112988-08-6; $\{[Mn^{II}(PA)_2]_2(N\text{-Oct-disal})\}^{2-}$, 112988-20-2; $\{[Mn^{IV}(PA)_2]_2(N\text{-Oct-disal})\}^{2+}$, 112988-21-3; $\{[Mn^{III}(PA)_2]_2(sal\text{-}m\text{-Xyln})\}$, 112988-09-7; $\{[Mn^{II}(PA)_2]_2(sal\text{-}m\text{-Xyln})\}^{2-}$, 113008-22-3; $\{[Mn^{IV}(PA)_2]_2(sal\text{-}m\text{-Xyln})\}^{2+}$, 112988-22-4; $\{[Mn^{III}(PA)_2]_2(salhn)\}$, 112988-10-0; $\{[Mn^{II}(PA)_2]_2(salhn)\}^{2-}$, 112988-23-5; $\{[Mn^{IV}(PA)_2]_2(salhn)\}^{2+}$, 112988-24-6; $\{[Mn^{III}(PA)_2]_2(disal)\}$, 112988-11-1; $\{[Mn^{II}(PA)_2]_2(disal)\}^{2-}$, 112988-25-7; $\{[Mn^{IV}(PA)_2]_2(disal)\}^{2+}$, 112988-26-8; $\{[Mn^{III}(salpn)]_2(sal\text{-}m\text{-Xyln})\}$, 112988-12-2; $\{[Mn^{II}(salpn)]_2(sal\text{-}m\text{-Xyln})\}^{2-}$, 113008-23-4; $\{[Mn^{IV}(salpn)]_2(sal\text{-}m\text{-Xyln})\}^{2+}$, 112988-29-1; $\{[Mn^{III}(salpn)]_2[C_3(PA)_2]\}$, 112988-13-3; $\{[Mn^{II}(salpn)]_2[C_3(PA)_2]\}^{2-}$, 112988-30-4; $\{[Mn^{IV}(salpn)]_2[C_3(PA)_2]\}^{2+}$, 113008-24-5; $\{(\mu\text{-}O)_2[Mn^{III/IV}(PA)(bpy)]_2\}^{+}$, 112988-14-4; $\{(\mu\text{-}O)_2[Mn^{III}(PA)(bpy)]_2\}$, 112988-31-5; $\{(\mu\text{-}O)_2[Mn^{IV}(PA)(bpy)]_2\}^{2+}$, 112988-32-6; H_2O, 7732-18-5; O_2, 7782-44-7; 4,4′-trimethylenebis(pyridine), 17252-51-6.

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Aromatic Hydroxylation via Cyclometalation. Metaloxylation of Palladated 2-(Alkylsulfinyl)azobenzenes

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Several azo sulfoxide ligands belonging to the class 2-(sulfinyl)azobenzenes (**3**) have been synthesized: $C_6H_4(R')—N{=}N—C_6H_4X$ (R′ = H, 4′-Me, 5′-Me; X = 2-S(O)R, R = Me, CH_2Ph). These react with Na_2PdCl_4 in ethanol, affording brown-red cyclopalladated species having the coordination sphere Pd(C,N,S)Cl (**4**). The mode of ligand binding is established with the help of high-resolution ^1H NMR and IR data. In chloroform solution **4** reacts with *m*-chloroperbenzoic acid (mCPBA), resulting in high-yield regiospecific oxidation (metaloxylation) of the C–Pd moiety into C–O–Pd. The resulting pink-violet Pd(O,N,S)Cl complexes (**5**) have been characterized spectroscopically and in one case by independent synthesis via a nonoxidative route. From **5** the free hydroxyazo ligand (**6**) can be liberated via reductive (hydrazine) elimination of the metal. The metalation–metaloxylation–demetalation sequence thus affords a high-yield route for regiospecific aromatic hydroxylation of the azobenzenes under consideration. The kinetics of the metaloxylation reaction has been examined in two cases. The rate law is $d[5]/dt = k[4]\cdot[mCPBA]$. The enthalpy of activation is small (~9 kcal). The large negative entropy of activation (~−30 eu) suggests an associative mechanism. It is proposed that in the transition state mCPBA binds to the metal center via peroxy oxygen followed by heterolytic cleavage of the O–O bond and oxygen insertion into the Pd–C bond.

Introduction

A major goal of current chemical research is to achieve metal-catalyzed activation of the C–H bond. So activated, the bond is a potent site for chemoselective transformations that are otherwise difficult or impossible to achieve. Hydroxylation of the aromatic ring (eq 1)is an example per se. Metal ion mediation

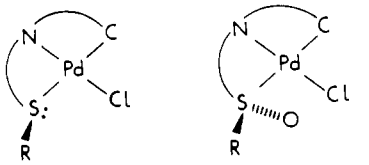
$$Ar–H \rightarrow Ar–OH \qquad (1)$$

of one form or another is frequently obligatory for this reaction to occur either in vivo or in vitro.[1-9] This work concerns the metal-promoted aromatic hydroxylation route stated in eq 2. In

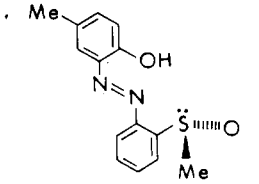
$$Ar–H \xrightarrow{i} Ar–M \xrightarrow{ii} ArOM \xrightarrow{iii} ArOH \qquad (2)$$

step i arene C–H activation[10] affords Ar–M into which oxygen is inserted in step ii. Subsequent demetalation (step iii) affords the net reaction of eq 1. Very little is however known about oxygen insertion into the Ar–M bond, step ii.[3,11-13] This has seriously limited practical application of eq 2 for achieving aromatic hydroxylation.

