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"Chelate-Assisted" Oxidative Addition of the Carbon-Sulfur Bond in 8-Quinoline Thioesters to Rh(PPh$_3$)$_3$Cl

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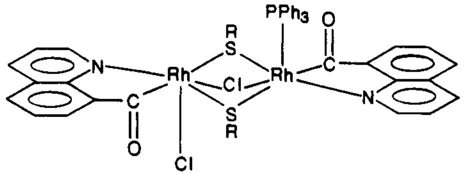
Received February 22, 1988

The 8-quinoline thioesters C$_9$H$_6$N-8-C(O)SR (R = *n*-Bu, CHMe$_2$, CH$_2$Ph, Ph, *p*-C$_6$H$_4$CH$_3$) reacted in refluxing toluene with RhCl(PPh$_3$)$_3$, leading to cleavage of the C(O)-SR bond, loss of PPh$_3$, and isolation of dimers of the type Rh$_2$(η^2-8-C$_9$H$_6$NC(O))$_2$(μ-Cl)(1-Cl)-μ,μ'-(SR)$_2$(1'-PPh$_3$) (**2**). The structure where R = *n*-Bu was determined: monoclinic, space group $P2_1/c$, a = 15.929 (3) Å, b = 17.218 (3) Å, c = 17.214 (3) Å, β = 98.793 (14)°, Z = 4. A precursor to this complex having an additional PPh$_3$ ligand was isolated and converted to its PF$_6$ salt. The complexes are examples of C-S bond cleavage wherein both the hydrocarbon- and sulfur-containing fragments are incorporated into one complex.



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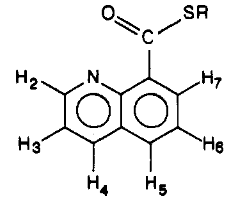
Introduction

"Chelate-assisted" oxidative-addition reactions of C-C,[1] C-H,[2] N-H,[3] and Si-H[4] bonds have been reported when such moieties have been brought near a low-valent metal atom by means of a pendant ligand. Cleavage of C-S bonds as in hydrodesulfurization is a topic of considerable interest. In order to study the oxidative addition of C-S bonds, the 8-quinoline thioesters **1a-e** were prepared and reacted with Rh(PPh$_3$)$_3$Cl. This led to C-S bond cleavage and the isolation of thiolato-bridged dimers, illustrating an interesting additional feature of these sulfur-containing systems consistent wih multiple-point bonding models[5] for metal-sulfide-catalyzed hydrosulfurization.



1a, R = CH$_2$CH$_2$CH$_2$CH$_3$
b, R = CH$_2$Ph
c, R = CHMe$_2$
d, R = Ph
e, R = 4-C$_6$H$_4$Me

Results

Compound **1b** does not react with Ir(PPh$_3$)$_2$(CO)Cl, and **1a** does not react with Rh(PPh$_3$)$_2$(CO)Cl in refluxing toluene; the starting materials are recovered. However, **1a-e** react with Rh(PPh$_3$)$_3$Cl in refluxing toluene or benzene to give a change in color of the solution from red to yellow and precipitation of the series of yellow complexes **2a-e**.

