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Metallosulfoxides and -sulfones: Sulfur Oxygenates of [1,5-Bis(2-mercaptoethyl)-1,5-diazacyclooctanato]palladium(II)

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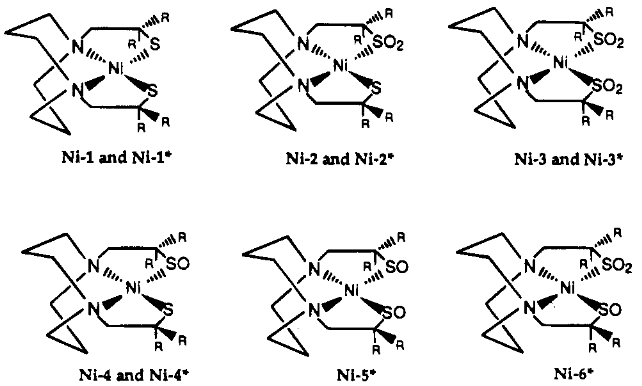
Successive sulfur-site oxygenation of the dithiolate complex [1,5-bis(mercaptoethyl)-1,5-diazacyclooctanato]-palladium(II), **Pd-1**, using H_2O_2 as an O atom source produced all but one member of the series of palladium(II) complexes containing sulfinate (metallosulfone) and sulfenate (metallosulfoxide) S-donor ligands: the monosulfoxide, PdS(=O)R or **Pd-4**; bis(sulfoxide), Pd(S(=O)R)$_2$ or **Pd-5**; sulfone/sulfoxide, Pd(SO$_2$R)S(=O)R or **Pd-6**; and the bis(sulfone) Pd(SO$_2$R)$_2$ or **Pd-3** complex. A unique site selectivity for the addition of a second O atom from H_2O_2 to thiolate sulfur of **Pd-4** producing the bis(sulfoxide), **Pd-5**, exclusively, precluded the preparation of the monosulfone complex, Pd(SO$_2$R)SR or **Pd-2**, via that route. However, the dithiolate **Pd-1** reacts with O_2 photochemically in aprotic solvents, giving access to this last member of the series, **Pd-2**. Further reaction of **Pd-2** with O_2 under UV photolysis gives the bis(sulfone) complex, **Pd-3**. The oxygenates were characterized by various spectroscopies, electrochemistry, and X-ray crystallography. Mass spectrometry delineated a single O atom loss pathway for the sulfoxide species, while SO_2 and O_2 loss is found in sulfone cases. Electrochemical studies show that the addition of an O atom to a thiolate sulfur to create a sulfoxide S-donor results in a stabilization of the Pd^{I} oxidation state in the range 50−70 mV, while the addition of an O atom to a sulfoxide sulfur to create a sulfone S-donor results in greater stabilization of the Pd^{I} oxidation state in the range 190−220 mV. Complex **Pd-2** crystallizes in the monoclinic $P2_1/c$ (No. 14) space group with $a = 8.362(11)$ Å, $b = 12.102(9)$ Å, $c = 12.990(14)$ Å, $\beta = 101.39(9)°$, $V = 1289(2)$ Å^3, and $Z = 4$. Complex **Pd-4** crystallizes in the orthorombic $P2_12_12$ space group with $a = 12.210(2)$ Å, $b = 15.931(4)$ Å, $c = 6.802(2)$ Å, $V = 1323.1(6)$ Å^3, and $Z = 4$. Complex **Pd-6** cocrystallizes with **Pd-3** in the monoclinic $C2/c$ space group with $a = 15.862(5)$ Å, $b = 8.146(2)$ Å, $c = 21.812(9)$ Å, $\beta = 107.82(2)°$, $V = 2683(2)$ Å^3, and $Z = 8$.

Introduction

In recent papers we have reported the synthesis, structural characterization, and properties of a series of nickel-bound sulfoxide (the sulfenato ligand, −S(=O)R) and sulfone (sulfinato, −SO$_2$R) ligands as derivatives of the *cis*-dithiolates [1,5-bis(mercaptoethyl)-1,5-diazacyclooctanato]nickel(II), designated as **Ni-1**,[1] and an analogue containing four methyl groups substituted on the carbon α to the sulfur donors, [1,5-bis(2-mercapto-2-methylpropyl)-1,5-diazacyclooctanato]nickel(II),[2] designated as **Ni-1***.[3−5] All of the oxygenates derived from the sterically encumbered **Ni-1*** indicated in Scheme 1, including the three examples containing the quite uncommon sulfoxide ligand, have been isolated and characterized by X-ray crystallography.[4] The **Ni-4** analogue of **Ni-4*** represents a fourth example of a structurally characterized nickel metallosulfoxide.[5]

Earlier literature reports of O atom addition to sulfur in metal-bound thiolates producing isolable metallosulfoxide complexes exist in the case of cobalt(III) complexes[6] (as in Co(en)$_2$(S(=O)CH$_2$CH$_2$NH$_2$)$^{2+}$)[6a] and is inferred for ruthenium(III) (as in (NH$_3$)$_5$RuS(=O)R^{2+}).[7] Oxidative addition of sulfinyl chloride to Ir^{I} and of *N*-(alkyl- or arylsulfinyl)phthalimides (R−S(=O)-Nphth) to Pt^{0} complexes yields examples of IrCl$_2$(S(=O)CH$_3$)(CO)L$_2$ (L = P(C$_6$H$_5$)$_3$ or P(C$_6$H$_5$)$_2$CH$_3$)[8] and ((C$_6$H$_5$)$_3$P)$_2$Pt(S(=O)R)(Nphth), respectively.[9] Especially germane to the work described below is a report of the crystal structure of a platinum thiolate/sulfoxide complex derived from the S---S oxidative addition of acyclic thiosulfinates R′− S(O)S−R to Pt(0).[10] Synthetic attempts to limit sulfur oxygenation to the mono-oxy stage making use of O_2 or O atom sources have

Scheme 1



R = H and (where starred *) CH$_3$

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resulted in the more common dioxy or metallosulfone products.[11] The dearth of examples of metallosulfoxides has limited explorations of their potential as precursors for the synthesis of asymmetric or chiral sulfoxides.[12]

The factors which lead to stable metallosulfoxides vs products of disproportionation, metallothiolates and metallosulfones, are not delineated. The possibility of gaining insight into such controlling factors is enhanced by the generation of a series whose electronic and steric makeup may be modified in known ways. In the case of the **Ni-1***, the ease of isolation of the sulfoxide derivatives was reasonably ascribed to steric encumbrance of sulfur which limits access to O atom abstracting agents. Hence the **Pd-1** complex, [1,5-bis(mercaptoethyl)-1,5-diazacyclooctanato]palladium(II),[13] offers the possibility to assess electronic effects on S-reactivity and $M-S(=O)R$ vs $M-SO_2R$ stability.

Sulfur-rich metal catalytic sites are frequently reported to be air-sensitive, sometimes reversibly deactivated on exposure to oxygen. Irreversible oxygen damage is generally regarded as formation of catalytically inactive metal oxides. In fact, O_2 reacts directly with **Ni-1** and **Ni-1*** to yield S-oxygenates, the chemistry of which is being explored for insight into ligand-site, oxygen-modified coordination spheres. Preliminary studies find the oxygenation processes exhibit a complicated dependency on solvent and concentration, which is apparently congruent with the oxygenation of organic sulfides by $^1\Delta\ O_2$.[14] In the latter case, examples of O−O cleavage are prominent in protic solvents. Indeed, ground state dioxygen ($^3\Sigma\ O_2$) reacts very slowly (weeks) with the rigidly square planar **Ni-1***;[4] as in the case of diamagnetic organic sulfides, $^1\Delta\ O_2$ is much more reactive.