Recently we have initiated a program for defining the scope and nature of the reaction Ar–M → Ar–OM, which has been called aromatic metaloxylation. Certain cyclopalladated azobenzenes were shown to undergo facile metaloxylation by *m*-chloroperbenzoic acid (mCPBA). In the particular case of azobenzene thioether complexes having coordination sphere **1**, the



1 **2**



6

Pd–C bond was selectively oxygenated but the sulfur center remained unreactive and sulfoxide formation did not occur.[3]

Herein we describe the successful synthesis of metalated azo sulfoxide species of coordination type **2** by metalation of preformed ligands. The major point of interest is that both in terms of high yields and mechanistic simplicity **2** represents a model substrate

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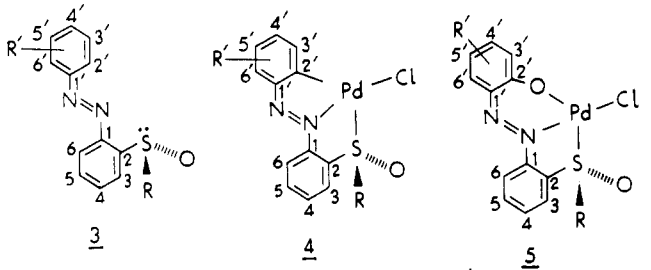
for metaloxylation by mCPBA. The metaloxylated complexes have been isolated in the pure state, and in one case the corresponding phenolic ligand has been liberated in the free state by reductive elimination of the metal ion. All steps of eq 2 have thus been realized. The metalated precursors (**2**) and their metaloxylated congeners have been structurally characterized with the help of spectroscopic techniques.

Results and Discussion

A. Azo Sulfoxide Ligands and Their Cyclopalladation. The azobenzene sulfoxide ligands used in the present work (**3a–d**) can



	R	R′
3a, 4a, 5a	Me	H
3b, 4b, 5b	CH_2Ph	H
3c, 4c, 5c	Me	4′-Me
3d, 4dα, 5dα	Me	5′-Me
4dβ	Metalation at 6′ (see text)	

be systematically named as 2-(alkylsulfinyl)azobenzenes. These were synthesized in good yields by oxidizing the corresponding sulfides with hydrogen peroxide in acetic acid. Azo sulfoxides of the present type do not appear to have been reported earlier.

Reaction of **3** with Na_2PdCl_4 in aqueous EtOH at room temperature affords the dark colored complexes **4** in excellent yield. In the case of ligand **3d**, ortho metalation can in principle occur at positions 2′ or 6′. Two isomers designated α and β are indeed formed in practice. These have been characterized with the help of ^1H NMR (see below). Attempted isomer separation by chromatography has, however, not succeeded. All complexes are electrical nonconductors in solution and display Pd–Cl stretches in the region 330–340 cm^{-1}.

B. Spectra and Bonding Mode. a. IR and UV–Vis Spectra. Sulfoxides are ambidentate in character and can bind palladium(II) through oxygen or sulfur atoms.[14] The free ligands (**3**) display a strong band near 1040 cm^{-1} assignable to ν_{SO}. This band is blue shifted to the region 1100–1160 cm^{-1} (Table I) in **4**, strongly suggesting that coordination occurs through sulfur and not through oxygen (oxygen binding shifts ν_{SO} to ~900 cm^{-1}).[14-17] Confirmatory NMR evidence is presented below. The complexes afford brown-red solutions in organic solvent and display characteristic spectra in the UV–vis region (Table I). Strong absorptions observed around 500 nm (absent in free ligands) are characteristic of ortho palladation and probably represent $\pi-\pi^*$ transitions localized on the metalated azobenzene fragment.[18]

b. High-Resolution ^1H NMR Spectra. Sulfur coordination of sulfoxide ligands to metals is reflected in two ways in high-resolution ^1H NMR spectra: (i) a downfield shift of the S–R (e.g. R = Me) signal from the free ligand position and (ii) an increase in the inequivalence of methylene protons of S–R (e.g. R = CH_2Ph) compared to the free ligand value.[14-16,19] Selected chemical shift ($CDCl_3$ solvent) data for **3** and **4** are collected in Table II. The S–Me signals of **4a** and **4c** occur at ~0.5 ppm downfield from those of **3a** and **3c**, respectively. The methylene protons are inequivalent in both **3b** (δ 4.12, 4.34) and **4b** (δ 4.62, 5.02). In each case they give rise to a well-resolved pair of doublets at 500 MHz. The geminal coupling constant is ~ 13 Hz. The **4b** methylene protons are shifted (by ~0.6 ppm) downfield and display greater (by ~0.2 ppm) separation compared to the **3b** protons. The complexes are thus S-bonded.

Table I. UV–vis[a] and IR[b] Spectral Data

compd	λ_{max}, nm (ε, M^{-1} cm^{-1})	$\nu_{S=O}$, cm^{-1}
3b	450 (500), 300 (19 000), 230 (19 200)	1040
3c	450 (700), 340 (22 000), 235 (15 500)	1040
4a	500 (3200),[d] 465 (3900), 410 (8700), 370 (11 050), 355 (11 000), 320 (9000)[d]	1115
4b	500 (2800),[d] 470 (3700), 410 (8000), 375 (10 800), 355 (11 400), 310 (11 600)[d]	1115
4c	500 (6000),[d] 470 (7000), 410 (10 500), 370 (10 700), 360 (10 600), 320 (9400)	1120
4d[c]	510 (2700),[d] 480 (3300), 415 (9300), 375 (10 100), 360 (10 400), 330 (9300)[d]	1115
5a	535 (7200), 390 (6600),[d] 370 (9500), 330 (10 400)	1140
5b	540 (6700), 390 (6300),[d] 370 (9000), 335 (10 400)	1145
5c	535 (6600), 400 (8700),[d] 380 (10 700), 335 (8600)	1145
5dα	565 (7100), 400 (6800),[d] 383 (9500), 345 (10 000)	1145
6	410 (8700), 325 (17 600), 240 (8000)	1030

[a] In dichloromethane. [b] In KBr disks. [c] Mixture of α and β isomers. [d] Shoulder.

