oxidation (Scheme II) proceeds in excellent yield,[31] and the violet complex **10** is isolated after chromatographic workup of the reaction mixture. The regiospecificity of the oxidation is firmly authenticated by the direct synthesis of **10b** and **10c** from the corresponding *o*-(alkylthio)-*o′*-hydroxyazobenzene (**3n** and **3o**) ligands (Scheme II) prepared by a nonoxidative route. Selected spectral data for **10** are in Tables I and II. Like **9**, **10** displays a strong ν_{PdCl} band in the range 330–340 cm^{-1}.

A notable feature of the reaction **9 → 10** is that the coordinated thioether function is left unaffected[32–35] by *m*-CPBA even when the latter is present in excess. Free thioethers are easily oxidized

Table III. Kinetic Data[a] for the Oxidation of **9c** by *m*-CPBA (at 295.8 K) in CH_3CN

10^3[*m*-CPBA], M	$10^{-1}k_{obsd}$, M^{-1} s^{-1}	$10^{-4}k$, M^{-2} s^{-1}
0.97	2.86	2.95
2.24	6.82	3.04
2.82	8.47	3.00
4.68	14.52	3.10

[a] In this set of measurements the initial concentration of complex **9c** is 0.8458×10^{-4} M.

(28) Thus the spectrum of **5b** in $CDCl_3$ has three methyl signals of unequal intensity (δ 2.21, 2.23, 2.31; the combined intensities of the first two signals are approximately equal to that of the third signal) and the spectrum in the aromatic region is very complex. The composition of the complex and its ^{1}H NMR spectrum remain invariant from preparation to preparation. On addition of 1 mol of PPh_3 to **5b** the spectrum becomes more simple and is compatible with a simple bridge-split PPh_3 adduct: 5′-Me, 2.22 ppm: 2,6-Me_2, 2.33 ppm: 3′-H, 6.25 ppm ($J_{4'3'}$ = 9.0 Hz). Overlap with PPh_3 signals precluded assignment of other aromatic signals. The phosphine complex can be isolated in the pure state. It appears to be structurally similar (Pd–C replaced by Pd–OC) to[20] the bridge-split PPh_3 adduct of **4b**.

(29) Ring-substituted complexes were generally not preferred since they could yield isomeric mixtures on oxidation—the isomers differing in the locations of the five-membered and six-membered chelate rings.[17] Indeed, the oxidation of **8** (R = 5-Me, R′ = H, D = py) was found to afford a mixture of two orange-yellow complexes, presumably isomeric homologues of **11** separable by chromatography. However, these were not fully characterized.

(30) Katritzky, A. R.; Lagowski, J. M. *Chemistry of the Heterocyclic N-Oxides*; Academic: London, New York, 1971; p 22. Karayannis, N. M.; Speca, A. N.; Chasau, D. E.; Pytlewski, L. L. *Coord. Chem. Rev.* **1976**, *20*, 37.

(31) Spectrophotometric examination of the reaction mixture shows that **10** is formed in yields of 90% or above. After chromatographic separation the actual yields of the isolated crystalline complexes are >70%.

(32) The coordinated chloride ion is also inactive as in other cases[33] although free chloride is reactive.[34]

(33) Balch, A. L.; Benner, L. S.; Olmstead, M. M. *Inorg. Chem.* **1979**, *18*, 2996.

(34) Hoots, J. E.; Lesch, D. A.; Rauchfuss, T. B. *Inorg. Chem.* **1984**, *23*, 3130.

(35) When **10** is left in the presence of excess *m*-CPBA, a very slow reaction occurs, the nature of which has not been investigated.