The bis(mercaptoethyl)diazacyclooctane (bme-daco) ligand presents an opportunity to fully elucidate sulfur-oxygenation pathways in metal thiolates, including both inter- and intramolecular O−O scission paths, provided that all products at all levels of oxygenation are identifiable. In a separate paper, comparisons of the reactivity of **Ni-1**, **Ni-1***, and **Pd-1** with dioxygen are made, and the requirements for metal dithiolates and O_2 activation are summarized.[15] The report below is of the characterization of a series of palladium-bound S-oxygenate analogues to those of Scheme 1 and uses H_2O_2 and ground state oxygen ($^3\Sigma\ O_2$) in the presence of UV light as oxygen sources.

Experimental Section

Materials. Reagent-grade solvents were dried using standard techniques.[16] The concentration of hydrogen peroxide (Mallinckrodt) used was 11.1 M measured by titration with $KMnO_4$. Oxygen was purchased from Bailey & Tool Co., Bryan, TX, and used with no further purification. All other chemicals were purchased from Aldrich Chemical Co. and used as obtained. Unless otherwise noted, standard Schlenk techniques using nitrogen and an argon glovebox were employed throughout to maintain anaerobic conditions during synthesis and isolation of products.

Table 1. Summary of X-ray Crystal Structure Data for **Pd-2**, **Pd-4**, and **Pd-3/Pd-6**

chemical formula	**Pd-2**	**Pd-4**$\cdot 0.5H_2O$	**Pd-3/Pd-6**$\cdot 0.5H_2O$
fw	370.80	363.81	402.89
space group	$P2_1/c$	$P2_12_12$	$C2/c$
a (Å)	8.632(11)	12.210(2)	15.862(5)
b (Å)	12.102(9)	15.931(4)	8.146 (2)
c (Å)	12.990(14)	6.80 (2)	21.812(9)
α (deg)			
β (deg)	101.39(9)		107.82(2)
γ (deg)			
V (Å^3)	1289(2)	1323.1(6)	2683(2)
Z	4	4	8
ρ (calcd, g/cm^3)	1.911	1.826	1.999
temp (K)	163(2)	293(2)	293(2)
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
abs coeff (mm^{-1})	1.756	1.705	1.706
R^a	0.0630	0.0447	0.0375
$R_w{}^a$	0.1271	0.1044	0.0914

[a] Residuals: $R = \Sigma|F_o - F_c|/\Sigma F_o$; $R_w = \{[\Sigma w(F_o - F_c)^2]/[\Sigma w(F_o)^2]\}^{1/2}$.

Chromatography. All of the neutral palladium complexes were purified and separated from mixtures by chromatography through a 12 × 1 in. column of silica gel (60−200 mesh, Aldrich grade 922 or EM science grade 22). Methanol was used as an eluant.

Physical Measurements. NMR spectra were recorded using a Varian XL-200 FT NMR spectrometer. Vis/UV spectra were obtained employing a Hewlett-Packard HP8452A diode array spectrophotometer. An IBM IR/32 Fourier transform spectrophotometer was used to record infrared spectra (KBr pellets). Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Mass spectra were determined at the Center of Chemical Characterization and Analysis, Texas A&M University. Positive ion fast atom mass spectra were recorded in thioglycerol and nitrobenzyl alcohol (NBA) matrices using a VG-70S spectrometer with a xenon source having particle energy of 10 keV. Data were collected by a VG11−250J data system.

Cyclic voltammographs were obtained using a Bio-Analytical Systems 100A electrochemical analyzer with a glassy carbon stationary electrode and a platinum wire auxiliary electrode. Samples were measured in acetonitrile solution with tetra-*n*-butylammonium hexafluorophosphate (TBAHFP) (0.25 M) as the supporting electrolyte and a $Ag/AgNO_3$ reference electrode. Potentials were standardized with Cp_2Fe^+/Cp_2Fe and referenced to NHE.

X-ray Crystal Structure Analyses. Single crystals of complexes **Pd-2**, **Pd-4**, and **Pd-6** were obtained as described below. The **Pd-3** complex cocrystallized with **Pd-6**; hence, its structural parameters were extracted from the solution of the structure of the latter. All X-ray crystal structures were determined at the Crystal & Molecular Structure Laboratory of the Center for Chemical Characterization and Analysis at Texas A&M University. X-ray crystallographic data were obtained on a Nicolet R3m/V single-crystal X-ray diffractometer operating at 50 kV and 30 mA, Mo Kα (λ = 0.710 73 Å) radiation, equipped with a Nicolet LT-2 cryostat. Diffractometer control software P3VAX 3.42 was supplied by Nicolet Analytical X-ray Instruments. The structures of the oxygenates were solved and refined using SHELXS-86 and SHELXL-93 computer programs, respectively.[17,18] A single crystal was mounted on a glass fiber with epoxy cement either at room temperature or at 163 K in an N_2 cold stream. X-ray experimental conditions and data collections for the oxygenated complexes **Pd-2**, **Pd-4**, and **Pd3/Pd-6** are given in Table 1.

Syntheses. The synthesis of **Pd-1** has been described previously.[13] In almost all cases of **Pd-1** oxygenation, a yellow compound assumed to be the trimetallic complex, $(\textbf{Pd-1})_2Pd^{2+}$, analogous to that structurally

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characterized as **(Ni-1)**$_2$Ni^{2+},[3] was a byproduct which, like **(Ni-1)**$_2$Ni^{2+},[3] did not easily elute from a silica gel column. The vis/UV spectrum of this compound from an independent preparation shows strong absorptions at 248, 268, and 320 nm, *vide infra*.

[1-(Mercaptoethyl)-5-(sulfinatoethyl)-1,5-diazacyclooctanato]palladium(II) (Pd-2). **Pd-1** (0.10 g, 0.29 mmol) was placed into a tap water-cooled cylindrical photolysis vessel (Ace Glass, catalog no. 7878) equipped with a 450 W Hanovia, medium-pressure, mercury vapor lamp. The cell was degassed and N_2 back-filled for three cycles, CH_2Cl_2 (100 mL) was added, and the vessel was wrapped with aluminum foil. Oxygen (1 atm regulated by an oil bubbler) was bubbled into the solution while irradiated for 25 min, during which time the temperature rose by ca. 10 °C. The solution was transferred, and solvent was removed by rotary evaporation. The remaining solid was redissolved in a minimum of CH_3OH and placed on a silica gel column. The separated compounds in order of elution were the starting **Pd-1** (10%), the monosulfone complex **Pd-2** (37%), and the bis(sulfone) complex **Pd-3** (3%). Another similar experiment performed in CH_3CN with a 40 min irradiation period also yielded **Pd-2** (27%).

A crystal suitable for crystallographic analysis was grown by ether diffusion into a concentrated **Pd-2**/CH_2Cl_2 solution. Anal. Calcd (found) for **Pd-2** ($C_{10}H_{20}N_2S_2O_2Pd$): C, 32.4 (31.8); H, 5.44 (5.27); N, 7.55 (7.41).