The presence of two isomers (α and β) in preparations of **4d** is clearly revealed in the methyl region. The free ligand shows S–Me and 5′-Me signals as sharp singlets at 2.87 and 2.48 ppm respectively. In **4d** two S–Me signals occur at 3.41 and 3.39 ppm (note the deshielding due to S-coordination in both cases) in the intensity ratio 2:3. The two corresponding 5′-Me signals are at 2.80 and 2.42 ppm. The following assignments have been made. **4dα**: S-Me, 3.39 ppm; 5′-Me, 2.42 ppm. **4dβ**: S-Me, 3.41 ppm; 5′-Me, 2.80 ppm. The sizable downfield shift of the 5′-Me signal in the β-isomer is due to the close proximity of the metal–carbon bond.[20] This isomer involves metalation at a hindered position and is therefore formed in lower percentage (40%) compared to the α-isomer (60%).

All aromatic proton signals of **3a**, **4a**, **3c**, and **4c** have been completely assigned on the basis of (i) spin–spin structure and changes therein on substitution, (ii) shift of signals to higher field upon aromatic ring methylation, and (iii) comparison with the spectra of corresponding thioether species, **1**. Regarding item (iii), we note that aromatic protons are systematically deshielded in going from **1** to **4**, the effect being particularly prominent in the case of 3-H, 4-H, and 5-H. The difference in δ values of **4c** and its corresponding thioether analogue[3] are as follows: 3-H, 0.50; 4-H, 0.24; 5-H, 0.30; 6-H, 0.13; 3′-H, 0.12; 5′-H, 0.04; 6′-H, 0.07 ppm. Assignments are shown schematically in Figure 1, and data are collected in Table II. Metalation at the 2′-position in **4c** is firmly expressed in the singlet nature of its 3′-H signal. This signal occurs as a doublet in **4a**. The spectra of both **3b** and **4b** in the aromatic region are complicated by signals from the CH_2Ph substituent. In the case of **4d** complications arise from the existence of α and β isomers. No attempt was made to assign spectra in these cases.

C. Reaction with mCPBA. a. Metaloxylation. Upon addition of mCPBA to solutions of **4** in chloroform, the color changes from

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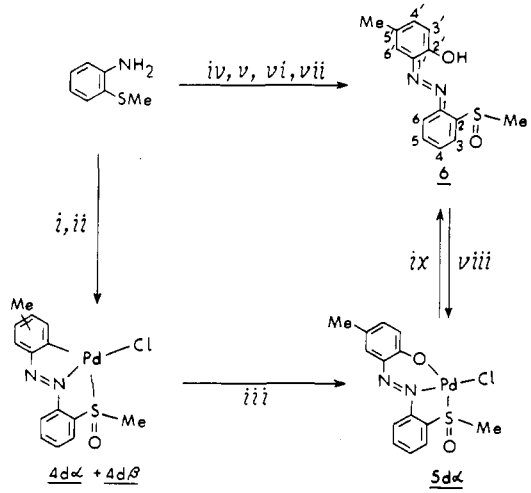
Table II. ^{1}H NMR Spectral Data in $CDCl_3$

	δ (J, Hz)										
compd	6-H[a]	5-H[b]	4-H[b]	3-H[a]	6′-H	5′-H	4′-H	3′-H	2′-H[a]	S-Me	others
3a	8.29 (8.0)	7.72 (8.0)	7.72 (8.0)	8.00 (8.0)	7.96[a] (8.0)	7.58[d] (8.0)	7.58[d] (8.0)	7.58[d] (8.0)	7.96 (8.0)	2.91	
3c	8.29 (8.0)	7.76 (8.0)	7.68 (8.0)	8.00 (8.0)	7.87[a] (8.0)	7.41[a] (8.0)		7.41[a] (8.0)	7.87 (8.0)	2.92	2.48[e]
3d	8.26 (8.0)	7.72 (8.0)	7.68 (8.0)	7.96 (8.0)	7.40[c]		7.40[a] (8.0)	7.64[b] (8.0)	7.68 (8.0)	2.87	2.48[f]
4a	8.35 (9.0)	7.85 (8.7)	7.83 (7.8)	8.20 (8.4)	8.06[a] (8.4)	7.37[b] (7.8)	7.41[b] (8.4)	7.93[a] (8.7)		3.41	
4c	8.32 (9.3)	7.83 (7.5)	7.80 (7.5)	8.20 (8.4)	7.94[a] (7.8)	7.16[a] (7.8)		7.72[c]		3.39	2.43[e]
5c	8.26 (8.0)	7.74 (8.0)	7.66 (8.0)	8.00 (8.5)	7.56[a] (8.0)	6.72[a] (9.0)		7.08[c]		3.72	2.32[e]
5dα	8.26 (8.0)	7.76 (8.0)	7.60 (8.0)	8.02 (8.0)	7.41[c]		7.08[a] (8.0)	7.34[a] (8.0)		3.70	2.28[f]
6	8.32 (8.0)	7.76 (8.0)	7.70 (8.0)	8.00 (8.0)	7.76[c]		7.00[a] (8.0)	7.28[a] (8.0)		2.80	2.36[f], 11.76[g]

[a] Doublet. [b] Triplet. [c] Singlet. [d] Center of complex multiplet. [e] 4′-Me. [f] 5′-Me. [g] 2′-OH.

