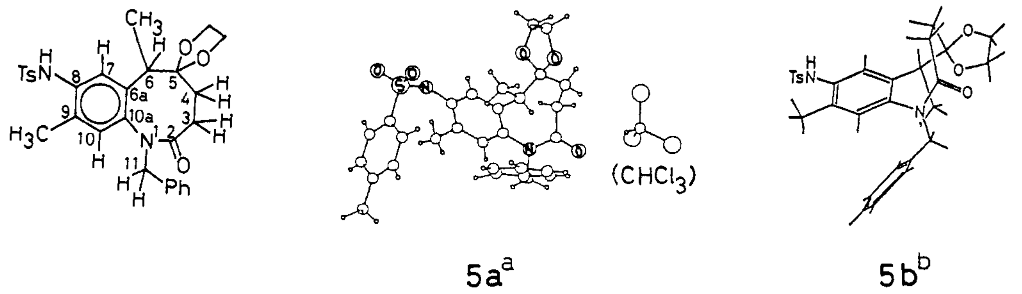
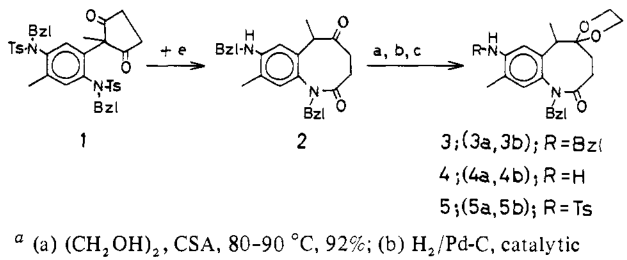


Figure 1. (a) X-ray crystal structure of **5a** (twist-boat-chair), (b) Presumed structure of **5b** (twist-boat, Dreiding model).

Scheme I[a]



[a] (a) $(CH_2OH)_2$, CSA, 80-90 °C, 92%; (b) H_2/Pd-C, catalytic AcOH, AcOEt, quantitative; (c) TsCl, pyridine, 94%.

The rotation of the benzyl group is restricted mainly by the steric hindrance in the structure of **5a** (Figure 1). Furthermore, the interesting folded conformation is also presumed to be caused by the spatial "attractive interaction" between the benzene ring and 6-H and also between the benzene ring and 6-Me due to the CH/π[5] or the van der Waals' attraction.[6]

The structure of **5b** was determined from the ^{1}H NMR spectral data and NOE's because of the difficulty of preparing a single crystal suitable for X-ray diffraction. Both 9-Me and 10-H signals were observed to be upfield compared to the case of **5a**. One of the four methylene protons (3-H, 4-H) was observed at higher field (δ 1.7–1.9) and distinct from the others (δ 2.1–2.4). Moreover a large NOE of 23% was observed for the 6-H signal, and none for the 6-Me signal on saturation of the 7-H signal.

Considering these data and the steric strain of the molecule, the structure of **5b** should be represented by the twist-boat form (TB, Figure 1), which has been known to be the metastable conformer of *cis,cis*-1,3-cyclooctadiene.[7] The 7-H is in close proximity to 6-H, and both the 9-Me and 10-H are close to the face of the benzene ring of the N substituent, probably caused by the CH/π interaction as discussed for **5a**. One 4-H (see **5b** in Figure 1) is situated directly over the benzene ring of the fundamental framework, accounting for the observed shielding. Thus, the signal at δ 1.7–1.9 is assigned to the endo-4-H.

The other conformers, e.g., twist-chair, boat, and twist-boat-chair[7] with the hindered oriented 6-Me (which was generated by the ring inversion of **5a**, TBC, Figure 1), were excluded for the following reasons. First, they seemed to be of high energy, labile because of the strain caused by the nonbonded interactions and/or by the large torsion of the lactam bond. Moreover, they could not explain the ^{1}H NMR spectral data and NOE's of **5b**.

Thus, there is no doubt that the two isomers (**5a**, **5b**) are not simply a pair of rotamers based on the restricted rotation of the benzyl group but a pair of conformational diastereoisomers of the eight-membered ring. The rates of interconversion between **5a** and **5b** were measured in Me_2SO-d_6 by monitoring the relative intensities of the 6-Me signals in the ^{1}H NMR spectra as a function of time. The free energies of activation for the interconversion were estimated to be 26.6 ($\Delta G^‡_{5a\to5b}$) and 25.2 kcal/mol ($\Delta G^‡_{5b\to5a}$) at 25 °C.

