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CYCLOPALLADATED ARYLSULFIDES AND SULFOXIDES: SYNTHESIS, CHARACTERIZATION AND REACTIVITY TOWARD *m*-CHLOROPERBENZOIC ACID

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Abstract—A number of stable di- μ -halogeno-bridged cyclopalladated complexes $[Pd_2L_2Cl_2]$ have been synthesized (where L = arylsulfides and their corresponding sulfoxides). The cyclopalladated compounds have been characterized on the basis of elemental analysis and spectroscopic (IR, UV–vis, and ¹H and ¹³C NMR) data. Regioselective aromatic metaloxylation (Pd—Ar \rightarrow Pd—O—Ar) or di- μ -halogeno-bridged cyclopalladated complexes occur with *m*-chloroperbenzoic acid at room temperature without any oxidation of sulfur atoms. Copyright © 1996 Elsevier Science Ltd

Cyclopalladated compounds are known to be important starting materials for organic synthesis and it is possible to observe selective functionalization of the metallated carbon atom which is otherwise difficult to achieve.¹⁻⁴ With this background we undertook a project to generate cyclopalladated complexes of simple organic substrates having a two-electron donor sulfur atom⁴⁻⁸ and to study their reactivity with an oxygen atom transfer reagent. It is well known that arylsulfides react with oxygen atom transfer reagents like hydrogen peroxide,^{9,10} organic peracids,¹¹ selenium dioxide¹² and iodosylbenzene¹³ to generate arylsulfoxides and, furthermore, sulfones are produced from sulfoxides.

The present report concerns the syntheses and characterization of cyclopalladated complexes of arylsulfides and arylsulfoxides,⁶ and the regio-selective metaloxylation^{14–17} of di- μ -halogeno-bridged cyclopalladated species by *m*-chloroperbenzoic acid.

EXPERIMENTAL

All chemicals and solvents used in syntheses were of reagent grade and were used without further purification unless stated otherwise. CH_2Cl_2 , npentane, benzene, MeCN, MeOH and Et_2O were purified or dried as described in the literature. Benzylphenyl sulfide (HL¹), dibenzyl sulfide (HL²) and benzylphenyl sulfoxide (HL³) were prepared as reported elsewhere.¹⁰ Dibenzyl sulfoxide (HL⁴) was synthesized following a reported method.¹⁸

Preparation of complexes

The synthetic procedure followed in this work is a modification of that reported⁶ for the complexes $[Pd_2L_2^2(OAc)_2]$ (2a) and $[Pd_2L_2^4(OAc)_2]$ (4a).

 $[Pd_2L_2^1(OAc)_2]$ (1a). Benzylphenyl sulfide (0.27) g, 1.35 mmol) was added to a suspension of palladium(II) acetate (0.2 g, 0.891 mmol) in acetic acid (15 cm^3) . The reaction mixture was kept at 363 K for 1 h and was evaporated to dryness. To remove excess acetic acid, the greenish yellow residue was washed with n-pentane and, finally, the residue was extracted with CH₂Cl₂. The CH₂Cl₂ solution was chromatographed over silica gel (60-120 mesh size). A vellow band containing complex 1a was eluted by a mixture of CH_2Cl_2 and $Et_2O(50:1, v/v)$. On removal of the solvent, bright yellow crystalline complex la was obtained and dried in vacuo. Yield : 50%. Found: C, 49.1; H, 3.8; S, 8.6. Calc. for $C_{30}H_{28}O_4Pd_2S_2$: C, 49.4; H, 3.8; S, 8.8%. IR: $v(CH_3COO)$ 1547, 1408 cm⁻¹.

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[Pd₂L¹₂C₂] (**1b**). To a solution of acetato-bridged compound **1a** (0.1 g, 0.137 mmol) in acetone (80 cm⁹), an aqueous solution of lithium chloride (0.04 g, 0.943 mmol) was added dropwise. The solution was stirred for 12 h at room temperature. On removal of the solvent, a bright yellow solid (**1b**) was obtained, which was washed thoroughly with Et₂O and water. Finally, it was dried *in vacuo*. Yield: 80%. Found: C, 45.6; H, 3.2; S, 9.2. Calc. for C₂₆H₂₂Cl₂Pd₂S₂: C, 45.8; H, 3.2; S, 9.4%. Absorption spectrum (CH₂Cl₂), λ /nm (ε /dm³ mol⁻¹ cm⁻¹): 355 (4000), 240 (39,180).