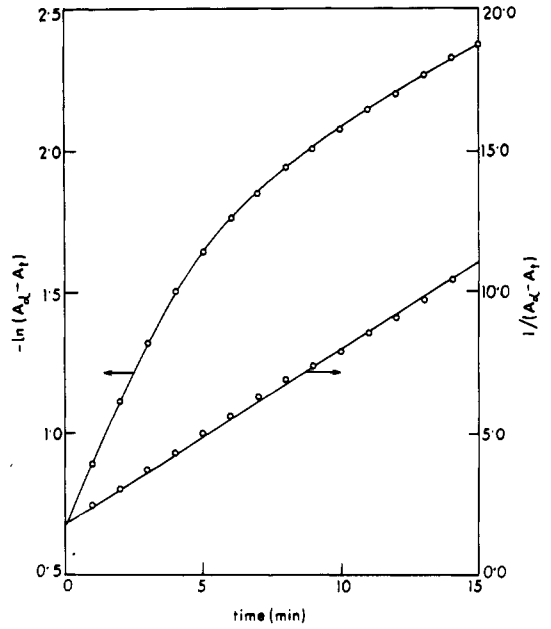


Figure 5. Plots of $-\ln (A_\infty - A_t)$ and $1/(A_\infty - A_t)$ vs. time: [**9c**] = 0.8458 × 10^{-4} M and [*m*-CPBA] = 2.24 × 10^{-3} M at 295.8 K in acetonitrile solvent.

by peroxo reagents, affording sulfoxides and sulfones via nucleophilic attack on the peroxo group by sulfur.[36,37] The coordinated thioether function is expected to be less nucleophilic than the free function. In practice the reactivity of **9** unlike that of certain ruthenium(II)-bound thioethers[38] is too slow to be observable in the present experiments.

F. Kinetics and Mechanism. The reaction of **9** with *m*-CPBA proceeds sufficiently slowly in acetonitrile (295.8 K) for the rate to be followed by conventional spectrophotometry even when *m*-CPBA is present in excess (see below). The corresponding reaction of complex **8** is too fast to be similarly followed. On the other hand, reaction of **4** with *m*-CPBA is complex (vide supra) and no attempts have yet been made to study its kinetics.

a. Rate Law. Complex **9c** was specifically chosen for detailed studies. It has an absorption maximum at 500 nm, which shifts to 545 nm on oxidation to **10c** (Table I). The growth of the 545-nm band was monitored as a function of time. In order to obtain the apparent rate constant, k_{obsd}, excess oxidant was used in all experiments.

The plot of $-\ln (A_\infty - A_t)$ vs. t was very distinctly curved. On the other hand, that of $1/(A_\infty - A_t)$ vs. t was excellently linear for at least 80% of the reaction (Figure 5). Here t, A_∞, and A_t represent time, absorbance at infinite time, and absorbance at time t, respectively. For all concentrations of *m*-CPBA (with a given initial concentration of **9c**) used in this study (selected data in Table III) the $1/(A_\infty - A_t)$ vs. t lines afforded identical intercepts, which when multiplied by $\Delta\epsilon$ correctly furnished the reciprocal of the initial concentration of **9c**, where $\Delta\epsilon$ is the difference in molar extinction coefficients of **10c** and **9c** at 545 nm.

We thus have the somewhat surprising result that the oxidation **9c** → **10c** is pseudo second order[39] in nature (eq 5). The plot

$$\text{rate} = d[\mathbf{10c}]/dt = k_{obsd}[\mathbf{9c}]^2 \quad (5)$$

of k_{obsd} vs. [*m*-CPBA] is linear, the quantity $k_{obsd}/[m\text{-CPBA}]$ being constant. The complete rate law is therefore given by eq 6, where k is a third-order rate constant of value 3.02 × 10^4 M^{-2} s^{-1} (Table III).

$$d[\mathbf{10c}]/dt = k[\mathbf{9c}]^2[m\text{-CPBA}] \quad (6)$$

b. Reaction Pathway. The rate law (6) basically means that in the rate-determining step two **9c** molecules must be associated with one *m*-CPBA molecule. The details of how this happens must be left to chemically logical guesswork. One model is expressed in eq 7–9, from which the rate law of eq 10 results. Here K_1 and

$$m\text{-CPBA} + \mathbf{9c} \overset{K_1}{\rightleftharpoons} \text{adduct 1} \quad \text{rapid} \quad (7)$$