Further studies on the conformational interconversions of **5** are in progress.

Acknowledgment. We thank Prof. E. Osawa, Faculty of Sciences, Hokkaido University, for helpful discussions. This work was supported by Grants-in-Aid from the Ministry of Education, Science and Culture, Japan, which is gratefully acknowledged.

Supplementary Material Available: Crystal data and tables of atomic coordinates, thermal parameters, bond angles, bond lengths, and structure factors for **5a** (7 pages). Ordering information is given on any current masthead page.

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Synthesis and Structure of a Stable Complex Featuring an S-Bound Dibenzothiophene Ligand: $RuCl_2(4\text{-}R_2P(DBT))_2$ (DBT = Dibenzothiophene)

Stella M. Bucknor, M. Draganjac, Thomas B. Rauchfuss,* and Charles J. Ruffing

School of Chemical Sciences, University of Illinois
Urbana, Illinois 61801

William C. Fultz and Arnold L. Rheingold*

Department of Chemistry, University of Delaware
Newark, Delaware 19711

Received April 16, 1984

This report describes the preparation and structural characterization of the first coordination complex of a dibenzothiophene (DBT) derivative. Dibenzothiophenes[1] are among the most abundant and refractory organosulfur compounds found in fossil fuel feedstocks, and the interaction of these aromatic heterocycles with metals is widely assumed to be central to the mechanisms of both catalytic desulfurization[2] and the poisoning of noble metal catalysts.[3] Given the deteriorating quality of available feedstocks, these mechanistic issues are of considerable current interest.

In 1975 Kuehn and Taube reported the isolation of $[Ru(NH_3)_5(\text{thiophene})](PF_6)_2$ wherein the thiophene is probably S bound to the ruthenium(II) center.[4] Although the instability of the Kuehn–Taube complex ($K_{H_2O} \approx 10$) limited its characterization, this report suggested that ruthenium(II) would be a good starting point for the preparation of more stable derivatives of

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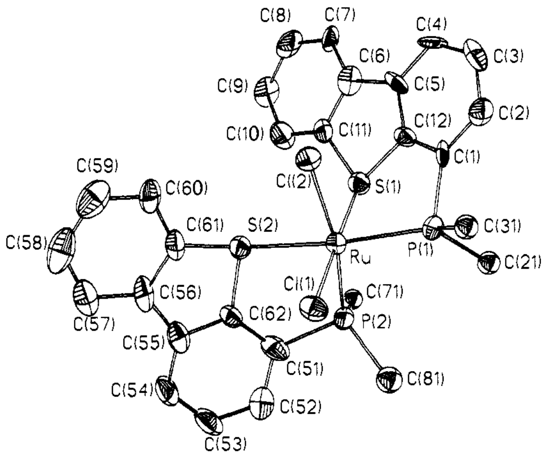
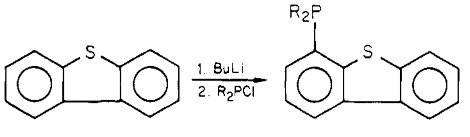


Figure 1. Structure of $RuCl_2((tol)_2P(DBT))_2$ showing atom labeling scheme. The hydrogen atoms and the *p*-tolyl groups have been omitted for clarity. Thermal ellipsoids drawn by ORTEP represent the 35% probability surfaces.

this otherwise unexplored class of ligands. Of particular interest to us was the coordination chemistry of the dibenzothiophenes.[5]

Treatment of 4-lithiodibenzothiophene[6] with diphenylphosphinous chloride or di-*p*-tolylphosphinous chloride gave, after an extractive workup, colorless crystals of $4\text{-}R_2P(DBT)$ (**1a**, R = Ph; **1b**, R = *p*-tol) in 55% yield (eq 1). Compounds **1a** and



(1)

1b were characterized by analysis, mass spectrometry, and ^1H and ^{31}P NMR spectroscopy.[7] These data as well as those obtained for their phosphine sulfide derivatives provided unambiguous characterization of these ligands.[8]