Table I. Selected Bond Lengths (Å) and Angles (deg) for **2a**

Rh(1)-Cl(1)	2.547 (3)	Rh(1)-S(1)	2.395 (3)
Rh(1)-S(2)	2.343 (3)	Rh(1)-P(3)	2.337 (3)
Rh(1)-C(4)	1.930 (10)	Rh(1)-N(4)	2.098 (8)
Rh(2)-Cl(1)	2.644 (2)	Rh(2)-S(1)	2.341 (3)
Rh(2)-S(2)	2.315 (3)	Rh(2)-Cl(2)	2.379 (3)
Rh(2)-C(5)	1.960 (10)	Rh(2)-N(5)	2.051 (8)
S(1)-C(11)	1.849 (11)	S(2)-C(21)	1.840 (9)
C(4)-C(42)	1.53 (2)	C(4)-O(4)	1.231 (12)
C(5)-O(5)	1.194 (11)	C(5)-C(52)	1.50 (2)
Cl(1)-Rh(1)-S(1)	84.1 (1)	Cl(1)-Rh(1)-S(2)	84.4 (1)
S(1)-Rh(1)-S(2)	78.3 (1)	Cl(1)-Rh(1)-P(3)	94.9 (1)
S(1)-Rh(1)-P(3)	173.1 (1)	S(2)-Rh(1)-P(3)	94.8 (1)
Cl(1)-Rh(1)-C(4)	170.8 (3)	S(1)-Rh(1)-C(4)	90.5 (3)
S(2)-Rh(1)-C(4)	101.8 (3)	P(3)-Rh(1)-C(4)	91.3 (3)
Cl(1)-Rh(1)-N(4)	90.3 (2)	S(1)-Rh(1)-N(4)	93.5 (2)
S(2)-Rh(1)-N(4)	170.6 (2)	P(3)-Rh(1)-N(4)	93.3 (2)
C(4)-Rh(1)-N(4)	82.6 (4)	Cl(1)-Rh(2)-S(1)	83.0 (1)
Cl(1)-Rh(2)-S(2)	82.8 (1)	S(1)-Rh(2)-S(2)	80.0 (1)
Cl(1)-Rh(2)-Cl(2)	94.1 (1)	S(1)-Rh(2)-Cl(2)	98.4 (1)
S(2)-Rh(2)-Cl(2)	176.6 (1)	Cl(1)-Rh(2)-C(5)	175.8 (3)
S(1)-Rh(2)-C(5)	99.3 (3)	S(2)-Rh(2)-C(5)	94.2 (3)
Cl(2)-Rh(2)-C(5)	89.0 (3)	Cl(1)-Rh(2)-N(5)	93.5 (2)
S(1)-Rh(2)-N(5)	173.4 (3)	S(2)-Rh(2)-N(5)	94.0 (2)
Cl(2)-Rh(2)-N(5)	87.5 (3)	C(5)-Rh(2)-N(5)	83.9 (4)
Rh(1)-Cl(1)-Rh(2)	75.0 (1)	Rh(1)-S(1)-Rh(2)	83.7 (1)
Rh(1)-S(1)-C(11)	110.3 (4)	Rh(2)-S(1)-C(11)	106.8 (4)
Rh(1)-S(2)-C(21)	109.8 (4)	Rh(1)-S(2)-Rh(2)	85.5 (1)
Rh(1)-C(4)-C(42)	112.4 (7)	Rh(2)-S(2)-C(21)	108.9 (4)
Rh(2)-C(5)-O(5)	128.3 (8)	Rh(1)-C(4)-O(4)	131.5 (9)
O(5)-C(5)-C(52)	121.2 (9)	O(4)-C(4)-C(42)	115.9 (9)
		Rh(2)-C(5)-C(52)	110.4 (6)

The presence of large amounts of PPh$_3$ in the ether washings was noted. The weight of the recovered PPh$_3$ corresponded to 2 equiv/equiv of Rh(PPh$_3$)$_3$Cl. The relatively small amount of PPh$_3$ in the complex was reflected in the elemental analyses. These were in agreement with the presence of one PPh$_3$ per two Rh atoms, consistent with the formulation of the complexes as dimers. In some cases, a discrepancy exists between the calculated and experimental values due to the inclusion of chlorinated solvent within the crystal lattice, the solvent being detected in the NMR spectrum. Another problem arises for **2b** (R = CH$_2$Ph) and **2d**

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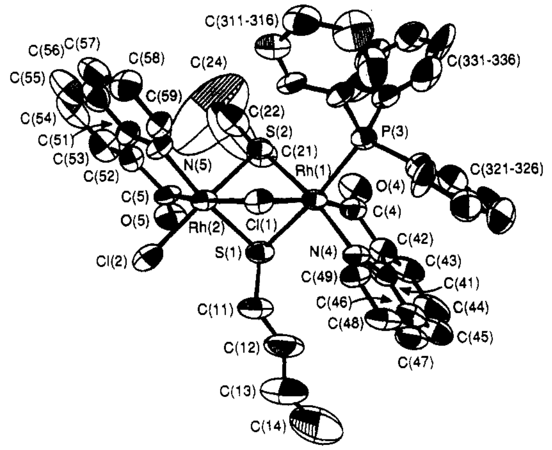

Figure 1. Computer-generated thermal ellipsoid drawing (probability level 50%) of the dimer $Rh_2(\eta^2\text{-}8\text{-}C_9H_6NC(O))_2(\mu\text{-}Cl)(1\text{-}Cl)\text{-}\mu,\mu'\text{-}(SR)_2(1'\text{-}PPh_3)$. The *U*(eq) value was used for atom C(323) of the phosphine ligand.

(R = Ph), where low C and H analyses are attributed to the cocrystallization of an additional product on the basis of the detection of additional peaks in the NMR spectra.