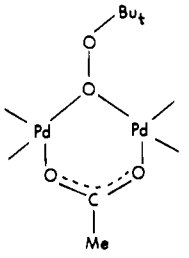
$$\text{adduct 1} + \mathbf{9c} \overset{K_2}{\rightleftharpoons} \text{adduct 2} \quad \text{rapid} \quad (8)$$

$$\text{adduct 2} \xrightarrow{k'} \mathbf{10c} + \mathbf{9c} + m\text{-CBA} \quad \text{rate determining} \quad (9)$$

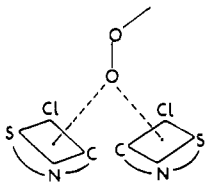
$$d[\mathbf{10c}]/dt = k'K_1K_2[\mathbf{9c}]^2[m\text{-CPBA}] \quad (10)$$

K_2 are equilibrium constants and *m*-CBA is *m*-chlorobenzoic acid. The equivalence between eq 6 and 10 is established by setting $k = k'K_1K_2$.

Equilibria 7 and 8 are not direct corollaries of the observed rate law. However, these provide a chemically rational pathway such that the direct ternary collisions (2 **9c** + 1 *m*-CPBA) are not required for reaction to occur. We have no convincing evidence for the formation of the adducts of eq 7 and 8, and pure **9c** is monomeric in solution.[40] However, a good indirect case can be made by using an analogy. The reaction of excess *tert*-butyl hydroperoxide with palladium(II) acetate is known to afford the tetrameric complex $[Pd(MeCO_2)(t\text{-}BuO_2)]_4$ of known structure.[41] Adjacent palladium atom pairs are peroxo and acetato bridged as in **12**. The existence of **12** gives credence to the reality of



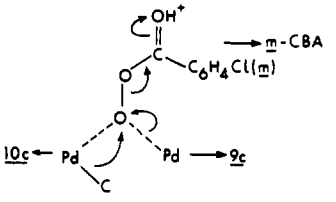
12



13

adduct 2 with a gross structure of type **13**, in which the dotted lines are meant to indicate weak coordinate bonds.

A logical set of electron movements that can result in the formation of **10c** (along with **9c** and *m*-CBA) from **13** is schematically depicted in **14**, where only the reactive bonds are shown.



14

The key step is the heterolytic dissociation of the O–O bond, allowing insertion of oxygen into the Pd–C bond of one **9c** molecule. The binding of *m*-CPBA to two electrophilic palladium centers is believed to be responsible for the initial activation (weakening) of the O–O bond. The peracid proton is taken to be dissociated in the formation of **13** and reinstated for carbonyl protonation (**14**). This is a logical but not essential feature of the mechanism proposed. The electron movements in **14** have

(36) House, H. O. *Modern Synthetic Reactions*; W. A. Benjamin: Menlo Park, CA, 1972; p 334.
(37) Curci, R.; Diprete, R. A.; Edwards, J. O.; Modena, G. *J. Org. Chem.* **1970**, *35*, 740. Barnard, D. *J. Chem. Soc.* **1956**, 489.
(38) Root, M. J.; Deutsch, E. *Inorg. Chem.* **1985**, *24*, 1464.
(39) Kassim, A. Y.; Sulfab, Y. *Inorg. Chem.* **1981**, *20*, 506. Toppen, D. L. *J. Am. Chem. Soc.* **1976**, *98*, 4023.
(40) The molecular weight of **9c** was determined by vapor pressure osmometry in $CHCl_3$. The observed value is 445 ± 20 against the calculated value of 459. Since the complex is monomeric in $CHCl_3$, it is very unlikely that molecular association will take place in CH_3CN.
(41) Mimoun, H.; Charpentier, R.; Mitschler, A.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1980**, *102*, 1047.

some analogy to those implicated in the Baeyer–Villiger oxidation[42] of ketones to esters by peracid.