 $[Pd_2L_2^2(OAc)_2]$ (2a). The compound was prepared using the method for 1a with the following variations. The temperature of the reaction mixture was maintained at 343 K for 8 h and benzene was used as eluent in the chromatographic separation of complex 2a. Yield: 45%. Found: C, 50.5; H, 4.2; S, 8.2. Calc. for $C_{32}H_{32}O_4Pd_2S_2$: C, 50.7; H, 4.2; S, 8.4%. IR: ν (CH₃COO) 1565, 1413 cm⁻¹.

[Pd₂L₂²Cl₂] (**2b**). The complex was prepared from **2a** and sodium chloride following the procedure described for **1b**. Yield: 76%. Found: C, 47.1; H, 3.6; S, 8.9. Calc. for C₂₈H₂₆Cl₂Pd₂S₂: C, 47.3; H, 3.7; S, 9.0%. Absorption spectrum (CH₂Cl₂), λ /nm (ϵ /dm³ mol⁻¹ cm⁻¹): 348 (4100), 240 (22,000).

[Pd₂L₂³(OAc)₂] (**3a**). Complex **3a** was prepared using the same method as for **1a**. A mixture of CH₂Cl₂ and MeOH (50:1, v/v) was used as eluent for the chromatographic separation of complex **2a**. Yield: 40%. Found: C, 47.0; H, 3.6; S, 8.1. Calc. for C₃₀H₂₈O₆Pd₂S₂: C, 47.3; H, 3.7; S, 8.4%. IR: ν (CH₃COO) 1543, 1409 cm⁻¹; ν (SO) 1113 cm⁻¹.

 $[Pd_2L_2^3Cl_2]$ (3b). This complex was prepared from 3a and lithium chloride using the method described for 1b. Yield: 45%. Found: C, 43.5 H, 3.0; S, 8.8. Calc. for C₂₆H₂₂Cl₂Pd₂O₂S₂: C, 43.7; H, 3.1; S, 9.0%. IR: ν (SO) 1124 cm⁻¹.

 $[Pd_2L_2^4Cl_2]$ (4b). Complex 4a was synthesized following the method for 2a. A mixture of benzene and MeCN (9:1, v/v) was used as eluent in the chromatographic isolation of 4a. Complex 4b was obtained from 4a following the method for 2b. Yield: 20%. Found: C, 44.9; H, 3.5; S, 8.4. Calc. for C₂₈H₂₆Cl₂Pd₂O₂S₂: C, 45.3; H, 3.5; S, 8.6%. IR: ν (SO) 1114 cm⁻¹.

Metaloxylation by m-chloroperbenzoic acid

Reaction of complex **1b** with m-chloroperbenzoic acid. To a stirred solution of complex **1b** (0.1 g, 0.146 mmol) in CH₂Cl₂ (30 cm³), a solution of *m*chloroperbenzoic acid (0.055 g, 0.318 mmol) in CH₂Cl₂ (5 cm³) was added dropwise. The colour of the solution changed from yellow to brown. The reaction mixture was stirred for 3 h at room temperature. After complete removal of the solvent under reduced pressure, the solid residue was washed with aqueous EtOH (1:1, v/v) followed by Et₂O to remove the organic acids. Complex **5** was obtained as a brown crystalline powder and dried *in vacuo*. Yield: 60%. Found: C, 43.6; H, 3.0; S, 8.8. Calc. for C₂₆H₂₂Cl₂Pd₂O₂S₂: C, 43.7; H, 3.1; S, 9.0%. Absorption spectrum (CH₂Cl₂), λ /nm (ϵ /dm³ mol⁻¹ cm⁻¹): 240 (60,000).