[1,5-Bis(sulfinatoethyl)-1,5-diazacyclooctanato]palladium(II) (Pd-3). Into a methanolic solution (30.0 mL) of **Pd-1** (0.10 g, 0.29 mmol) was added an excess of H_2O_2 (0.10 mL, 1.11 mmol) in one aliquot. The reaction was stirred at room temperature for 24 h. A greenish yellow solid precipitated out of the reaction and was isolated by filtration (yield = 64%). The solid was characterized by FAB MS in a thioglycerol matrix and shows a molecular ion at *m/z* 403 as expected. Anal. Calcd (found) for **Pd-3**$\cdot$2H$_2$O ($C_{10}H_{24}N_2S_2O_6Pd$): C, 27.4 (27.6); H, 5.51 (4.85); N, 6.38 (6.30).

[1-(Mercaptoethyl)-5-(sulfenatoethyl)-1,5-diazacyclooctanato]palladium(II), (Pd-4). A methanolic solution (100 mL) of **Pd-1** (0.10 g, 0.29 mmol) under N_2 was cooled to −78 °C (dry ice/acetone), and hydrogen peroxide (27.0 μL, 0.29 mmol) was added. The yellow solution was allowed to gradually warm to room temperature and was stirred overnight. The solvent was removed by rotary evaporation, and the residue was dissolved in a minimum of CH_3OH (5.0 mL) and purified by silica gel chromatography with CH_3OH elution. The separated products in order of elution were the monosulfoxide complex **Pd-4** (28%) and the bis(sulfoxide) complex **Pd-5** (22%).

X-ray quality crystals of **Pd-4** were grown by ether diffusion into its saturated methanolic solution. Anal. Calcd (found) for **Pd-4**$\cdot$H$_2$O ($C_{10}H_{22}N_2S_2O_2Pd$): C, 32.2 (32.1); H, 5.95 (5.45); N, 7.51 (7.12).

Another synthesis was performed by irradiation of a methanolic solution of **Pd-1** (2.95 mmol) with oxygen bubbling for 15 min, producing **Pd-4** (20%) with recovery of **Pd-1** (37%).

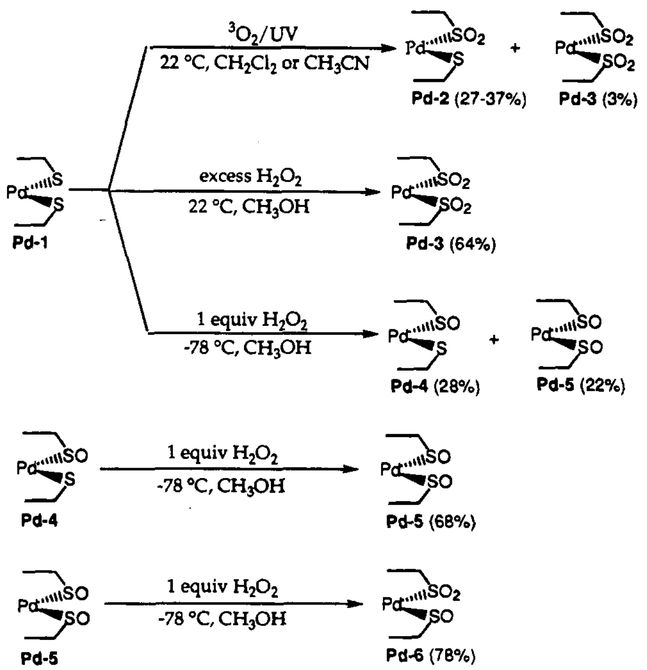
[1,5-Bis(sulfenatoethyl)-1,5-diazacyclooctanato]palladium(II) (Pd-5). Under N_2, a portion of H_2O_2 (53.0 μL, 0.59 mmol) was added to a methanolic solution (100 mL) of **Pd-1** (0.10 g, 0.29 mmol), and the mixture was stirred for 12 h. The solvent was subsequently removed by rotary evaporation, and the residue was dissolved in a minimum of methanol and transferred to a silica gel column. Two products separated with methanol elution: the bis(sulfoxide) complex **Pd-5** (37%) and the sulfone/sulfoxide complex **Pd-6** (5%).

A better yield of **Pd-5** was obtained by conversion of **Pd-4** (50.0 mg, 0.14 mmol in 30.0 mL of MeOH) in the presence of 1 equiv of H_2O_2 (13.0 μL, 0.14 mmol aliquot). A similar workup procedure as described above gives the bis(sulfoxide) complex **Pd-5** in 68% yield.

Analytical samples of **Pd-5** were obtained by addition of dry Et$_2$O into its saturated methanolic solution under anaerobic conditions. Anal. Calcd (found) for **Pd-5**$\cdot$3H$_2$O ($C_{10}H_{26}N_2S_2O_5Pd$): C, 28.27 (28.11); H, 6.17 (6.11); N, 6.59 (6.37).

[1-(Sulfenatoethyl)-5-(sulfinatoethyl)-1,5-diazacyclooctanato]palladium(II) (Pd-6). Under anaerobic conditions 80.0 μL of H_2O_2 (0.89 mmol) was added to a methanolic solution of **Pd-1** (0.10 g, 0.29 mmol in 100 mL). The reaction was stirred overnight (ca. 12 h). The solvent was subsequently removed by rotary evaporation, and the residue was dissolved in a minimum of methanol and transferred to a silica gel column. The product obtained with methanol elution was the sulfone/sulfoxide complex **Pd-6** (43%).

Scheme 2



A higher yield of **Pd-6** may be obtained with **Pd-5** as precursor. Under anaerobic conditions, H_2O_2 (3.00 μL, 0.03 mmol) was added to a methanolic solution (20.0 mL) of **Pd-5** (12.5 mg, 0.03 mmol). The reaction was stirred overnight (ca. 12 h). A workup procedure similar to that described above gave the sulfone/sulfoxide complex **Pd-6** (78%).

Compound **Pd-6** was crystallized by ether diffusion into a concentrated methanolic solution. The X-ray crystal structure analysis revealed that **Pd-6** cocrystallized with **Pd-3**, in which the unit cell contained 56% of **Pd-6** and 44% of **Pd-3**. Anal. Calcd (found) for (44/56%) **Pd-3/Pd-6**$\cdot$0.5H$_2$O ($C_{10}H_{21}N_2S_2O_{3.94}Pd$): C, 29.8 (29.9); H, 5.22 (5.26); N, 6.96 (6.91).

Reactions of Pd-2, Pd-4, Pd-5, and Pd-6 with Oxygen Sources: (A) Hydrogen Peroxide and (B) Dioxygen. These reactions were carried out on small samples with quantification made possible by use of tared 10 or 25 mL flasks in the final product isolation.

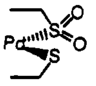
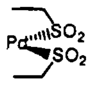
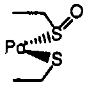
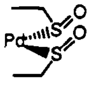
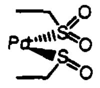
(A) Into a 50 mL Schlenk flask containing a methanolic solution (10.0 mL) of **Pd-2** (10.0 mg, 0.027 mmol) under N_2 was added a portion of H_2O_2 (2.40 μL, 0.027 mmol). The mixture was stirred overnight (ca. 12 h) at room temperature before the solvent was removed by rotary evaporation. The residue was transferred to a silica gel column, and one band, identified as the sulfone/sulfoxide complex, **Pd-6**, eluted with CH_3OH. The solution of **Pd-6** was concentrated, transferred to a tared flask, and dried in vacuo, resulting in an approximate yield of 80%.