G. Concluding Remarks. In this work we have dealt with three groups of cyclopalladated azobenzenes. Tridentate binding of *o*-hydroxyazobenzenes (in **8**) and *o*-(alkylthio)azobenzenes (in **9**) is established for the first time. The specific lability of the Pd–O bond to proton attack in the *o*-hydroxyazobenzene species makes **8** species useful as acid–base indicators in nonaqueous media. The major result of the present study is the first detailed demonstration that the high-yield metaloxylation reaction (4) is applicable to palldated azobenzenes in acetonitrile media. There is a claim[43] that an air-sensitive Pd–OC complex is formed by *m*-CPBA oxidation of palladated dimethylbenzylamine. We also take note of the known[44] oxidative cleavage of M–C (M = Pd, Ni) bonds by peroxo reagents. A review of the use of cyclopalldated complexes in organic synthesis has recently appeared.[45]

We have briefly examined the efficacy of other peroxo reagents such as hydrogen peroxide and *tert*-butyl hydroperoxide. The reactions are generally very sluggish, and details remains to be worked out. In aqueous dioxane the metallacycle **4a** is oxidized by excess H_2O_2 to afford the bis complex **6a**, the yield being only ~10% after 4 days. Excess *tert*-butyl hydroperoxide oxidizes **8b** to **11** in acetonitrile, but completion of reaction takes several days. In contrast the metaloxylation of **8b** by *m*-CPBA is complete in <2 min at room temperature.

The observed third-order kinetics of the **9c** → **10c** reaction was somewhat unexpected. But a post facto molecular rationalization has been devised by taking into account the known bridging ability of the peroxo function. The present result in no way proves that the metaloxylation reactions of **4** and **8** described in the work proceed by the same route. Further studies in this area as well as on the generalization of the metaloxylation reaction to other cyclometalated species are in progress.

Experimental Section

Materials. Disodium tetrachloropalladate(II) was prepared by reacting palladium(II) chloride with sodium chloride in water and evaporating the aqueous solution. Commercial *m*-chloroperbenzoic acid was purified by a reported procedure[46] and was used after determining active oxygen content by iodometric titrations. All other chemicals and solvents used for the preparative works were of reagent grade and were used without further purification. Commercially available BDH silica gel (60–120 mesh) was used for column chromatography and in other experiments.

Equipment. Visible and ultraviolet spectra were taken with a Hitachi 330 spectrophotometer fitted with a thermostated cell compartment. Infrared spectra were taken on a Perkin-Elmer 783 spectrophotometer, and ^1H NMR data were collected in $CDCl_3$ solvent with the help of Varian XL200 and Bruker 270-MHz FT spectrometers. Molecular weights were determined by using a Knauer vapor pressure osmometer with benzil as calibrant.

Synthesis of Compounds: Azobenzenes. The unsubstituted compound **3a** was prepared from nitrobenzene by following a reported method.[47] **2,6,5′-Trimethylazobenzene (3b)** was prepared by condensing equimolar quantities of 3-methylnitrosobenzene and 2,6-dimethylaniline in glacial acetic acid.[48] The pure ligand was isolated by column chromatography of the ether extract of the condensed product using benzene as eluant. Subsequent evaporation of the eluant in vacuo afforded the ligand as a dense brown-red liquid. For the synthesis of **2-hydroxyazobenzene (3c)**, 2-methoxyazobenzene was first prepared by a reported method[48] and subsequently demethylated in dichloromethane solvent with the help of a diethyl ether solution of BBr_3. The crude product so obtained was recrystallized from aqueous ethanol (95%), affording brown-red crystals melting[49] at 83 °C. The compounds **2-hydroxy-5-methylazobenzene (3d)**, **2-hydroxy-5,4′-dimethylazobenzene (3e)**, and **2-hydroxy-5,2′,6′-trimethylazobenzene (3f)** were prepared[17,24] by coupling the appropriately substituted diazotized aniline with *p*-cresol. The compounds **2-(methylthio)azobenzene (3g)**, **2-(methylthio)azo(*m*- or *p*-)toluene (3h or 3i)**, **2-(benzylthio)azobenzene (3j)**, and **2-(benzylthio)azo(*m*- or *p*-)toluene (3k or 3l)** were synthesized[24,27] by condensing the appropriate 2-(alkylthio)aniline with nitrobenzene or *m*- or *p*-nitrotoluene. **2,2′-Dihydroxyazobenzene (3m)** was synthesized by fusing 2-nitrophenol, potassium hydroxide, and potassium acetate together as is reported in the literature.[49] The recrystallized (from alcohol) compound melts at 170 °C (lit.[49] mp 171–172 °C). The ligands **2-(methylthio)-2′-hydroxy-5′-methylazobenzene (3n)** and **2-(benzylthio)-2′-hydroxy-5′-methylazobenzene (3o)** were prepared by condensing *p*-cresol with the diazotized solution of 2-(alkylthio)aniline and 2-(benzylthio)aniline, respectively.[50]