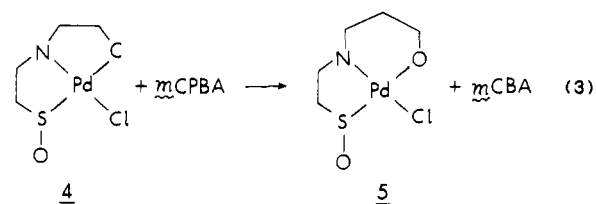
Scheme I[a]



[a] Key: (i) *m*-$CH_3C_6H_4NO$/AcOH, H_2O_2; (ii) Na_2PdCl_4; (iii) mCPBA, chromatography; (iv) $NaNO_2$/HCl, 273–277 K; (v) *p*-$CH_3C_6H_4OH/OH^-$; (vi) H_2O_2/OH^-; (vii) H^+; (viii) Na_2PdCl_4; (ix) $N_2H_4 \cdot H_2O$.

brown-red to pink-violet. Removal of solvent followed by purification affords complex **5** in high yields. Complex **4d** was shown above to consist of α and β isomers. In reaction with mCPBA each isomer is presumably metaloxylated to the corresponding oxidized isomer (e.g. **4dα** → **5dα**). Chromatography on silica gel afforded one isomer in the pure form in 50% yield bases on **4d**. High-resolution ^{1}H NMR spectra showed this to be the α isomer (see below). The species eluted from the chromatography column at a later stage (presumably the other isomer) forms a gum that could not be purified.

The metaloxylation reaction is stated in eq 3 where mCBA is *m*-chlorobenzoic acid. The stoichiometric formation of mCBA in the reaction was confirmed by its isolation.



That the reaction of **4** with mCPBA indeed results in metaloxylation as depicted in eq 3 was confirmed in the case of the oxidation of **4dα** to **5dα** by nonoxidative synthesis of **5dα** using preformed hydroxyazo sulfoxide ligand (**6**) as shown in Scheme I.

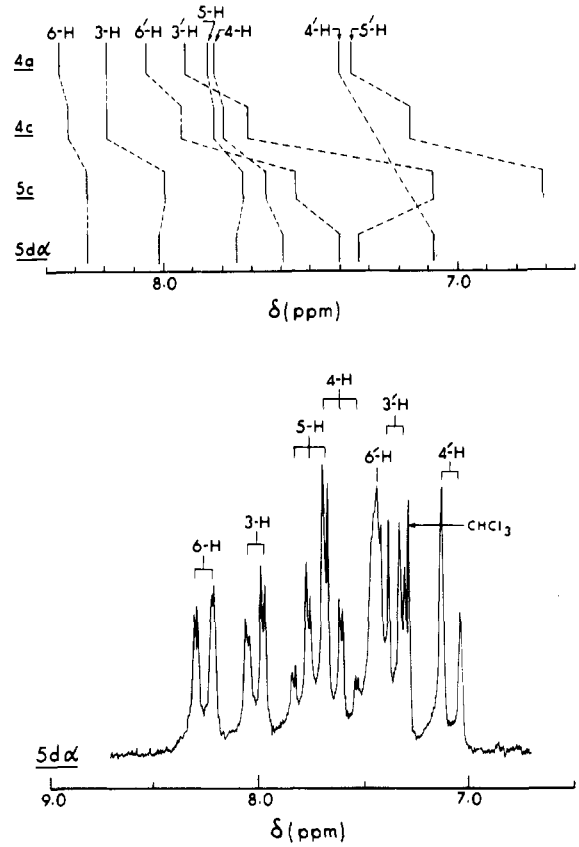


Figure 1. Schematic ^{1}H NMR spectra of **4a**, **4c**, **5c**, and **5dα** and observed spectrum of **5dα** in $CDCl_3$.

Complexes of type **5** lose metallic palladium upon treatment with hydrazine hydrate. In the case of **5dα** the liberated hydroxyazo sulfoxide ligand was isolated and shown to be identical with **6** (Scheme I). With this isolation, the regiospecific hydroxylation of **3d** into **6** via the metalation–metaloxylation–demetalation route defined in eq 2 is achieved.

b. Characterization of 5. The binding of palladium(II) through sulfur in **5** was established in the usual manner. The SO stretch is observed at ~1140 cm^{-1} (Table I). The methyl ^{1}H NMR signal displays a downfield shift of 0.90 ppm in going from **6** to **5dα** (Table II). Aromatic signals have been completely assigned in selected cases (Figure 1, Table II). These signals are generally shifted upfield in going from **4** to **5** (compare **4c** and **5c**)—the effect being particularly dramatic for the protons of the metaloxylated ring. This is expected in view of the electron-releasing function of the phenolic oxygen. Complexes of type **5** absorb strongly around 550 nm as well as at higher energies (Table I).

