Notes

A Novel Example of Metal-Mediated Aromatic Thiolation in a Ruthenium Complex. Crystal Structure of $Ru^{II}(SC_6H_4N{=}NC_6H_4N)_2$[†]

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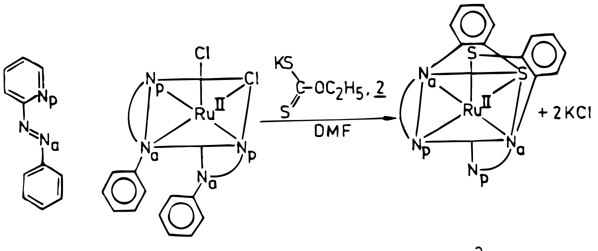
Received June 28, 1995

Introduction

Aromatic thiols constitute a very important class of organic compounds.[2a] The available synthetic routes for the thiolation of an aromatic ring ($C_6H_5{-}H \rightarrow C_6H_5{-}SH$) involve multistep process.[2b] In the present article we report an unusual reaction where the pendant phenyl ring of the ligand pyridine-2-azobenzene (**L**) in **1** has been selectively (ortho carbon atom of the phenyl ring) and directly thiolated, **3** by *O*-ethyl dithiocarbonate (**2**). To our knowledge this is the first example of a transition metal mediated regiospecific thiolation of an aromatic ring. Metal-assisted facile C−S bond cleavage and the concomitant formation of a selective new carbon−sulfur center are extremely important in biological systems[3] as well as in industry[4] and in synthetic organic chemistry.[5]

Results and Discussion

The reaction of *ctc*-Ru(L)$_2$(Cl)$_2$, **1** (*cis*−*trans*−*cis* with respect to chlorides, pyridine, and azo nitrogens respectively) with the potassium salt of *O*-ethyl dithiocarbonate (**2**) in boiling DMF for 3 h. affords a dark red brown solution corresponding to **3**, eq 1. The pure thiolated product, **3** has been isolated as dark colored crystalline solid in 70% yield by chromatographic purification of the above red brown solution in silica gel column using chloroform−acetonitrile (10:1) as eluant followed by evaporation of the solvents. A 1:2 ratio of **1** and **2** is required to get the maximum yield in minimum time period. The reaction (eq 1) does not take place in alcohol, benzene, or acetonitrile solvents; possibly the high boiling point and dielectric constant of DMF solvent plays an important role in the course of the thiolation reaction. In absence of dithiocarbonate (**2**), **1** remains unchanged in boiling DMF. Carbon disulfide, the precursor of **2**, does not react with **1**.



L 1 3

(1)

Under identical experimental conditions the free ligand **L** fails to react with dithiocarbonate (**2**). Thus both **2** and DMF appear to be the suitable components for the thiolation of the pendant phenyl ring of **L** in complex **1**.

Microanalytical data (C, H, N) of **3** are in good agreement with the calculated values (see Experimental Section). **3** is soluble in common polar and nonpolar solvents. In solution (acetonitrile/dimethylformamide) it shows nonconducting behavior. Solid state magnetic moment measurement at 298 K indicates that the complex **3** is diamagnetic (t_{2g}^6, $S = 0$). In its infrared spectrum the N=N stretching frequency of the coordinated ligand is appreciably lowered (1280 cm^{-1}) compared to that in free ligand, **L** (1425 cm^{-1}), evidently due to Ru(II)→**L**π^* back-bonding.[6] In CHCl$_3$ solution the complex **3** displays two intense transitions at 710 nm ($\epsilon = 7970$ M^{-1} cm^{-1}) and 560 nm ($\epsilon = 21\,170$ M^{-1} cm^{-1}) which are assigned to $t_2(Ru^{II}) \rightarrow \pi^*(\mathbf{L})$ MLCT transitions.[7] In the UV region it shows three other transitions [λ, 375 nm ($\epsilon = 43\,200$ M^{-1} cm^{-1}); λ, 344 nm ($\epsilon = 41\,100$ M^{-1} cm^{-1}); λ, 263 nm ($\epsilon = 60\,770$ M^{-1} cm^{-1})] which are believed to represent intraligand ($\pi-\pi^*$ and n−π^*) transitions.[8]

The X-ray crystal structure of the final product (**3**) is shown in Figure 1. Selected bond lengths and bond angles are displayed in Table 1. The RuS$_2$N$_4$ coordination sphere is distorted octahedral although the two meridional planes are very nearly orthogonal (dihedral angle 90.5°). The Ru^{II}−S distances (2.376(2) and 2.359(2) Å) compare well with the reported Ru^{II}−S distances.[9] The two C−S distances are almost equal, 1.734(6) and 1.731(6) Å. The shortness of the Ru−N(azo) bonds [Ru−N(3) = 1.975(4), Ru−N(6)=1.976(4) Å] compared to Ru−N(pyridine) bonds [Ru−N(1) = 2.066(5), Ru−N(4) = 2.090(4) Å] reflects the back-bonding interaction, Ru^{II} (dπ)→**L**(π^*) where the **L**(π^*) level is predominantly azo in character.[8]

In the starting complex, **1** (the structure of **1** was confirmed

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[†] Dedicated to Professor Animesh Chakravorty on the occasion of his 60th birthday.