Under similar conditions, a methanolic solution (10.0 mL) of 10.0 mg (0.03 mmol) of **Pd-6** was added to 2.30 μL (0.03 mmol) of H_2O_2. The mixture was stirred for 24 h at room temperature before the solvent was removed by rotary evaporation. The residue was extracted with a minimum of methanol and found to contain starting material **Pd-6**. The product **Pd-3** was insoluble in methanol and was separated from the supernatant by careful decantation. The **Pd-3** complex was then dried under vacuo and weighed (3.6 mg, 35%).

(B) With $^3O_2$ under Photolysis. A CH_3CN solution (30.0 mL) of **Pd-2** (11.3 mg, 0.030 mmol) was placed in the photolysis vessel described above. With a purge of O_2, the yellow solution was irradiated for 40 min at room temperature. The solvent was removed by rotary evaporation. The residue was taken up in a minimum of methanol and transferred to a small, preweighed flask. The supernatant was decanted away from insoluble **Pd-3**, which was subsequently dried in vacuo and weighed (5.5 mg, 45%). The supernatant was characterized to be a mixture of the starting **Pd-2** and **(Pd-1)**$_2$Pd^{2+}.

Under similar conditions, a methanolic solution (50.0 mL) of **Pd-4** (25.0 mg, 0.07 mmol) was irradiated for 15 min at room temperature. The residue was chromatographed on a silica gel column, obtaining, in order of elution with methanol, the reactant **Pd-4** (47%) and **Pd-6** (22%).

Table 2. Physical and Spectroscopic Properties of Compounds **Pd-1** through **Pd-6**

	 **Pd-1**	 **Pd-2**	 **Pd-3**	 **Pd-4**	 **Pd-5**	 **Pd-6**
Color	yellow	yellow	yellow	yellow	yellow	yellow
IR[a] ν(SO) (cm^{-1})						
Pd-SO				920	909, 929	932
Pd-SO$_2$		1188, 1055	1202, 1074, 1042			1055, 1190
UV[b] (nm(ε))[c]	343 (1000)	212 (10100), 236 (14300), 260 (15200), 328 (2900)	264 (14200), 320 (4300)	246 (15300), 364 (4200)	270 (8000), 316 (5100), 388 (5600)	208 (6500), 266 (11600), 370 (5800)
Parent ion (m/z)[d]	339	371	403	355	371	387

[a] KBr pellets. [b] Measured in methanolic solution except for **Pd-3** (in water). [c] ε in M^{-1} cm^{-1}. [d] FAB MS, thioglycerol matrix for **Pd-1**, **Pd-2**, and **Pd-3**; nitrobenzyl alcohol matrix for **Pd-4**, **Pd-5** and **Pd-6**.

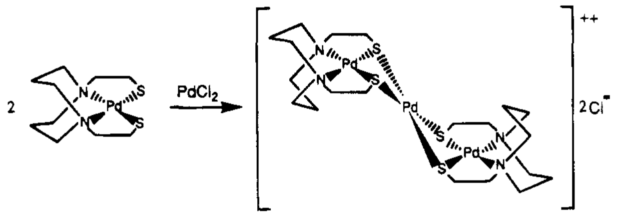
A similar reaction was carried out with O_2 and **Pd-5** (13.00 mg, 0.035 mmol in 30 mL of MeOH) under photolysis for 1 h. The products were separated by silica gel chromatography with **Pd-5** recovered to the extent of 74%; no other oxygenate was observed.

Results and Discussion

Synthesis. The *cis*-dithiolate complex **Pd-1** is best obtained by addition of the sodium salt of the ligand, Na_2(bme-daco), into a slurry of $PdCl_2$ in methanol.[13] The yellow product was purified by silica gel chromatography. **Pd-1** has been structurally characterized by X-ray crystallography to be a square planar N_2S_2 monomeric complex analogous to the nickel analogues.[1] The complex is air stable, diamagnetic, soluble in both protic and aprotic solvents, and, unlike the deep purple **Ni-1** and **Ni-1***, is a bright yellow/orange in color.

Scheme 2 is a summary of the optimal conditions for preparing the oxygenates; details are given in the Experimental Section. The oxidant of choice for isolation of metallosulfoxides is the O atom source hydrogen peroxide in slight stoichiometric deficiency. The monosulfone complex **Pd-2** can only be accessed through reaction of **Pd-1** with molecular oxygen in aprotic solvents under photolysis; in this case, O_2 is expected to add in a pairwise fashion to a single sulfur site as has been established for reaction of O_2 with **Ni-1**.[3] The bis(sulfone) **Pd-3** is best prepared by reaction of H_2O_2 in greater than 4-fold excess with **Pd-1** in MeOH, from which it precipitates. **Pd-3** is, however, water soluble, as are all complexes in the series.

In most cases mixtures of S-oxygenates are obtained, requiring separation by silica gel column chromatography; methanol is the eluant of choice. Column retention of the products roughly correlates with the extent of oxygenation. The dithiolate **Pd-1** is the fastest moving fraction, while the monosulfoxide **Pd-4** and the monosulfone **Pd-2** elute next and, in mixtures, together. Fortunately, the synthetic methods employed rarely produce **Pd-2** and **Pd-4** concurrently (the former is obtained only from reaction of dioxygen, while the latter is best prepared from hydrogen peroxide, *vida supra*). Interestingly, the monosulfoxide complex of the nickel analogue of **Pd-4**, **Ni-4**, is more acid-sensitive and cannot survive silica gel column chromatography; its separation can only be pursued on a neutral Al_2O_3 column.[5] The three-oxy species, **Pd-6**, elutes after **Pd-4** along with the bis(sulfoxide) **Pd-5**; such mixtures of **Pd-5** and **Pd-6** can be separated using 1:1 mixtures of ethanol/methanol. The bis(sulfone) complex **Pd-3** is only slightly soluble in MeOH and elutes slowly. A common additional product of oxidation reactions is charged and remains on the top of the column. This compound is expected to result from occasional production of free Pd(II), which is scavenged by **Pd-1**, producing a trimetallic analogous to that structurally characterized for **Ni-1** produced under similar conditions.[3] Its electronic spectrum and chromatographic properties are identical to that of the compound from deliberate addition of 1 equiv of $PdCl_2$ to 2 equiv of **Pd-1**, eq 1.



(1)

Characterization. All **Pd-1** oxygenates are obtained after solvent evaporation as yellow solids and typically contain waters of hydration. Their spectroscopic signatures are collected in Table 2. Consistent with X-ray crystal structure data, *vide infra*, which show longer S–O bonds for the palladium sulfoxides as compared to the sulfones, all sulfoxides have ν(SO) stretches between 910 and 930 cm^{-1}, while the sulfone complexes show a two-band set, $\nu(SO)_{asym}$ and $\nu(SO)_{sym}$, in the 1050–1200 cm^{-1} range. These values are very similar to those of analogous S-oxygenates based on **Ni-1***.[4] The electronic spectral bands in the range 320–390 nm, assigned as d–d transitions, are blue shifted compared to similar nickel derivatives in the **Ni-1*** series. Absorptions in the range 200–270 nm are assigned as LMCT transitions,[19] and their intensities are relatively greater than the nickel analogues. The ^{1}H NMR spectra of **Pd-1** and derivatives show complicated, and as yet unassigned, multiplets in the 2–3 ppm range.