Table III. Rate Constants and Activation Parameters for the Metaloxylation of **4** in $CHCl_3$[a]

compd	T, K	10^3[mCPBA], M	$10^3 k_{obsd}$, s^{-1}	k, $M^{-1} s^{-1}$	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
4a	289	0.960	0.258 (1)	0.244 (4)	10.2 (7)	−26.4 (2.4)
		2.360	0.550 (2)			
		3.760	0.930 (2)			
		5.160	1.270 (2)			
	294	0.811	0.297 (3)	0.337 (5)		
		2.222	0.740 (2)			
		3.633	1.200 (2)			
		5.044	1.730 (4)			
	300	1.120	0.453 (2)	0.407 (6)		
		2.590	1.070 (3)			
		4.060	1.600 (1)			
		5.530	2.270 (2)			
	307	0.970	0.800 (2)	0.767 (9)		
		2.390	1.790 (1)			
		3.810	2.900 (2)			
		5.230	4.060 (1)			
4c	289	1.730	0.647 (4)	0.332 (6)	8.2 (7)	−32.6 (2.3)
		3.820	1.263 (2)			
		5.900	1.951 (2)			
		7.970	2.723 (2)			
	294	0.656	0.315 (2)	0.469 (5)		
		1.154	0.548 (4)			
		1.650	0.797 (6)			
		2.150	1.010 (2)			
	300	0.994	0.631 (6)	0.692 (22)		
		1.651	1.210 (2)			
		2.309	1.620 (1)			
		2.966	2.010 (6)			
	307	1.360	1.180 (18)	0.793 (33)		
		2.720	2.550 (15)			
		4.080	3.660 (35)			
		5.400	4.370 (20)			

[a] Least-squares deviations are given in parentheses.

c. Rate Law, Activation Parameters, and Mechanism. The kinetics of the metaloxylation reaction (eq 3) was studied in chloroform solvent at several temperatures in the range 289–307 K for the complexes **4a** and **4c**. Good isosbestic points were observed throughout the course of the reaction as illustrated for one case in Figure 2. Rates were followed by monitoring absorption (A_t) changes at 540 nm as a function of time (t). Under pseudo-first-order conditions (excess oxidant), the plot of $-\ln (A_\alpha - A_t)$ vs t for at least 85% of the reaction was excellently linear in each case. Thus the rate law of eq 4 applies. The observed

$$\text{rate} = d[\mathbf{5}]/dt = k_{obsd}[\mathbf{4}] \quad (4)$$

rate constant (k_{obsd}) varied linearly (Figure 3) with the concentration of mCPBA (eq 5). The metaloxylation of cyclopalladated

$$k_{obsd} = k[\text{mCPBA}] \quad (5)$$

azo sulfoxides thus follow a straightforward second-order rate law. This is in contrast to the more complex behavior (third-order rate law) of the thioether species of type **1**.[3] The origin of this difference is unclear at present, but the larger steric demand of the sulfoxide function (compared to thioether function) may have a role to play.

Variable-temperature rate constants and activation parameters are collected in Table III. The large negative entropy of activation supports an associative transition state. It is plausible that association occurs between the metal center and mCPBA peroxo oxygen as shown schematically in structure **7**. Binding of *tert*-butyl hydroperoxide to palladium(II) through peroxo oxygen has been documented.[21] Axial binding of perbenzoic acids to an iron(III) porphyrin is known.[22] In **7**, the proton is positioned so as to correspond ultimately to mCBA (eq 6). The electron movements suggested in **7** correspond to heterolytic cleavage of the O–O bond. The facile nature of this cleavage is reflected in

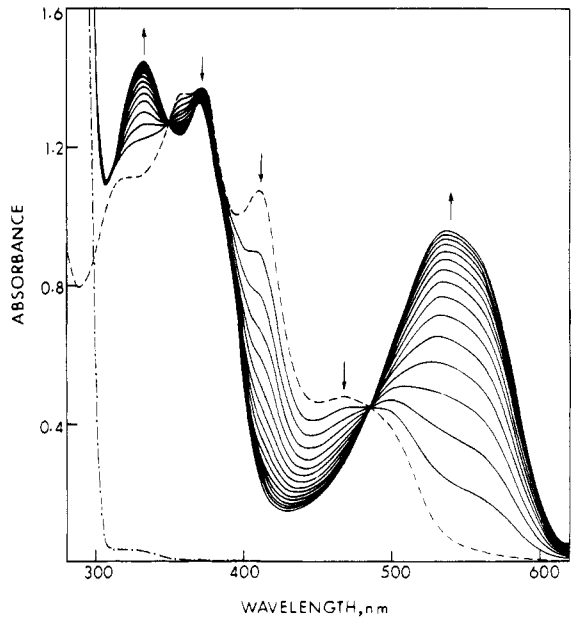
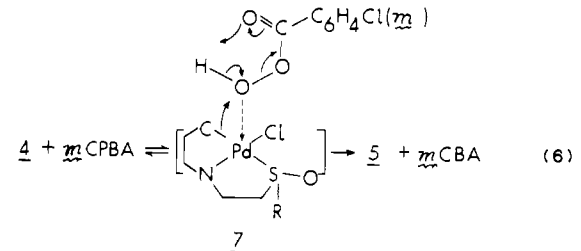


Figure 2. Spectra of pure 4a (- -), pure mCPBA (−·−), and a reaction mixture thereof (—) at 300 K in $CHCl_3$ solution. The arrows indicate increase and decrease of band intensities as reaction proceeds.