Preparation of Complexes. ***trans*-Bis(μ-chloro)bis(((5′-methylphenyl)azo)-2,6-dimethylphenyl-*C*$^{2'}$,*N*)dipalladium(II) (4b).** An ethanolic solution (10 mL) of 2,6,5′-trimethylazobenzene (224 mg, 1 mmol) was added to an ethanolic solution (10 mL) of Na_2PdCl_4 (294 mg, 1 mmol), and the reaction mixture was kept in air for 12 h. Yellow-orange crystals thus obtained were filtered, washed successively with water and ethanol, and dried over P_4O_{10}; yield 50%. Anal. Calcd for $Pd_2C_{30}H_{30}N_4Cl_2$: C, 49.34; H, 4.11; N, 7.67; Cl, 9.72. Found: C, 49.41; H, 4.05; N, 7.70; Cl, 9.85. Complex **4a** was prepared similarly in 90% yield. In the reported preparation[15] of **4a** aqueous dioxane was used as solvent.

Bis((phenylazo)-2-phenolato-*N*,*O*)palladium(II) (6a) was synthesized by following a general reported method,[22] and **6b** was prepared similarly. The yield of **6a** was 80%. Anal. Calcd for $PdC_{24}H_{18}N_4O_2$: C, 57.55; H, 3.60; N, 11.19. Found: C, 57.45; H, 3.60; N, 10.90. The yield of **6b** was 78%. Anal. Calcd for $PdC_{30}H_{30}N_4O_2$: C, 61.60; H, 5.13; N, 9.58. Found: C, 61.55; H, 5.09; N, 9.55.

Bis(μ-chloro)bis(((2-hydroxyphenyl)azo)phenyl-*C*$^{2'}$,*N*)dipalladium(II) (7a). 2-Hydroxyazobenzene (200 mg, 1.01 mmol) was dissolved in dry ethanol (20 mL). The solution was heated, and to the hot solution was added a Na_2PdCl_4 (295 mg, 1.00 mmol) solution in dry ethanol (10 mL). The reaction mixture was heated to reflux for 6 h. The solution was concentrated and filtered, and the solvent was then completely evaporated in vacuo. The dry mass was washed with hexane (3 × 5 mL), and the residue was dried in vacuo; yield 90%. Complex **7b** was also prepared similarly; yield 80%. Anal. Calcd for $Pd_2C_{24}H_{18}N_4O_2Cl_2$ (**7a**): C, 42.50; H, 2.66; N, 8.26. Found: C, 42.40; H, 2.56; N, 8.40. Anal. Calcd for $Pd_2C_{28}H_{26}N_4O_2Cl_2$ (**7b**): C, 45.80; H, 3.54; N, 7.63. Found: C, 46.00; H, 3.60; N, 7.65.