Fast atom bombardment mass spectroscopy, FAB MS, analyses were carried out for all complexes in two matrices, nitrobenzyl alcohol (NBA) and thioglycerol. The NBA matrix unfortunately contaminates the mass spectra with an intense signal of m/z = 307, where a fragment corresponding to **Pd-1** with loss of a sulfur atom might occur. The thioglycerol matrix, however, appears to react with the sulfoxide oxygen, abstracting an oxygen atom presumably in a manner similar to the reaction of $[Ir(Se_2O)(dppe)_2]^+$ with RSH, producing $[Ir(Se_2)(dppe)_2]^+$,

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[19] (a) Weschler, C. J.; Deutsch, E. *Inorg. Chem.* **1973**, *12*, 2682. (b) Weschler, C. J.; Deutsch, E. *Inorg. Chem.* **1976**, *15*, 139. (c) Adzamli, I. K.; Deutsch, E. *Inorg. Chem.* **1980**, *19*, 1366.

Scheme 3

Sulfinates (thioglycerol)

$\textbf{Pd-2} \xrightarrow{-SO_2} m/z = 307$

$\textbf{Pd-3} \xrightarrow{-O_2} \textbf{Pd-2} \text{ or } \textbf{Pd-5}$

Sulfenates (NBA)

$\textbf{Pd-4} \xrightarrow{-O} \textbf{Pd-1}$

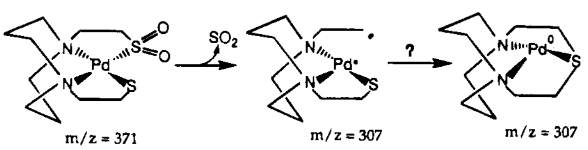
$\textbf{Pd-5} \xrightarrow{-O} \textbf{Pd-4} \xrightarrow{-O} \textbf{Pd-1}$

$\textbf{Pd-6} \xrightarrow{-O} \textbf{Pd-2} \xrightarrow{-SO_2} m/z = 307$

RSSR, and H_2O.[20] Therefore, the MS analyses for sulfone complexes are performed in a thioglycerol matrix, while sulfoxide complexes are examined in an NBA matrix.

Two main points from our interpretation of mass spectral data for complexes **Pd-2** through **Pd-6** are embodied in Scheme 3. The loss of SO_2 from the monosulfone **Pd-2** is expected to result in a radical metallofragment analogous to that proposed in **Ni-2*** fragmentation studies.[4] Examples of sulfur dioxide deinsertion or loss in solution chemistry are precedented. For example, Wojcicki et al. reported that benzene solutions of the α-toluenesulfonate, $(\eta^5\text{-}C_5H_5)Mo(CO)_3SO_2CH_2C_6H_5$, lose SO_2 when irradiated to give a 35% yield of $(\eta^5\text{-}C_5H_5)Mo(CO)_3CH_2C_6H_5$.[21]

An intriguing recent study found SO_2 extrusion from a nickel sulfone in the presence of an adjacent *cis* thiolate ligand resulted in the formation of a thioether.[22] The analogous possibility for **Pd-2** is expressed by eq 2 below. Interestingly, the MS data available to us now show evidence of O_2, but not SO_2, loss from the bis(sulfone) **Pd-3** complex. Also, under these conditions, there has been no indication of SO loss from any of the palladium sulfoxides.



(2)

X-ray Crystal Structure Analyses. A summary of X-ray crystal structure collection and refinement data for **Pd-2**, **Pd-3/Pd-6**, and **Pd-4** is given in Table 1, and their molecular structures are shown as thermal ellipsoid (**Pd-2** and **Pd-4**) and ball and stick (**Pd-3/Pd-6**) plots in Figures 1−3, respectively. Selected bond dimensions are compared in Table 3, and additional metric data are presented in the figure captions. Full crystallographic reports for these complexes are available in the supporting information.

All structures were solved by direct methods[17] and refined by full-matrix least-squares anisotropic refinement for all non-hydrogen atoms.[18] Hydrogen atoms were placed in idealized positions with isotropic thermal parametrs fixed at 0.08 Å^3. Neutral atom scattering factors and anomalous scattering factors were taken from the *International Tables for X-ray Crystallography*, Vol. C.[23]

All complexes in the series show fundamentally similar structures, comprised of square planar palladium(II) coordination with *cis* nitrogens and *cis* sulfurs. Deviation from square planarity as defined by the tetrahedral twist, the angle of the intersection between PdN_2 and PdS_2 planes, is 10.2° for **Pd-2**, 2.8° for **Pd-3/Pd-6**, and 4.5° for **Pd-4**. The diazacyclooctane portion of the ligand is incorporated into two fused metallodiazacyclohexane rings that occupy a chair/boat configuration in all S-oxygenates. Interestingly, the parent dithiolate **Pd-1** differs in that the metallodiazacyclohexane rings are oriented in the chair/chair conformation, the usual conformation seen in hexacoordinate, pseudo-octahedral complexes.[24,25]

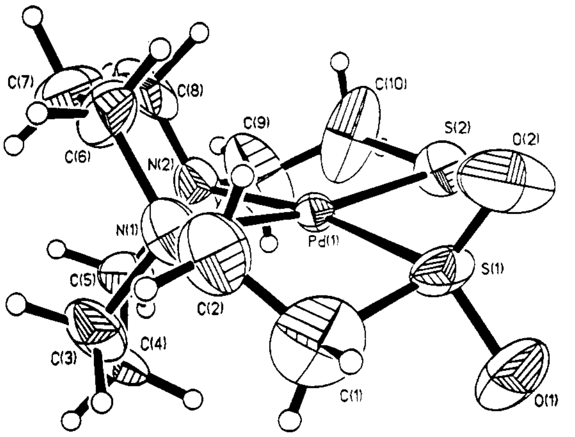


Figure 1. 50% probability thermal ellipsoid plot of **Pd-2**. Selected bond lengths (Å): Pd(1)−S(1) 2.207(4); Pd(1)−S(2) 2.251(4); Pd(1)−N(1) 2.113(11); Pd(1)−N(2) 2.103(10); S(1)−O(1) 1.434(10); S(1)−O(2) 1.412(11). Selected bond angles (deg): S(1)−Pd(1)−S(2) 96.7(2); S(1)−Pd(1)−N(1) 89.4(3); S(2)−Pd(1)−N(1) 170.8(3); S(1)−Pd(1)−N(2) 171.1(3); S(2)−Pd(1)−N(2) 88.8(3); N(1)−Pd(1)−N(2) 86.1(5); Pd(1)−S(1)−O(1) 115.0(5); Pd(1)−S(1)−O(2) 117.7(4).