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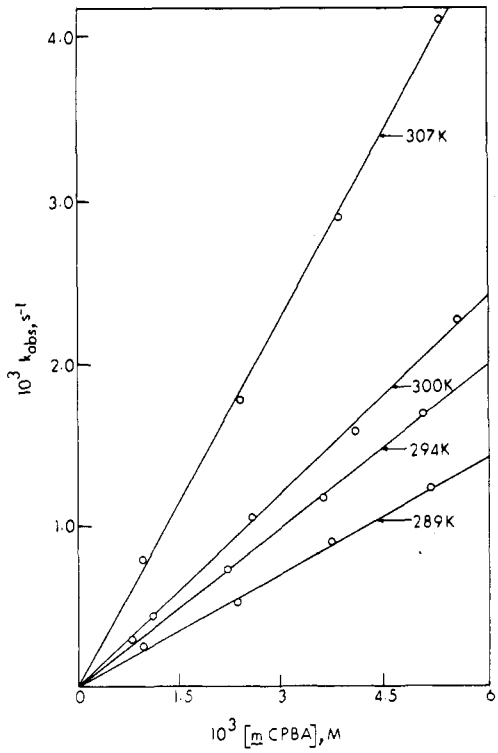

Figure 3. Variable-temperature k_{obsd} vs [mCPBA] for the oxidation of **4a** to **5a**.

the small enthalpy of activation ($\leq$10 kcal M^{-1}). Complex **4c** carries an electron-releasing methyl group in the metalated ring. Oxygen insertion into the Pd–C bond may therefore be expected to be more facile in **4c** than in **4a**. The metaloxylation of the latter complex is indeed slightly slower than that of the former. Further work on the proposed mechanism is in progress.

The kinetic data do not necessarily require that O–O bond cleavage and oxygen insertion into the metal–carbon bond are in strict concert. It is possible that a higher valent palladium oxo complex is transiently formed and undergoes very rapid internal oxygen transfer affording **5**. Formation of relatively stable higher valent oxo species via heterolytic O–O bond cleavage is well documented in the reaction of percarboxylic acids with complexes of 3d ions.[22-24] Such species are potent catalysts for organic oxidations such as olefin epoxidation.

D. Concluding Remarks. Azo sulfoxide ligands of the type 2-(alkylsulfinyl)azobenzenes have been synthesized and cyclopalladated. The resulting organometallics have proved to be model substrates for metaloxylation (C–Pd → C–OPd) by mCPBA. Using a metalation–metaloxylation–demetalation sequence, we have achieved the regiospecific hydroxylation of an azobenzene in high yield. The metaloxylation reaction involves heterolytic O–O bond cleavage, and the rate is first order in both complex and oxidant. The activation process is attended with a small enthalpy and large negative entropy. Ongoing studies include examination of the effects of systematic variation of percarboxylic acid and ligand substituents on the rate and nature of the metaloxylation reaction.

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 and was used after determining active oxygen content by iodometric titrations.[24,25] Aqueous H_2O_2 was standardized just prior to use. All other common chemicals were reagent grade and were used as received. Commercially available BDH silica gel (60–120 mesh) was used for column chromatography.

Instrumentation. Visible and ultraviolet spectra were recorded on a Hitachi 330 spectrophotometer equipped with a thermostated cell holder. Infrared spectra were recorded on a Perkin-Elmer 783 spectrophotometer. ^1H NMR data were collected in $CDCl_3$ solvent by using Varian XL 200 and Bruker 500-MHz FT NMR spectrometers.

Synthesis of Ligands. The sulfoxide ligands were synthesized from the corresponding sulfide ligands by oxidizing the latter with hydrogen peroxide. Representative cases are detailed below. Available information on hydrogen peroxide oxidation of thioethers served as guides for setting experimental conditions.[26]

2-(Methylsulfinyl)-4′-methylazobenzene (3c). A solution of 150 mg (0.58 mmol) of 2-(methylthio)-4′-methylazobenzene in glacial acetic acid (15 mL)[3,27] was cooled in ice bath and hydrogen peroxide (0.10 mL, 23% w/v) was added to the above solution dropwise. The reaction mixture was stirred for 36 h. The solvent was removed in vacuo, and the resulting gummy residue was washed with water (5 × 5 mL). A benzene extract (10 mL) of this residue was chromatographed on a silica gel column (50 × 1.5 cm) prepared in petroleum ether (bp 60–80 °C). A light orange band of the unreacted ligand was eluted with a benzene–petroleum ether (1:6) mixture. The pure sulfoxide ligand **3c** was then eluted as an orange band by using an acetonitrile–benzene (1:4) mixture. Pure crystalline ligand (mp 85 ± 1 °C) was obtained in 74% yield by evaporation of solvent and was then dried over P_4O_{10} under vacuum. Anal. Calcd for $C_{14}H_{14}N_2SO$ (**3c**): C, 65.12; H, 5.43; N, 10.85. Found: C, 65.07; H, 5.43; N, 10.90.

The other compounds of type **3** were synthesized similarly by using appropriate precursor ligands.[3,27] Yields varied in the range 70–85%. Anal. Calcd for $C_{13}H_{12}N_2SO$ (**3a**): C, 63.93; H, 4.92; N, 11.48. Found: C, 63.89; H, 4.90; N, 11.45. Calcd for $C_{19}H_{16}N_2SO$ (**3b**): C, 71.25; H, 5.00; N, 8.75. Found: C, 71.22; H, 4.98; N, 8.80. Calcd for $C_{14}H_{14}N_2SO$ (**3d**): C, 65.12; H, 5.43; N, 10.85. Found: C, 65.07; H, 5.45; N, 10.91.