Reaction of complex **2b** with m-chloroperbenzoic acid. The reaction between complex **2b** and *m*chloroperbenzoic acid was carried out in a similar manner as stated above. The crude product was purified by chromatography on silica gel and complex **6** was eluted using a mixture of CH₂Cl₂ and MeOH (25:1, v/v). After the removal of the solvent, compound **6** was collected as dark brown solid and dried *in vacuo*. Yield: 30%. Found: C, 45.1; H, 3.5; S, 8.5. Calc. for C₂₈H₂₆Cl₂Pd₂O₂S₂: C, 45.3; H, 3.5; S, 8.6%. Absorption spectrum (CH₂Cl₂), λ/nm ($\epsilon/dm^3mol^{-1} cm^{-1}$): 230 (46,700).

Reaction of complex **4b** with m-chlorperbenzoic acid. The reaction between complex **4b** and *m*chloroperbenzoic acid, and the isolation of the brown complex **7** were carried out following the same procedure as stated for complex **1b**. Yield : 40%. Found : C, 43.2 ; H, 3.3 ; S, 8.2. Calc. for $C_{28}H_{26}Cl_2Pd_2O_4S_2$: C, 43.4 ; H, 3.4 ; S, 8.3%. IR : ν (SO) 1118 cm⁻¹. Absorption spectrum (CH₂Cl₂), λ/nm (ϵ/dm^3 mol⁻¹ cm⁻¹) : 335 (sh, 4448), 230 (35,400).

Physical measurements

The IR spectra were recorded either with Perkin– Elmer 783 or Perkin–Elmer 983 (with DS system) spectrophotometers as KBr discs. ¹H and ¹³C NMR spectra were recorded using a Jeol GSX 400 NB spectrometer. Electronic spectra were measured on a Shimadzu UV-240 spectrophotometer. Carbon and hydrogen analyses were maded by RSIC, Chandigarh, India. Sulfur contents were estimated following reported methods.¹⁹

RESULTS AND DISCUSSION

The acetato-bridged cyclopalladated complexes **1a–4a** were synthesized by reacting palladium(II) acetate with the appropriate arylsulfides (HL¹, HL²) or arylsulfoxides (HL³, HL⁴) in acetic acid in the temperature range 343–363 K. Here, palladium (II) acetate acts as an electrophile^{7,20} in the cyclopalladation process. The di- μ -halgeno-bridged cyclopalladated complexes **1b–4b** were obtained by treating the respective acetato-bridged compounds with alkali halides. The elemental analyses of com-

plexes 1-4 are in full agreement with their formulations.

Complexes **1a**, **2a** and **3a** display strong bands around 1570 and 1420 cm⁻¹ characteristic of acetato bridging,²¹ which are absent in the corresponding chloro-bridged compounds. Free sulfoxides show an intense band in the region 1040– 1060 cm⁻¹ due to v(SO). Sulfoxide can bind the metal centre via the sulfur or oxygen atom.²² Here, complexes **3** and **4** show a v(SO) stretch in the higher energy region, 1114–1118 cm⁻¹. Therefore, this clearly indicates^{22,23} that the sulfoxides bind palladium(II) centres through the sulfur atom in complexes **3** and **4**.

The ¹H NMR spectra of **1a** (in DMSO- d_6) and **2a** (in $CDCl_3$) show signals of the methyl protons of acetato groups at 2.0 (s) and 2.14 (s) ppm, respectively. The methylene protons of complex 1a appear as a broad peak at 4.00 ppm. The signals for two non-equivalent methylene groups of complex 2a are observed as four doublets at 3.73, 4.05, 4.35 and 4.42 ppm.⁷ The ¹H NMR spectrum of complex 1b (in DMSO-d₆) exhibits signals for methylene, H—C(3) and H—C(4) protons at 4.52 (br, s), 6.80(d) and 6.9 (t) ppm, respectively. The appearance of a broad peak at room temperature for two inequivalent protons of a methylene group which is attached to a palladium(II)-coordinated sulfur atom is well known in the literature.^{4,5} The highfield shift of H—C(3) on *ortho*-metallation is well documented.¹⁴ The other aromatic proton signals of complex 1b appear in the range 7.01-7.82 ppm. The signals for two non-equivalent methylene groups of chloro-bridged complex 2b in DMSO- d_6 are observed at 4.05 (s) and 4.27 (s) ppm. The signals for H—C(3) and H—C(4) protons of the metallated phenyl ring of 2b resonate at comparatively high field, 6.84 (d) and 6.92 (t) ppm. Other aromatic proton signals for complex 2b appear in the range 7.0–7.62 ppm. The ¹H NMR spectra of 3b and 4b could not be recorded due to the poor solubility of the compounds in common organic solvents.