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S0020-1669(95)00810-X CCC: $12.00

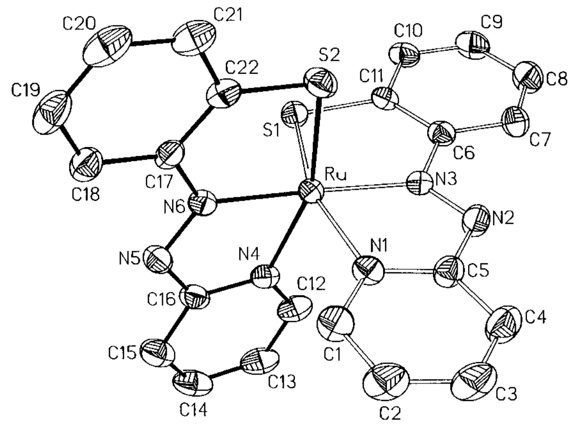

Figure 1. Perspective view of the complex $Ru(SC_6H_4N{=}NC_6H_4N)_2$, **3**.

Table 1. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for $Ru(SC_6H_4N{=}NC_6H_4N)_2$, **3**

	Distances		
Ru−S(1)	2.376(2)	Ru−N(6)	1.976(4)
Ru−S(2)	2.359(2)	S(1)−C(11)	1.734(6)
Ru−N(1)	2.066(5)	S(2)−C(22)	1.731(6)
Ru−N(4)	2.090(4)	N(2)−N(3)	1.301(7)
Ru−N(3)	1.975(4)	N(5)−N(6)	1.311(6)
	Angles		
S(1)−Ru−S(2)	92.4(1)	S(2)−Ru−N(4)	159.9(1)
S(1)−Ru−N(1)	158.6(1)	S(2)−Ru−N(6)	84.1(1)
S(1)−Ru−N(3)	83.7(1)	Ru−S(1)−C(11)	96.7(2)
S(1)−Ru−N(4)	89.5(1)	Ru−S(2)−C(22)	97.3(2)
S(1)−Ru−N(6)	103.4(1)	N(4)−Ru−N(6)	76.0(2)
S(2)−Ru−N(1)	94.4(1)	N(1)−Ru−N(3)	75.7(2)
S(2)−Ru−N(3)	92.3(1)	N(1)−Ru−N(4)	91.0(2)

crystallographically earlier[10]), the phenyl rings of both **L** units (which are the active sites of the thiolation reaction) exist far away from the chlorides with the pyridine and azo nitrogens being mutually *trans* and *cis*, respectively. In the final product, **3**, however, the relative orientation of the respective nitrogens are exactly the reverse. Thus a geometrical reorganization has been taken place internally during the thiolation reaction to attain the meridional configuration of **3**.

Ruthenium has a very rich and developed chemistry with the pyridine-2-azobenzene ligand[11] but in none of the cases the coordinated ligand **L** showed any further transformation as it is being observed in the present case. It has been observed earlier that in Pd-**L** complex the aromatic $-C_6H_5$ moiety of **L** can be regiospecifically oxidized to $-C_6H_4(OH)$ (hydroxyl group *cis* to azo function)[12] and rhenium mediated reductive cleavage of **L** leads to very rare semibent organoimido, $Re^{V/VI}(N-C_6H_5)$ species.[13] Thus this work further demonstrates that the pyridine-2-azobenzene ligand (**L**) is susceptible to undergo a fascinating important metal-mediated reaction.

The mechanism of this reaction and the nature of the other fragment(s) of **2** are not clear at present. This along with the general applicability of this type of reaction in other systems are under scrutiny.

Experimental Section

Materials. The *ctc*-$Ru(L)_2(Cl)_2$ complex and the potassium salt of *O*-ethyl dithiocarbonate (KSSCOEt) were prepared according to the reported procedures.[11a,14] Chemicals and solvents were reagent grade and used as received.