(Triphenylphosphine)((phenylazo)-2-phenolato-*C*$^{2'}$,*N*,*O*)palladium(II) (8a). A mixture of Na_2PdCl_4 (300 mg, 1.02 mmol) (or $PdCl_2$; 180 mg, 1.02 mmol) and 2-hydroxyazobenzenes (200 mg, 1.01 mmol) were heated to reflux in dry ethanol (30 mL) for 6 h. The reaction mixture was filtered hot. The filtrate was concentrated over a steam bath to 20 mL. An equal volume of water was then added, and the mass was stirred magnetically for 2 h. The precipitate was collected by filtration and washed successively with hexane (3 × 2 mL) and dichloromethane (3 × 2 mL). It was then suspended in ethanol (20 mL), and triphenylphosphine (270 mg, 1.03 mmol) was added in pinches over 15 min. The solution color changed from pink to blue. Stirring was continued for 1 h. The mass was evaporated to dryness and extracted with dichloromethane (5 × 3 mL). The extract was chromatographed on a silica gel column (50 × 1 cm) prepared in benzene. Pure acetonitrile was used as eluant. A deep blue band separated out. The blue eluant was evaporated in vacuo. It was recrystallized from a 1:5 dichloromethane–hexane mixture to yield dark-colored shining crystals, yield 70%. Anal. Calcd for $PdC_{30}H_{23}N_2OP$: C, 63.78; H, 4.08; N, 4.96. Found: C, 63.95; H, 3.95; N, 5.00.

Other complexes of type **8** were synthesized similarly by using appropriate ligands and by substituting triphenylphosphine with pyridine and γ-picoline where required. Yields varied in the range 70–80%. Anal. Calcd for $PdC_{17}H_{13}N_3O$ (**8b**): C, 53.49; H, 3.41; N, 11.01. Found: C, 53.52; H, 3.45; N, 10.95. Calcd for $PdC_{31}H_{25}N_2OP$ (**8c**): C, 64.32; H, 4.32; N, 4.84. Found: C, 64.30; H, 4.40; N, 4.80. Calcd for $PdC_{19}H_{17}N_3O$ (**8d**): C, 55.69; H, 4.15; N, 10.26. Found: C, 55.50; H, 4.12; N, 10.30. Calcd for $PdC_{32}H_{27}N_2OP$ (**8e**): C, 64.82; H, 4.56; N, 4.73. Found: C, 64.75; H, 4.61; N, 4.62. Calcd for $PdC_{19}H_{17}N_3O$ (**8f**): C,

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55.69; H, 4.15; N, 10.26. Found: C, 55.70; H, 4.10; N, 10.20.

Chloro(((2-(methylthio)phenyl)azo)phenyl-$C^{2'},N,S$)palladium(II) (9a). To an ethanolic (10 mL) solution of Na_2PdCl_4 (100 mg, 0.34 mmol) was added slowly a warm (313 K) ethanolic (20 mL) solution of 2-(methylthio)azobenzene (80 mg, 0.35 mmol). The color of the solution gradually changed from yellow to brown-red. The reaction mixture was heated on a water bath for 1.5 h. The hot solution was then left in air to evaporate. Shining crystals were collected by filtration, washed with 25% ethanol in water, and then dried over P_4O_{10} under vacuum; yield 70%. Anal. Calcd for $PdC_{13}H_{11}N_2ClS$: C, 42.29; H, 2.98; N, 7.59. Found: C, 42.35; H, 3.00; N, 7.60.

The substituted analogues of **9a** were synthesized similarly. Yields varied in the range 65–75%. Anal. Calcd for $PdC_{14}H_{13}N_2ClS$ (**9b**): C, 43.88; H, 3.40; N, 7.31. Found: C, 43.85; H, 3.40; N, 7.35. Calcd for $PdC_{20}H_{17}N_2ClS$ (**9c**): C, 52.30; H, 3.70; N, 6.10. Found: C, 52.40; H, 3.75; N, 6.12. Calcd for $PdC_{14}H_{13}N_2ClS$ (**9d**): C, 43.88; H, 3.40; N, 7.31. Found: C, 44.00; H, 3.45; N, 7.25.