2-(Methylsulfinyl)-2′-hydroxy-5′-methylazobenzene (6). Hydrogen peroxide (5 mL; 23% w/v) was added dropwise in 2 h to a magnetically stirred suspension of 2-(methylthio)-2′-hydroxy-5′-methylazobenzene (200 mg, 0.78 mmol)[28] in 10% aqueous NaOH solution (50 mL). Stirring was continued for 48 h over a freezing mixture. The solution was filtered, and the filtrate was acidified with H_2SO_4 (2 N) at 0–5 °C. The yellow precipitate thus obtained was dissolved in dichloromethane (5 mL) and was subjected to chromatography over a silica gel column (50 × 1.5 cm) prepared in petroleum ether (bp 60–80 °C). The deep orange-yellow band of the desired product was eluted from the column by using benzene as eluant. The eluant on evaporation in vacuo gave a powdered compound, which was recrystallized from methanol, affording dark yellow crystals of mp 132 °C. Yield: 35%. Anal. Calcd for $C_{14}H_{14}N_2SO_2$ (**6**): C, 61.31; H, 5.11; N, 10.22. Found: C, 61.28; H, 5.09; N, 10.20.

Preparation of Complexes. Chloro(((2-(methylsulfinyl)phenyl)azo)phenyl-*C*²′,*N*,*S*)palladium(II) (4a). To an ethanolic (15 mL) solution of Na_2PdCl_4 (55 mg, 0.19 mmol) was added slowly an ethanolic (15 mL) solution of (2-methylsulfinyl)azobenzene (40 mg, 0.16 mmol). The reaction mixture was stirred continuously for 20 h. The color of the solution changed gradually from light brown to brown-red. The solution was evaporated in air, and the residue was washed thoroughly first with water (2 × 4 mL) and then with 50% aqueous ethanol (3 × 5 mL). The residue was dissolved in dichloromethane (10 mL) and the solution was chromatographed over a silica gel column (45 × 1 cm) prepared in benzene. The first orange-yellow band, eluted by benzene, consisted of free ligand and was rejected. An acetonitrile–benzene (1:9) mixture was then used to elute the desired compound as a deep brown-red band. The eluted solution on evaporation in vacuo gave pure compound in 75% yield. Anal. Calcd for $PdC_{13}H_{11}N_2ClSO$ (**4a**): C, 40.54; H, 2.86; N, 7.28. Found: C, 40.57; H, 2.83; N, 7.29.

The substituted analogues of **4a** were synthesized similarly. Yields varied in the range 70–90%. Anal. Calcd for $PdC_{19}H_{15}N_2ClSO$ (**4b**): C, 49.47; H, 3.25; N, 6.08. Found: C, 49.50; H, 3.20; N, 6.03. Calcd

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for $PdC_{14}H_{13}N_2ClSO$ (**4c**): C, 42.12; H, 3.26; N, 7.02. Found: C, 41.90; H, 3.23; N, 6.83. Calcd for $PdC_{14}H_{13}N_2ClSO$ (**4d**, α and β isomers): C, 42.12; H, 3.26; N, 7.02. Found: C, 42.16; H, 3.22; N, 6.83.

Chloro((2-(methylsulfinyl)phenyl)-5-methyl-2-phenolato-*O*,*N*,*S*)palladium(II), α Isomer (5dα). An ethanolic solution (25 mL) of 2-(methylsulfinyl)-2'-hydroxy-5'-methylazobenzene (**6**) (100 mg, 0.36 mmol) was added to an ethanolic solution (25 mL) of Na_2PdCl_4 (150 mg, 0.50 mmol). When the mixture was stirred, the color of the solution gradually changed from yellow-brown to pink-violet. Stirring was continued for 8 h, and the solution was then evaporated in vacuo. The maroon powder was washed with water (3 × 5 mL) and then with 50% aqueous ethanol (3 × 5 mL). The dichloromethane extract (3 × 5 mL) of the solid was next subjected to chromatography on a silica gel column (45 × 1 cm) prepared in benzene. The light orange band of unreacted ligand was eluted first by using benzene as eluant. The required complex (**5dα**) was then eluted as a pink-violet band by an acetonitrile–benzene (1:9) mixture. Evaporation of the eluant left a solid residue, which was recrystallized from a dichloromethane–methanol mixture (3:1; 15 mL), affording dark violet crystals in 90% yield. Anal. Calcd for $PdC_{14}H_{13}N_2SO_2Cl$ (**5dα**): C, 40.50; H, 3.13; N, 6.75. Found: C, 40.45; H, 3.10; N, 6.70.

Oxidation of 4a to 5a by mCPBA. To a chloroform solution (30 mL) of **4a** (100 mg, 0.27 mmol) was added dropwise with magnetic stirring a solution of mCPBA (90 mg, 0.39 mmol) in the same solvent (20 mL). The reaction mixture was stirred for 4 h. The color of the solution was changed from brown-red to pink-violet. After the completion of the reaction, the solvent was evaporated to dryness in vacuo. The residue was thoroughly washed with 50% aqueous ethanol (5 × 3 mL) and then with diethyl ether (3 × 3 mL) to remove any unreacted mCPBA and its reduced product mCBA. The dichloromethane solution (10 mL) of the residue was then chromatographed over a silica gel column (45 × 1 cm) made in benzene. The pink-violet band of **5a** was eluted by an acetonitrile–benzene (1:9) mixture. Evaporation of this solution in vacuo gave the dark violet solid compound in 85% yield. Anal. Calcd for $PdC_{13}H_{11}N_2SO_2Cl$ (**5a**): C, 38.92; H, 2.74; N, 6.99. Found: C, 38.98; H, 2.71; N, 6.90.