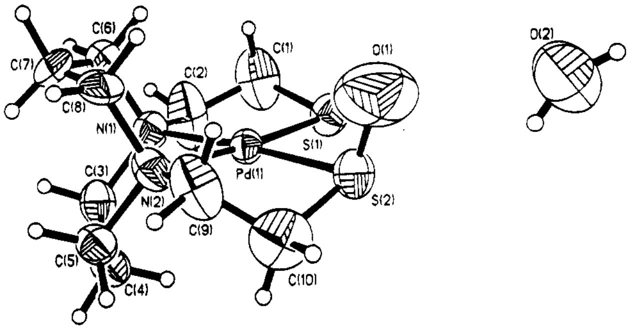


Figure 2. The 50% probability thermal ellipsoid plot of **Pd−4**·$0.5H_2O$. Selected bond lengths (Å): Pd(1)−S(1) 2.281(3); Pd(1)−S(2) 2.265(3); Pd(1)−N(1) 2.122(9); Pd(1)−N(2) 2.125(9); S(2)−O(1) 1.47(2). Selected bond angles (deg): S(1)−Pd(1)−S(2) 95.12(11); S(1)−Pd(1)−N(1) 88.4(3); S(2)−Pd(1)−N(1) 175.5(3); S(1)−Pd(1)−N(2) 174.7(3); S(2)−Pd(1)−N(2) 88.9(3); N(1)−Pd(1)−N(2) 87.7(4); Pd(1)−S(2)−O(1) 109.8(6).

The larger palladium atom leads to Pd−S and Pd−N distances that are on average 0.1 Å larger than the Ni−S and Ni−N distances of analogous NiN_2S_2 derivatives. A greater effect on ligand cavity is seen in the spread of the *cis* sulfurs, leading to an average S---S distance in the Pd series of 3.3 Å, about 0.3 Å larger than in the Ni series.[4]

The molecular structures of **Pd-2** and **Pd-4** show that the pendant sulfur-donor arms are staggered relative to each other across the N_2S_2 plane, while those of the **Ni-2**[3] and **Ni-2***[4] or **Ni-4**[5] and **Ni-4***[26] analogues are eclipsed. Similar to the **Ni-2** and **Ni-2*** derivatives, in **Pd-2** the $Pd{-}S_{\text{thiolate}}$ distance, 2.251(4)

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

(21) Graziani, M.; Bibler, J. P.; Montesano, R. M.; Wojcicki, A. *J. Organomet. Chem.* **1969**, *16*, 507.

(22) Cao, R.; Hong, M.; Jiang, F.; Xie, X.; Liu, H. *J. Chem. Soc., Dalton Trans.* **1994**, 3459.

(23) *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, 1992; Vol. C.

(24) Darensbourg, M. Y.; Font, I.; Mills, D. K.; Pala, M.; Reibenspies, J. H. *Inorg. Chem.* **1992**, *31*, 4965.

(25) Goodman, D. C.; Tuntulani, T.; Reibenspies, J. H.; Farmer, P. J.; Darensbourg, M. Y. *Angew. Chem., Int. Ed. Engl.* **1992**, *32*, 116.

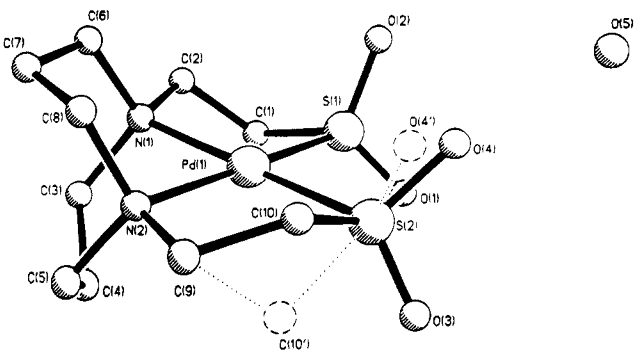
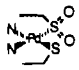
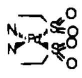
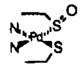
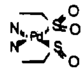
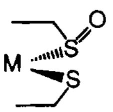


Figure 3. Molecular structure of **Pd-3/Pd-6**·0.5H_2O. Selected bond lengths (Å): Pd(1)−S(1) 2.242(2); Pd(1)−S(2) 2.247(2); Pd(1)−N(1) 2.121(5); Pd(1)−N(2) 2.124(5); S(1)−O(1) 1.410(7); S(1)−O(2) 1.462(5); S(2)−O(3) 1.330(7); S(2)−O(4) 1.476(8); S(2)−O(4′) 1.465(7); S(2)−C(10) 1.800(7); S(2)−C(10′) 1.833(8). Selected bond angles (deg): S(1)−Pd(1)−S(2) 95.87(7); S(1)−Pd(1)−N(1) 88.23(14); S(2)−Pd(1)−N(1) 175.60(14); S(1)−Pd(1)−N(2) 174.55(13); S(2)−Pd(1)−N(2) 89.03(13); N(1)−Pd(1)−N(2) 86.9(2); Pd(1)−S(1)−O(1) 119.2(3); Pd(1)−S(1)−O(2) 112.5(2); Pd(1)−S(2)−O(3) 124.7(5); Pd(1)−S(2)−O(4) 110.0(5); Pd(1)−S(2)−O(4′) 112.4(4); O(4′)−S(2)−C(10′) 105.1(5); O(4)−S(2)−C(10) 104.3(5); O(3)−S(2)−C(10) 111.1(6); O(1)−S(1)−C(1) 104.4(4); O(2)−S(1)−C(1) 105.9(3).

Table 3. Comparison of Metric Data of **Pd-1**, **Pd-4**, and **Pd-3/Pd-6**

Compound	Pd-N (Å)	Pd-S (Å)		S-O (Å)	S--S (Å)
Pd-1	2.093(3) 2.093(3)	2.2795(11) 2.2796(11)			3.353
Pd-2	2.113(11) 2.103(10)	2.207(4) 2.251(4)		1.434(10) 1.412(11)	3.327
Pd-3	2.121(5) 2.124(5)	2.242(2) 2.247(2)		1.410(7) 1.462(5) 1.330(7) 1.476(8)	3.333
Pd-4	2.125(9) 2.122(3)	2.265(3) 2.281(3)		1.47(2)	3.355
Pd-6	2.121(5) 2.124(5)	2.242(2) 2.247(2)		1.410(7) 1.462(5) 1.465(7)	3.333

Å, is longer than that of the Pd−$S_{sulfone}$ (2.207(4) Å). This order of M−SO_2R vs M−SR bond distance is attributed to the decrease in sulfur size in the formal oxidation state +2 in the former as opposed to the oxidation state of −2 in the latter.[4,27] However, as seen below, in the metallosulfoxides **Ni-4**, **Ni-4***, and **Pd-4** there are no statistically significant differences between the M---S and M---S(O)R distances in the metallosulfoxides **Ni-4**, **Ni-4***, and **Pd-4**.

	Ni-4	**Ni-4***	**Pd-4**
	1.549(2) Å	1.548(8) Å	1.47(2) Å
	2.153(1)	2.162(3)	2.265(3)
	2.153(2)	2.148(3)	2.281(3)

The S−O distances are statistically the same in the sulfones, **Pd-2**, **Ni-2**, and **Ni-2***, and their ν(SO) stretching frequencies are within a narrow range. In the sulfoxides, the S−O distance of **Pd-4**, 1.47(2) Å, is substantially shorter than that of the **Ni-4** and **Ni-4*** analogues and indeed closer to the values of S=O in the sulfones, **Pd-2** and **Pd-3** (1.45, 1.46 Å). Whereas this might suggest, in corroboration with the ease of isolation of **Pd-4** as compared to **Ni-4**, that the S=O bond is stronger in the former, the IR ν(SO) stretching frequencies, Table 2, are however similar for all monosulfoxide complexes! The relevant Pt thiolate/sulfoxide complex, $((C_6H_5)_3P)_2Pt(S(=O)C_4H_8S)$,[10] has a S−O distance of 1.448(7) Å, which is comparable to that of the **Pd-4** complex. In this case, the S−O stretching frequency is higher (977 cm^{-1}), consistent with a stronger bond. A possible explanation for the lower than expected ν(SO) stretching frequency in the case of **Pd-4** is the H-bonding interaction of water with sulfoxide oxygens, bridging two adjacent complexes in the solid state, while there is no water of hydration in the Pt complex.