Treatment of CH_2Cl_2 solutions of $RuCl_2(PPh_3)_3$ (1 mmol/60 mL) with 2 equiv of **1a** or **1b** afforded bright orange slurries (**1a**) or solutions (**1b**). Dilution with hexanes gave air-stable orange microcrystalline products in >80% yields. The products were formulated as $RuCl_2(R_2P(DBT))_2$ (**2a**, R = Ph; **2b**, R = *p*-tol) on the basis of microanalytical and fast atom bombardment[9] mass spectral data[10] (eq 2). The $^{31}P\{^1H\}$ NMR spectrum of **2b** shows

$$RuCl_2(PPh_3)_3 + 2(4\text{-}R_2P(DBT)) \rightarrow RuCl_2(4\text{-}R_2P(DBT))_2 + 3PPh_3 \quad (2)$$

an AB quartet ($J_{AB} = 30$ Hz) indicative of mutually cis phosphines. Furthermore, the 360-MHz ^1H NMR spectrum of **2b** features four tolyl methyl singlets requiring the all-cis geometry.

An X-ray diffraction study on single crystals of **2b**, grown by slow evaporation of an acetone solution, confirmed the structural assignment[11] (see Figure 1). A distorted octahedral geometry is observed about the Ru atom. The two $tol_2P(DBT)$ ligands chelate such that like atoms are cis. The Ru–S distances are 2.343 (5) and 2.402 (5) Å for sulfur trans to the chloride and phosphine ligands, respectively. Although there exist no precedents for M···S(thiophene) distances, comparable Ru–S distance of 2.449 (1) Å (trans to P) in $Ru(S_2CH)_2(PPh_3)_2$[13] are considerably longer than that observed in **2b**. The observed $Ru\text{–}S_1$ distance is in the range of Ru–S bond lengths found for ruthenium(II) dithiocarbamates[14] and is slightly shorter than the axial Ru–S distance (N trans, 2.383 (1) Å) in $Ru^{IV}(SR)_4(NCCH_3)$[15] (SR = 2,3,5,6-tetramethylbenzenethiolate).

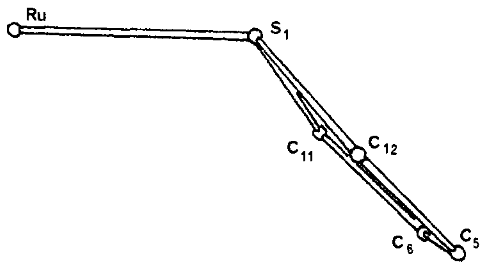


Figure 2. Coordination sphere of S(1) showing its pyramidal geometry; S(2) has a similar coordination geometry.

The average C–S bond length in **2b** of 1.755 (25) Å is similar to those observed for dibenzothiophene (1.747 Å).[16] The individual five- and six-membered rings of the $tol_2P(DBT)$ ligand are planar; however, the tricyclic ligand core is bowed significantly. The six-membered rings deviate from planarity by ~9° and 3.5° for the substituted and unsubstituted rings, respectively. The sulfur atoms are pyramidal; the midpoint of the biphenyl linkage, the sulfur, and the ruthenium atoms define angles of 132.0 and 130.1° (Figure 2). Distances of 2.336 (5) and 2.314 (5) Å are found for the Ru–P bond lengths when trans to the S and Cl ligands, respectively. Long and short Ru–Cl distances are also observed depending on the atom trans to the chloride ligand (S, 2.414 (4); P, 2.459 (5) Å).

The weak donor ability of the DBT ligand is indicated by the electrochemical and chemical properties of compounds **2a** and **2b**. In 10^{-3} M Et_4NClO_4/CH_3CN, compound **2b** undergoes irreversible oxidation at 0.88 V (vs. SCE) as well as ligand-based oxidations at 1.36 and 1.64 V. By comparisons with $RuCl_2(Ph_2PCH_2CH_2PPh_2)_2$ (0.48 V) and $RuCl_2(o\text{-}Ph_2PC_6H_4OCH_3)_2$ (0.94 V), it appears that the donor ability of the sulfur moiety is comparable to that of an ether. Although air stable, solutions of **2a** react readily with carbon monoxide affording the yellow crystalline monocarbonyl adduct, $RuCl_2(CO)(4\text{-}Ph_2P(DBT))_2$[17] whose X-ray structural analysis is scheduled for the near future.