Chloro(((2-(benzylthio)phenyl)azo)-5′-methyl-2′-phenolato-O,N,S)palladium(II) (10c). A hot ethanolic (15 mL) solution of 2-(benzylthio)-2′-hydroxy-5′-methylazobenzene (100 mg, 0.30 mmol) was added to an ethanolic (15 mL) solution of Na_2PdCl_4 (88 mg, 0.30 mmol). The reaction mixture was heated over a water bath for 2.5 h. A violet crystalline precipitate that was formed was filtered and washed with a 1:1 ethanol–water mixture (3 × 5 mL). The crude product was dissolved in acetonitrile (10 mL) and adsorbed in 2 g of silica gel. The mass was then dried in air and transferred over to a silica gel column (30 × 1 cm) prepared in benzene. The orange band of unreacted ligand was eluted with benzene. The red-violet band of pure compound was then eluted with a benzene–acetonitrile mixture (15% acetonitrile). Crystals were obtained by complete evaporation of the solution in vacuo; yield 70%. Anal. Calcd for $PdC_{20}H_{17}N_2OClS$: C, 50.54; H, 3.58; N, 5.90. Found: C, 50.50; H, 3.55; N, 5.95. Complex **10b** was also prepared similarly; yield 72%. Anal. Calcd for $PdC_{14}H_{13}N_2OClS$: C, 42.12; H, 3.26; N, 7.02. Found: C, 42.10; H, 3.30; N, 7.05.

Complex 5b. To an ethanolic solution (20 mL) of 2,6,5′-trimethyl-2′-hydroxyazobenzene (240 mg, 1.00 mmol) was added $PdCl_2$ (177 mg, 1.00 mmol) (or Na_2PdCl_4; 294 mg, 1.00 mmol). The reaction mixture was then heated to reflux for 6 h under a dinitrogen atmosphere. The solvent was removed under vacuum. The dry mass was washed with hexane (3 × 5 mL) and was extracted with dichloromethane (3 × 5 mL). The extract was subjected to column chromatography. The yellow band of unreacted ligand was eluted first by benzene. The desired compound was then eluted from the column by a 5% solution of acetonitrile in benzene. The brown-red solution on evaporation in vacuo gave shining crystals of the pure compound, yield 40%. Anal. Calcd for $PdC_{15}H_{15}N_2OCl$: C, 47.26; H, 3.94; N, 7.35; Cl, 9.31. Found: C, 47.20; H, 3.90; N, 7.30; Cl, 9.61.

(Pyridine)(2,2′-dihydroxyazobenzenato-O,N,O)palladium(II) (11). The ligand 2,2′-dihydroxyazobenzene was reacted with Na_2PdCl_4 by following the reported method[17] with some minor modifications. Ethanol was used in place of dimethyl sulfoxide, and the reaction time was 3 h; yield 85%. Anal. Calcd for $PdC_{17}H_{13}N_3O_2$: C, 51.33; H, 3.27; N, 10.57. Found: C, 50.22; H, 3.20; N, 10.60.

Reaction on Silica Gel Surface: 6a → 8a. Complex **6a** (100 mg) was dissolved in dichloromethane (15 mL) and was adsorbed on silica gel (15 g). The solvent was removed in air. The colored mass was heated at (353 ± 5) K for 24 h. A solution of triphenylphosphine (52 mg) in acetonitrile (20 mL) was added to the cooled silica gel. The acetonitrile extract (3 × 10 mL) on evaporation (in vacuo) gave the crude complex. This was dissolved in dichloromethane (15 mL) and was subjected to chromatography on a silica gel column (30 × 1 cm) in benzene. A deep blue band was eluted with acetonitrile. On evaporation of the solvent dark shining crystals were deposited; yield 12%.

Oxidation by *m*-CPBA. (a) 4b → 5b + 6b. To an acetonitrile solution (70 mL) of **4b** (100 mg, 0.14 mmol) was added dropwise with magnetic stirring a solution of *m*-CPBA (78 mg, 0.45 mmol) in the same solvent (15 mL). Stirring was continued for 3 h. The reaction mixture was then evaporated to dryness in vacuo. The residue was thoroughly washed with a 1:1 ethanol–water mixture (5 × 5 mL) and then with diethyl ether (2 × 3 mL) to remove any unreacted *m*-CPBA and its reduced product, *m*-CBA. The residue so left was then dissolved in chloroform (10 mL), and the solution was chromatographed over a silica gel column (45 × 1 cm) in benzene. The pink-violet band of **6b** was eluted first by benzene. Evaporation (in vacuo) of the eluant gave the solid compound in 10% yield. The complex **5b** was eluted by a 5% solution of acetonitrile in benzene. Evaporation of this solution in vacuo yields pure crystalline compound in 50% yield. Anal. Calcd for $PdC_{15}H_{15}N_2OCl$: C, 47.26; H, 3.94; N, 7.35. Found: C, 47.40; H, 4.10; N, 7.40.