The structures of **Pd-3/Pd-6** were determined from cocrystallized units, leading to an overlay of Pd−S features as noted in Table 3. Molecules of both **Pd-3** and **Pd-6** were found together at the same positions in the unit cell. The molecules are isostructural, and their combined structures resulted in the positional disorder of one of the two mercaptoethyl arms pendant to diazacyclooctane. The pendant arm for **Pd-6** contains the atoms C(9)−C(10′)−S(2)=O(4′), while the pendant arm for **Pd-3** contains the atoms C(9)−C(10)−S(2)O(3)O(4). The elbow carbons C(10), C(10′) and O(4), O(4′) of both pendant arms are disordered over two positions with site occupancy factors of 44% for C(10) and O(4) and its complement of 56% for C(10′) and O(4′). The oxygen atom O(3) was tied to the site occupation of O(4). The sulfur atom, S(2), was also disordered; however, the difference in the positional parameters for the two disordered atoms was less than 0.1 Å, and the two disordered sites could not be resolved. A single averaged position was chosen and restrained in such a manner as to return structurally reasonable atomic distances for both disordered structures.

Electrochemical Studies. A compilation of the electrochemical data for the series of complexes **Pd-1** to **Pd-6** is given in Table 4. These data are quite similar to those of the analogous **Ni-1*** series.[4] All complexes show reversible one-electron events in the cathodic region which are assigned to the $Pd^{II/I}$ couple. Complexes **Pd-2**, **Pd-3**, and **Pd-6**, which contain a sulfone moiety, show a second reversible wave, indicating a $Pd^{I/0}$ reduction. At an $E_{1/2}$ of −2105 mV (vs NHE), the $Pd^{II/I}$ couple is comparable to the $Ni^{II/I}$ couple of **Ni-1***, but is 160 mV more difficult to attain than for **Ni-1** (at −1944 mV). *This indicates that the overall electronic effect of four methyl groups is similar to that achieved on exchanging Pd for Ni in the parent bme-daco complex.* Analogously to the **Ni-1** and **Ni-1*** oxygenates, an oxidation event, from 2 to 3 V removed from the reduction event, is irreversible for palladium complexes containing a thiolate sulfur, but reversible and assignable to $Pd^{II/III}$ (in analogy to the $Ni^{II/III}$ assignment)[28] for the bis(sulfone) complexes.

The progression of accessiblity of the $Pd^{II/I}$ couple (and, in italics, the loss of accessibility of the oxidation event) with each oxygen atom added to sulfur is summarized in Scheme 4. The overall stabilization of the $Pd^{II/I}$ couple on going from **Pd-1** to the fully oxygenated **Pd-3** is more than 500 mV. That stabilization is partitioned as follows: The addition of an oxygen to a thiolate sulfur, creating a sulfoxide S-donor in the three cases of Scheme 4, results in a stabilization of the Pd^I oxidation

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(26) Font, I.; Buonomo, R.; Reibenspies, J. H.; Darensbourg, M. Y. *Inorg. Chem.* **1993**, *32*, 5897.

(27) (a) Mirza, S. A.; Pressler, M. A.; Kumar, M.; Day, R. O.; Maroney, M. J. *Inorg. Chem.* **1993**, *32*, 977. (b) Kumar, M.; Colpas, G. J.; Day, R. O.; Maroney, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 8323.

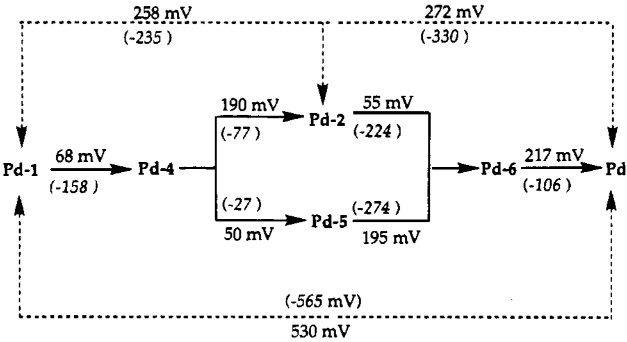
(28) Farmer, P. J.; Reibenspies, J. H.; Lindahl, P. A.; Darensbourg, M. Y. **1993**, *115*, 4665.

Table 4. Electrochemical Data[a] from Cyclic Voltammetry in CH_3CN[b] for Complexes **Pd-1** through **Pd-6**

complex	rev Pd^{III}/Pd^{II} $E_{1/2}$ (ΔE_p) (mV)	i_{p_a}/i_{p_c}	rev Pd^{II}/Pd^{I} $E_{1/2}$ (ΔE_p) (mV)	i_{p_a}/i_{p_c}	rev Pd^{I}/Pd^{0} $E_{1/2}$ (ΔE_p) (mV)	i_{p_a}/i_{p_c}	irrev$_{ox}$ E_{p_a} (mV)	E_{p_a} (mV)
Pd-1			−2105 (60)	0.95			747	
Pd-2			−1847 (95)	0.75	−2005 (78)	0.52	512	895
Pd-3	1329 (98)	0.83	−1575 (71)	0.76	−1995 (81)	0.62	182	
Pd-4			−2037 (76)	0.54			589	
Pd-5			−1987 (74)	0.66			562	1543
Pd-6			−1792 (98)	0.76	−2066 (102)	0.82	288	913

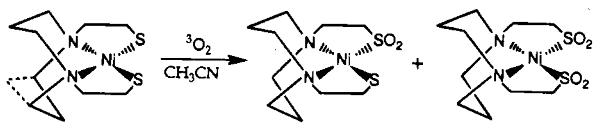
[a] All potentials scaled to NHE referenced to a Cp_2Fe^+/Cp_2Fe standard ($E_{1/2}^{NHE}$ = 400 mV). [b] 0.25 M TBAHFP electrolyte measured vs a Ag/$AgNO_3$ reference electrode.

Scheme 4



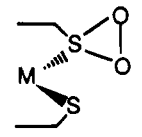
state in the range 50−70 mV; the addition of an oxygen to a sulfoxide sulfur, creating a sulfone S-donor in the three cases of Scheme 4, results in a much greater stabilization of the Pd^I oxidation state, in the range 190−220 mV. The destabilization of the oxidation event over the complete oxygenation range (i.e., **Pd-1** → **Pd-3**) is equal to the stabilization of the reduction event.