Physical Measurements. The UV−vis spectrum was recorded by using a Shimadzu UV-265 spectrophotometer. IR spectra (in KBr disks) were taken on a Perkin-Elmer 783 spectrophotometer. Diamagnetism was checked with the help of a PAR 155 vibrating sample magnetometer fitted with a Walker Scientific L75FBAL magnet. Microanalyses (C, H, N) were done by using a Perkin-Elmer 240C elemental analyzer.

Preparation of Compound 3, $Ru(SC_6H_4N{=}NC_6H_4N)_2$. A 100 mg (0.186 mmol) sample of *ctc*-$Ru(L)_2(Cl)_2$, **1** was dissolved in 20 mL of DMF. To this solution the potassium salt of *O*-ethyl dithiocarbonate (**2**) (60 mg, 0.38 mmol) was added. The resulting solution was heated to reflux for 3 h. The initial blue solution was gradually turned to red brown color. It was evaporated to dryness under reduced pressure and the solid mass thus obtained was dried in vacuo. The dried product was dissolved in a small volume of chloroform and was subjected to chromatography on a silica gel (60−120 mesh, BDH) column (30 × 1 cm). On elution with benzene a light yellow band separated out first and was rejected. A red brown band was then eluted with chloroform−acetonitrile (10:1). The collected eluant was evaporated to dryness to afford a dark crystalline solid, which was stored over P_4O_{10} in vacuo. Yield is 70%.

Anal. Calcd for **3**, $RuC_{22}H_{16}N_6S_2$: C, 49.90; H, 3.02; N, 15.88. Found: C, 49.85; H, 3.09; N, 15.79.

Single crystals were grown by slow diffusion of a dichloromethane solution of **3** into hexane.

X-ray Structure Determination. A dark crystal of dimension 0.22 × 0.28 × 0.30 mm^3 was mounted on a glass fibre. Unit cell parameters were determined by the least-squares fit of 25 machine-centered reflections having 2θ values in the range 15−30° . Lattice dimensions and Laue group were checked by axial photography. Systematic absences led to the identification of the space group as $P2_1/n$. Data were collected by the ω scan method over the 2θ range 3−45° ($\pm h,+k,+l$) on a Siemens R3m/V diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å) at 295 K. Significant crystal data and data collection parameters are listed in Table 2. Two check reflections were measured after every 198 reflections during data collection to monitor crystal stability. No significant intensity reduction was observed in the exposure to X-ray radiation. All data were corrected for Lorentz polarization effects and an empirical absorption correction was done on the basis of azimuthal scans[15] of eight reflections. The absorption coefficient and the minimum transmission coefficient (maximum normalized to 1.0) were 9.53 cm^{-1} and 0.90 respectively. Of

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Table 2. Crystallographic Data for $Ru(SC_6H_4N{=}NC_6H_4N)_2$, **3**

chem formula	$C_{22}H_{16}N_6S_2Ru$
fw	529.6
space group	$P2_1/n$
a, Å	14.102(9)
b, Å	11.297(8)
c, Å	14.411(9)
β, deg	111.70(5)
V, Å^3	2133(2)
Z	4
T, K	295
λ, Å	0.710 73
ρ_{calcd}, g cm^{-3}	1.649
μ, cm^{-1}	9.53
trans coeff	0.84−0.93
R^a	0.0314
$R_w{}^b$	0.0396

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/w|F_o|^2]^{1/2}$. $w^{-1} = \sigma^2(|F_o|) + 0.0005|F_o|^2$.

the 3116 reflections collected, 2808 were unique; 2108 satisfying the $F > 6.0\sigma(F)$ criterion were used for structure solution.

All calculations for data reduction, structure solution and refinement were done on a Micro Vax II computer using the SHELXTL-PLUS program package.[16] The metal position was located from a Patterson map, and the non-hydrogen atoms emerged from the difference Fourier syntheses. The structure was then refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added at their respective calculated positions with fixed $U = 0.08$ Å^2 in the last cycle of refinement. The number of variable parameters was 280, affording a data-to-parameter ratio of 7.5. The refinement converged to $R = 3.14\%$, $R_w = 3.96\%$, and GOF = 1.28, with the largest difference peak of 0.37 e Å^{-3} near the metal atom.

Acknowledgment. Crystallography was done at the National Single Crystal Diffractometer Facility, Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta, India. Financial support received from the Department of Science and Technology, New Delhi, India, is gratefully acknowledged.

Supporting Information Available: Atomic coordinates and equivalent isotropic displacement coefficients (Table 3), full listings of bond distances (Table 4), bond angles (Table 5), anisotropic thermal parameters (Table 6), and hydrogen atom coordinates (Table 7) and a summary of structure determination data (Table 8) (8 pages). Ordering information is given on any current masthead page.

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