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(11) Crystal data for $Ru[(p\text{-tol})_2P(DBT)]_2Cl_2\cdot 2(CH_3)_2CO$: cell dimensions, $a = 14.164$ (4) Å, $b = 14.478$ (4) Å, $c = 25.663$ (8) Å, $\beta = 91.28$ (3)°, $V = 5261$ (3) Å^3; space group $P_{21/n}$, $Z = 4$; $d_{calcd} = 1.365$ gm/cc, $d_{obsd} = 1.372$ gm/cc; $\mu = 5.73$ cm^{-1}. Intensity data on a single crystal of **2b** sealed in epoxy were collected on a Nicolet R3 automated diffractometer using the ω scan technique and employing Mo Kα radiation ($\lambda = 0.7107$ Å). The solution of the structure was obtained by conventional direct methods and Fourier techniques. Final refinement used a blocked cascade, least-squares routine (3203 unique reflections, $F > 3.0\sigma|F|$). Hydrogen atoms were input at calculated positions (C–H, 0.96 Å) and were included in the structure factor calculations but were not refined. Final R value was 0.1019; weighted $R_W = 0.1063$.[12] The structure was solved by using the programs SOLV and SHELXTL VERSION 4.0.

(12) Two molecules of acetone per asymmetric unit in the unit cell were observed with one of the solvate molecules disordered. Crystal decomposition, possibly due to loss of solvent molecules, occurred during initial data collection. The *p*-tolyl groups were refined with rigid phenyl units and with isotropic thermal parameters.

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(17) Anal. Calcd for $C_{49}H_{34}Cl_2OP_2RuS_2$: C, 62.82; H, 3.63; Cl, 7.59. Found: C, 63.34; H, 3.79; Cl, 7.66. IR (CH_2Cl_2 soln) 1988 cm^{-1}. ^{31}P NMR ($CDCl_3$) 50.63, 41.56, 20.64, 11.62 ppm; $\delta_A = 45.38$, $\delta_B = 16.84$, $J = 366$ Hz.

In summary, the present results provide the first unambiguous example of a thiophenic moiety functioning as a sulfur donor ligand. Although the Ru-S interaction is obviously influenced by the geometric constraints imposed by the chelate ring, our findings indicate that stable complexes of nonchelating S-bound thiophene ligands are feasible.[18]

Acknowledgment. This work was supported by the National Science Foundation and the Illinois Coal Research Board. T.B.R. is a fellow of the Camille and Henry Dreyfus and Alfred P. Sloan Foundations. Mass spectra were obtained in the Mass Spectrometry Laboratory, University of Illinois, supported in part by the National Institute of General Medical Sciences (GM 27029). 360-MHz NMR spectra were measured at the University of Illinois NSF Regional NMR Facility.

Registry No. 1a, 91281-15-1; **1b**, 91281-16-2; **2a**, 91281-17-3; **2b**$\cdot$2-$(CH_3)_2CO$, 91310-93-9; Ph_2PCl, 1079-66-9; (*p*-tol)$_2$PCl, 1019-71-2; 4-lithiodibenzothiophene, 75288-58-3.

Supplementary Material Available: Structure factor tables for $RuCl_2(tol_2P(DBT))_2\cdot 2(CH_3)_2CO$, positional and thermal parameters, and bond distances and angles (24 pages). Ordering information is given on any current masthead page.