Reactivity of Pd-1 and Oxygenate Series with Molecular O_2. In contrast to the **Ni-1** complex, which slowly (half-life of a day) reacts with $^3O_2$ in CH_3CN solution under ambient conditions to give mono- and bis(sulfone) complexes, eq 3, no



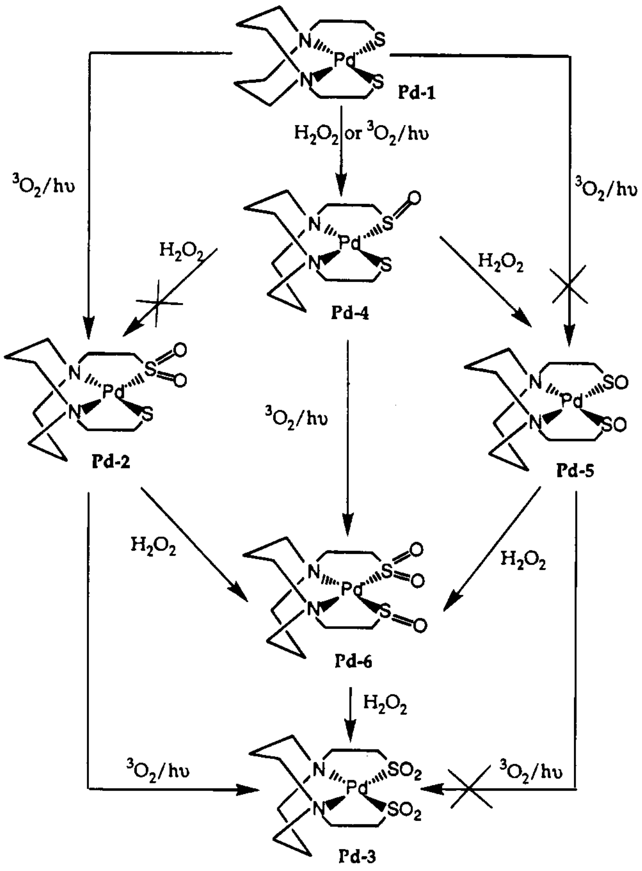
(3)

reaction at all is seen for **Pd-1** with $^3O_2$ over a period of 7 days in both aprotic and protic solvents. As indicated in the Synthesis section, oxygen reactivity can be promoted by UV photolysis, and in fact, such an approach is the only way that the monosulfone **Pd-2** could be prepared. A thiadioxirane[27,29] similar to that proposed to account for the established pairwise addition of molecular oxygen to **Ni-1** is expected to also be involved in the production of **Pd-2**; however, the definitive isotopic labeling experiments are not yet available.



thiadioxirane

Scheme 5



A full comparison of the reactivity of **Ni-1**, **Ni-1***, and **Pd-1** with $^3O_2$ and with $^1O_2$ will be presented in a separate report.[15] Scheme 5 summarizes results of experiments carried out to contrast the reactivity of O_2 and H_2O_2 with **Pd-1**. The preparation of the sulfones **Pd-2** and **Pd-3** from molecular O_2 is effected in aprotic solvents under photolysis, while O_2 seems to serve as an O atom source to photochemically activated **Pd-1** in MeOH, producing a sulfoxide, **Pd-4**, as indicated in Scheme 5. In addition to the important observation that **Pd-2** can be uniquely prepared by reaction with O_2 under photolysis, the further reactivity of **Pd-2** with O_2 to yield **Pd-3** is unprecedented in analogous Ni chemistry.[3,30] Although the oxygen atom of palladium sulfoxides can be removed in the presence of strong O atom abstracting agents such as *n*-Bu_3P and SO_2, they appear to be less reactive than the nickel analogues. Certainly, the ease of handling and isolation of the Pd−S(=O)R derivatives suggests a robustness greater than the Ni−S(=O)R analogues.

Concluding Remarks. The major conclusions of this work are as follows. (1) A second group VIII *cis*-dithiolate series demonstrating all levels of S-oxygenation has been achieved, and characteristic features have been determined. Included are three more examples of the uncommon metallosulfoxides.

(2) The synthetic accessibility and stability of the palladium sulfoxides, **Pd-4**, **Pd-5**, and **Pd-6**, rival those of the **Ni-4***, **Ni-**

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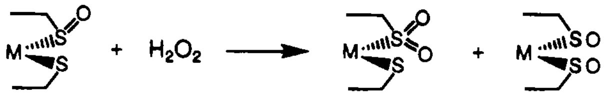
(29) Darensbourg, M. Y.; Farmer, P. J.; Soma, T.; Russel, D. H.; Solouki, T.; Reibenspies, J. H. In *The Activation of Dioxygen and Homogeneous Catalytic Oxidation*; Barton, D. H. R., Martell, A. E., Sawyer, D. T., Eds.; Plenum Press: New York, 1993; p 209.

(30) Farmer, P. J.; Solouki, T.; Soma, T.; Russell, D. H.; Darensbourg, M. Y. *Inorg. Chem.* **1993**, *32*, 4171.

Scheme 6



Ni-4	**Ni-2** (100%)	–
Ni-4*	**Ni-2*** (~50%)	**Ni-5*** (~50%)
Pd-4	–	**Pd-5** (100%)

5*, and **Ni-6*** complexes. Whereas the stability toward disproportionation and the recalcitrant oxygen transfer reactions from the sulfoxide ligands in the derivatives of **Ni-1*** was ascribed to the steric effect of the four methyl groups adjacent to the sulfurs, the isolation and robust character of the palladium sulfoxides can only be ascribed to an inherent thermodynamic stability, based on electronic factors.

(3) The apportionment of O atom addition from H_2O_2 to thiolate sulfur vs sulfoxide sulfur lay on the side of the latter in the **Ni-4** synthetic scheme and was fairly equally distributed in the case of the sterically encumbered **Ni-4***. As indicated in Schemes 5 and 6, the site selection for the addition of a second oxygen atom to **Pd-4** is decidedly for the second thiolate sulfur. At this stage, it is unclear as to whether the product distribution expressed in Scheme 6 reflects kinetic or thermodynamic control. Futhermore, the mechanism of oxygen transfer from H_2O_2 may follow a manifold of reaction possibilities, including metal-based (that is, H_2O_2 serves as nucleophile), followed by intramolecular S−O bond formation from the more internally labile or reactive S-site, or S- or O-based (that is, H_2O_2 serves as electrophile to thiolate-S or sulfoxide-O). Notably, both **Ni-5*** and **Pd-5** withstand refluxing CH_3CN without isomerization, or intramolecular disproportionation, to the sulfone/thiolate complex. This can be rationalized by a greater rigidity of the former, due to the sterically restrictive methyl substituents, and of the latter, due to a stronger square planar ligand field preference.

(4) Although it is stable, the bis(sulfoxide) complex, **Pd-5**, could not be produced by photooxygenation, i.e., the use of molecular O_2 in the presence of UV photolysis, whereas **Ni-5*** can be synthetically accessed by either H_2O_2 or $^1\Delta$ O_2. We propose that cross site addition of O_2 to the *cis* thiolate sulfurs in **Pd-1** at a distance of 3.3 Å is unlikely, whereas the S---S distance of 3.1 Å in **Ni-1*** is amenable to cross site O_2 addition, resulting in **Ni-5***. Proof of the latter hypothesis requires $^1\Delta$ O_2 production from $^{18}O_2/^{16}O_2$ mixtures. Experiments in this area are underway.

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Supporting Information Available: Tables of a summary of crystallographic data and refinement, atomic coordinates, bond lengths, bond angles, anisotropic displacement parameters, and H atom coordinates and packing diagrams of **Pd-2**, **Pd-4**, and **Pd-3/Pd-6** (21 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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