The oxidations of **4b** to **5b**, **4c** to **5c** and **4d** to **5dα** were carried out similarly. Yields were respectively 84%, 80%, and 50%. In the case of **4d**, which consists of α and β isomers the oxidation product was also found to consist of a mixture. The oxidized solution (after removing mCPBA and mCBA) when subjected to column chromatography first afforded the pink-violet band of **5dα**. The second pink-violet band followed, but it furnished only a gummy mass that could not be purified. Anal. Calcd for $PdC_{19}H_{15}N_2SO_2Cl$ (**5d**): C, 47.81; H, 3.15; N, 5.87. Found: C, 48.01; H, 3.18; N, 5.90. Calcd for $PdC_{14}H_{13}N_2SO_2Cl$ (**5c**): C, 40.50; H, 3.13; N, 6.75. Found: C, 40.46; H, 3.11; N, 6.70. Calcd for $PdC_{14}H_{13}N_2SO_2Cl$ (**5dα**): C, 40.50; H, 3.13; N, 6.75. Found: C, 40.40; H, 3.10; N, 6.70.

Demetalation of 5dα to 6. To an acetonitrile solution (20 mL) of **5dα** (60 mg, 0.14 mmol) was added dropwise with magnetic stirring a solution of 99% hydrazine hydrate (75 mg) in the same solvent (2 mL). The reaction mixture was stirred for 0.5 h. The color of the solution changed from pink-violet to orange-yellow, and metallic palladium precipitated. The solution was filtered, and the filtrate was evaporated in vacuo. The gummy residue was dissolved in dichloromethane (5 mL) and subjected to chromatography on a silica gel column (40 × 1 cm) prepared in petroleum ether. An orange-yellow band was eluted with benzene. The eluant on evaporation in vacuo gave **6** in pure form (mp 132 °C) in 89% yield. Anal. Calcd for $C_{14}H_{14}N_2SO_2$: C, 61.31; H, 5.11; N, 10.22. Found: C, 61.25; H, 5.05; N, 10.18. The compound so obtained was identical in all respects with the compound synthesized by hydrogen peroxide oxidation of the corresponding thioether (vide supra).

Kinetic Measurements. Thermostated solutions of reactants were mixed, diluted to required volumes, and transferred to an absorption cell of 1 cm path length. Increase in absorption of the reactants at 540 nm was digitally recorded as a function of time. A_α was measured when intensity changes leveled off. In all experiments the concentration of mCPBA was kept high so as to maintain pseudo-first-order conditions. Values of pseudo-first-order rate constants (k_{obsd}) were obtained from the slopes of the plots of $-\ln(A_\alpha - A_t)$ vs t lines. Values of second-order rate constants, k, were obtained from the slopes of the plots of k_{obsd} vs [mCPBA]. Activation parameters were obtained from the Eyring equation. Values of k_{obsd}, k, $H^\ddagger$, and $S^\ddagger$ and their deviations were calculated by using the usual least-squares methods.[29] A minimum of 30 A_t–t data points were used in each calculation.

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Registry No. **3a**, 112945-72-9; **3b**, 112945-73-0; **3c**, 112945-74-1; **3d**, 112945-75-2; **4a**, 112968-76-0; **4b**, 112968-77-1; **4c**, 112968-78-2; **4dα**, 112968-79-3; **4dβ**, 112968-80-6; **5a**, 112968-81-7; **5b**, 112968-82-8; **5c**, 112968-83-9; **5dα**, 112945-77-4; **6**, 112945-76-3; Na_2PdCl_4, 13820-53-6; 2-(methylthio)azobenzene, 101418-85-3; 2-(benzylthio)azobenzene, 101418-87-5; 2-(methylthio)-4'-methylazobenzene, 101418-86-4; 2-(methylthio)-5'-methylazobenzene, 102073-18-7; 2-(methylthio)-2'-hydroxy-5'-methylazobenzene, 85261-27-4.

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Platinum(II) Phosphine Complexes Containing 1,3,5-Triazine and Related Ligands

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Solution studies of the complexes $\{PtCl_2(PEt_3)\}_n$-1,3,5-triazine (n = 1–3), $\{PtCl_2(PR_3)\}_n$-pyrimidine (R = Et, *n*-Bu; n = 1, 2), and *trans*-$PtCl_2L(PR_3)$ (L = pyridine, 4-chloropyridine; R = Et, *n*-Bu) are reported. It is shown that (a) coordination of the "$PtCl_2(PR_3)$" fragment does not greatly weaken the donor capacity of the still-uncoordinated nitrogen atom of the heterocycle and (b) these complexes are dynamic in solution and the degree of lability increases in the order pyridine < pyrimidine < 1,3,5-triazine. The X-ray crystal structure of $\{PtCl_2(PEt_3)\}_3$-1,3,5-triazine was determined. The crystals are triclinic and belong to the space group $P\bar{1}$ with unit cell dimensions a = 13.020 (3) Å, b = 13.098 (2) Å, c = 13.251 (2) Å, α = 62.75 (1)°, β = 65.95 (2)°, γ = 75.49 (2)°, V = 1828.8 (1) Å^3, and Z = 2. The structure was refined to R = 0.036. Each platinum atom shows normal square-planar geometry with bonding parameters that are typical for compounds of the type *trans*-$PtCl_2$(N-ligand)(PR_3). There does not appear to be any significant change in the triazine structural parameters upon coordination.

Introduction

The coordination chemistry of 1,3,5-triazine (tri) has been investigated very little. The first reported complex appears to be $[Ru(NH_3)_5(tri)](ClO_4)_2$, described in 1968 by Ford et al.[2] In a later publication, Allenstein et al.[3] reported some "addition products" of the composition $(SbCl_5)_2(tri)$, $\{TiCl_4(tri)\}_x$, $SbCl_5(tri)$, $TiCl_4(tri)_2$, $AlCl_3(tri)$, $AlCl_3(tri)_2$, and $SnCl_4(tri)_2$. The first two complexes seem to be the only compounds described so far in which tri coordinates to more than one metal center. All subsequent

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