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[1.1]Ferrocenophanes as Effective Catalysts in the Photoelectrochemical Hydrogen Evolution from Acidic Aqueous Media

Ulrich T. Mueller-Westerhoff*[1] and Adel Nazzal

Physical Science Department
IBM Research Laboratory
San Jose, California 95193

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We wish to report the successful application of a new type of catalyst in the photoelectrochemical production of hydrogen from aqueous media in an electrolytic cell where the externally applied potential is reduced by a photogenerated potential, thus leading to a conversion of light to electrical and consequently chemical energy in the form of hydrogen gas. In such a cell, the photoreduction of hydrogen on a semiconductor photocathode such as p-type silicon is thermodynamically allowed, but it is kinetically inhibited: silicon and many other semiconductors show a high overvoltage for hydrogen evolution, which means that additional energy must be supplied to overcome this barrier. Previous work[1-7] in this area has remedied this problem in a temporary way through a variety of schemes. Our recent investigations of the synthesis[8] and properties[9,10] of the binuclear metallocene [1.1]ferrocenophane (**1**, "FCP") have now led us to a novel and useful polymeric material, with which p-type semiconductor electrodes can be modified in such a way that they continuously and over extended periods of time liberate hydrogen when irradiated by visible light. At this time, we have been concerned only with this part of the water splitting reaction, ignoring for the moment the need to improve the efficiency of oxygen generation at a suitable photoanode.

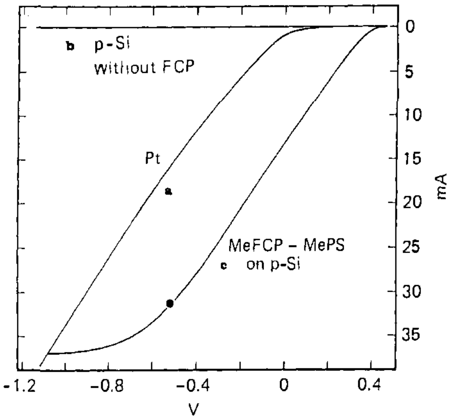
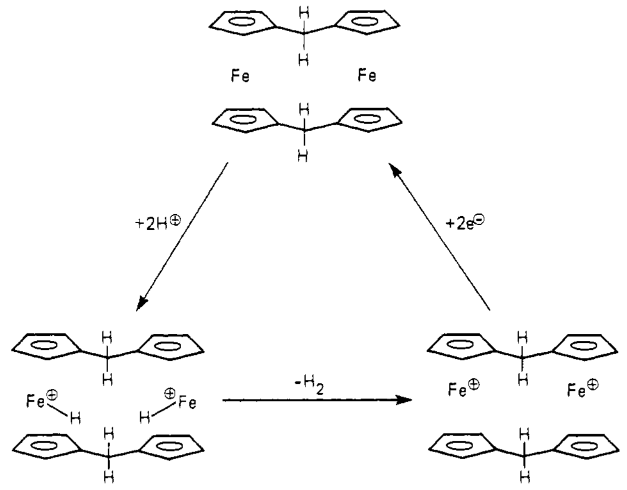


Figure 1. Current/voltage (vs. SCE) plots in neat HBF_3OH at scan rates of 50 mV/s of (a) a Pt cathode with the same surface area as that of the electrode in (b) and (c); (b) a p-Si photocathode in the absence of FCP, whether illuminated or in the dark; the same curve is obtained when a modified electrode is not illuminated; (c) illuminated MeFCP-polymer coated p-Si cathode. The same Pt anode was used in all cases. Note especially that no hydrogen evolution is observed (i.e., a flat line at 0 mA is shown in the I/V curve) within the above range for two cases: when a nonmodified p-type Si cathode is illuminated or when a modified cathode is kept in the dark.

FCP readily dissolves in strong, nonoxidizing acids such as boron trifluoride hydrate (HBF_3OH) with liberation of hydrogen. Quantitative studies in this laboratory have confirmed an earlier observation[11] that exactly 1 mol of hydrogen is evolved per mol of FCP. The dication **2** resulting from the reaction $2H^+ + FCP \rightarrow H_2 + FCP^{2+}$ can be converted back to neutral FCP by various reducing agents, such as $TiCl_2$ or $SnCl_2$. Because of the low basicity[12,13] of ferrocenes, no hydrogen evolution is observed from more dilute HBF_3OH or other aqueous acids.



The reduction of **2** to **1** can also be effected electrochemically and photoelectrochemically so that **1** can serve as a means to partially eliminate the overpotential problems. Effective photoelectrochemical catalysis of hydrogen production by FCP in solution was demonstrated by the following experiments: the onset

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(1) Present address: Department of Chemistry, University of Connecticut, Storrs, CT 06268

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