The reaction of *m*-CPBA with **4a** proceeded similarly, affording **5a** and **6a** both in 30% yield. Anal. Calcd for $PdC_{12}H_9N_2OCl$ (**5a**): C, 42.50; H, 2.66; N, 8.26. Found: C, 42.60; H, 2.52; N, 8.30.

(b) 8b → 11. Complex **8b** (15 mg, 0.038 mmol) was dissolved in acetonitrile (10 mL). To this solution was added an acetonitrile (5 mL) solution of *m*-CPBA (7 mg, 0.040 mmol). The reaction mixture was stirred for 10 min. The color changed from bluish green to orange-yellow. The solvent was then evaporated in vacuo. The dry mass so obtained was washed with 1:1 ethanol–water (5 × 3 mL), and the residue was again dried over P_4O_{10} under vacuum. Pure orange-red crystals were obtained by slow diffusion of the dichloromethane solution (2 mL) of the compound into hexane (10 mL); yield 80%. Anal. Calcd for $PdC_{17}H_{13}N_3O_2$: C, 51.33; H, 3.27; N, 10.57. Found: C, 51.30; H, 3.30; N, 10.55.

(c) 9c → 10c. A solution of *m*-CPBA (52 mg, 0.30 mmol) in acetonitrile (15 mL) was added dropwise with magnetic stirring to a solution of complex **9c** (120 mg, 0.26 mmol) in the same solvent (60 mL). Stirring was continued for 1.5 h. The purification steps are same as in (a) above; yield of **10c** 82%. Anal. Calcd for $PdC_{20}H_{17}N_2OClS$: C, 50.54; H, 3.58; N, 5.90. Found: C, 50.50; H, 3.60; N, 5.86.

The oxidations **9a → 10a** and **9b → 10b** were carried out similarly with similar yields. Anal. Calcd for $PdC_{13}H_{11}N_2OClS$ (**10a**): C, 40.53; H, 2.86; N, 7.28. Found: C, 40.50; H, 2.90; N, 7.31. Calcd for $PdC_{14}H_{13}N_2OClS$ (**10b**): C, 42.12; H, 3.26; N, 7.02. Found: C, 42.15; H, 3.21; N, 6.95.

Kinetic Measurements. All the kinetic experiments were performed at 295.8 K in acetonitrile. Desired volumes of the thermostated reactants were mixed, diluted to required volumes, and transferred to an absorption cell of 1 cm path length. All operations were done quickly. Absorbance (A_t) at 545 nm was recorded (directly from the digital display of the spectrophotometer) as a function of time. A_∞ was measured when intensity changes leveled off. Values of pseudo-second-order rate constants (k_{obsd} = slope × $\Delta\epsilon$) were obtained from the slope of the plots of the $1/(A_\infty - A_t)$ vs. t line.

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Registry No. **3a**, 103-33-3; **3b**, 102073-17-6; **3c**, 2362-57-4; **3g**, 101418-85-3; **3h**, 102073-18-7; **3k**, 102073-19-8; **4a**, 54865-84-8; **4b**, 93492-92-3; **5a**, 102109-71-7; **5b**, 102109-73-9; **6a**, 15632-65-2; **6b**, 102109-74-0; **7a**, 102109-75-1; **7b**, 102132-68-3; **8a**, 93492-96-7; **8b**, 102109-76-2; **8c**, 102109-77-3; **8d**, 102109-78-4; **8e**, 102132-69-4; **8f**, 102109-79-5; **9a**, 102109-80-8; **9b**, 102109-81-9; **9c**, 102109-82-0; **9d**, 102109-83-1; **10a**, 102109-84-2; **10b**, 102109-85-3; **10c**, 102109-86-4; **11**, 69968-22-5; *m*-CPBA, 535-80-8; Na_2PdCl_4, 13820-53-6.