The ¹H-decoupled ¹³C NMR spectrum of **1b** in DMSO- d_6 exhibits a signal for a methylene carbon at 47.40 ppm. The signal for palladated carbon [C(2)] is observed in the low-field region as a singlet at 150.42 ppm, as expected.⁸ The other signals for aromatic rings are observed at 123.38, 123.42, 124.59, 125.15, 129.46, 129.74, 131.07 and 131.60 ppm.

The ¹H-decoupled ¹³C NMR spectrum of **2b** in DMSO- d_6 exhibits signals for two non-equivalent methylene groups at 41.53 and 42.75 ppm. The signal for the palladated carbon C(2) also appears in the lower field region at 148.95 ppm. The other

signals for aromatic rings are observed at 123.56, 124.67, 125.24, 128.07, 128.78, 129.66 and 134.55 ppm.

The electronic spectra of the halogeno-bridged cyclopalladated complexes in CH_2Cl_2 solution show intense absorption bands around 240 and 350 nm, which are tentatively assigned to intraligand and ligand-to-metal charge transfer transitions, respectively. The electronic spectra of **3b** and **4b** could not be recorded due to poor solubility.

Metaloxylation reaction of orthopalladated arylsulfides and arylsufoxide with m-chloroperbenzoic acid

Complexes 1b, 2b and 4b react with *m*-chloroperbenzoic acid (1:2 mole ratio) in CH_2Cl_2 at room temperature and produce complexes 5, 6 and 7 respectively. The elemental analyses of complexes 5–7 are in full agreement with the formulations.

The IR spectra of the metaloxylated complexes 5 and 6 show the complete absence of any v(SO)stretch, which excludes the possibility of oxidation of metal-bound sulfur centres^{14,24,25} by *m*-chloroperbenzoic acid. In the IR spectrum of complex 7, the v(SO) stretch is observed at 1118 cm⁻¹. All the complexes 5–7 show a new band at *ca* 1245 cm⁻¹. Grigor and Nielson²⁶ reported that the v(CO)stretch of bis(*N*,*N*-dimethylsalicylaldiminato) palladium(II) appears at 1270 cm⁻¹. On this



	R	х	Y
1a	Ph	OAc	S
1b	Ph	Cl	S
2a	PhCH ₂	OAc	S
2b	PhCH ₂	Cl	S
3a	Ph	OAc	S = 0
3b	Ph	Cl	S = 0
4 a	PhCH ₂	OAc	S = 0
4 b	PhCh ₂	Cl	S = 0

Scheme 1.



basis, the new band near 1245 cm^{-1} may be assigned to a v(CO) stretch. The ¹H NMR spectrum of complex **5** (in DMSO- d_6) exhibits signals for two inequivalent protons of the methylene group as two doublets¹⁵ at 4.25 and 4.55 ppm ($J \sim 13$ Hz). The aromatic proton signals appear in the range 5.3–8.2 ppm. Each of the two different methylene groups of complex **6** (in DMSO- d_6) appear as an AB quartet;⁷ one is centred at 4.05 ($J \sim 13$ Hz) and the other at 4.27 ($J \sim 13$ Hz) ppm. The two different methylene groups of complex **7** (in DMSO- d_6) also appear as two AB quartets⁷ centered at 4.45 ($J \sim 13$ Hz) and 4.85 ($J \sim 13$ Hz) ppm. The aromatic proton signals for complexes **6** and **7** are observed in the region 6.8–8.5 ppm.

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