Structure of $[Rh_2(\eta^2\text{-}8\text{-}C_9H_6NC(O))_2(\mu\text{-}Cl)(1\text{-}Cl)\text{-}\mu,\mu'\text{-}(S\text{-}{}^nBu)_2(1'\text{-}PPh_3)]$ (2a). The structures of **2a**-**e** could not be established unequivocally from their IR, NMR, and mass spectra. Therefore, the structure of **2a** was determined via X-ray analysis and is shown in Figure 1. It consists of two Rh(III) atoms bridged by two thiolato groups and one chlorine atom. Also present are two carbonylquinolinate residues, a terminal chlorine, and one triphenylphosphine.

The crystal consists of discrete molecules of the Rh dimer. The complex is asymmetric and adopts a distorted-octahedral geometry around each Rh atom. Selected bond lengths and angles and the refined atomic coordinates are listed in Tables I and II, respectively. The presence of three bridging ligands results in a noticeable decrease in the angles between these ligands from the ideal 90° (e.g., Cl(1)–Rh(1)–S(1) = 84.1 (1)°, Cl(1)–Rh(1)–S(2) = 84.4 (1)°, and S(1)–Rh(1)–S(2) = 78.3 (1)°). The plane about Rh(1) is comprised of C(4) and N(4) of the chelating carbonylquinolinate S(2), and Cl(1), with S(1) and P(3) at the axial sites. The coordination sphere of Rh(2) consists of C(5) and N(5) from a carbonylquinolinate, Cl(1), and S(1) in the plane with Cl(2) and S(2) in the axial positions.

The Rh---Rh distance (3.161 Å) is longer than the range for a Rh–Rh single bond (2.62–2.84 Å),[6] as expected. However, 3.161 Å is considerably shorter than the Rh–Rh distance observed for other bridged Rh(III) dimers such as $Rh_2I_2(SMe_2)_3(CH_3)_4$ (3.38 Å)[7] and $[RhCl(H)(SH)(PPh_3)_2]_2$ (3.637 Å).[8] The bonding of the bridging ligands in **2a** is nonsymmetric. The strong trans influence[9] of PPh_3 results in a long Rh(1)–S(1) distance (2.395 (3) Å) compared to Rh(2)–S(1) (2.341 (3) Å). The two Rh–S distances trans to the N atoms (i.e., Rh(2)–S(1) and Rh(1)–S(2)) are similar in length (2.341 (3) and 2.343 (3) Å, respectively). The short Rh(2)–S(2) distance (2.315 (3) Å) may be due to the relatively weak trans influence of Cl. Comparable bridging Rh^{III}–S distances have been observed in other complexes. The bridging Rh–Cl distances are longer than expected[10] possibly due to the strong trans influence of the acyl group as observed in $[Rh_2Cl_3(C(O)Me)_2(PMe_2Ph)_4]PF_6$.[11] The terminal Rh(2)–Cl(2) bond length of 2.379 (3) Å lies within the range consistent with the intermediate trans influence of the SR^- ligand.[12] The bond lengths and angles found in the five-membered rings formed by the rhodium atoms and the 8-carbonylquinolinate ligands were in agreement with those found for other systems.[1b,c]

Table II. Fractional Atomic Coordinates (×10⁴; ×10⁵ for Rh) and Equivalent Isotropic Temperature Factors ($Å^2 \times 10^3$; $Å^2 \times 10^4$ for Rh) for **2a**

	x/*a*	*y*/*b*	*z*/*c*	*U*(eq)
Rh(1)	23216 (5)	49318 (5)	13362 (4)	390 (4)
Rh(2)	24547 (5)	31011 (5)	14247 (5)	433 (5)
Cl(1)	1386 (1)	3973 (2)	471 (1)	48 (1)
S(1)	2193 (2)	4019 (2)	2361 (1)	50 (2)
C(11)	1067 (6)	3909 (8)	2486 (6)	67 (8)
C(12)	873 (8)	4380 (9)	3181 (8)	87 (11)
C(13)	−33 (11)	4342 (11)	3242 (10)	134 (17)
C(14)	−220 (13)	4883 (12)	3880 (10)	188 (26)
S(2)	3415 (2)	4055 (2)	1203 (1)	42 (1)
C(21)	4249 (6)	4119 (7)	2067 (5)	55 (7)
C(22)	4999 (6)	3622 (8)	1954 (7)	66 (8)
C(23)	5611 (11)	3620 (16)	2733 (16)	113 (21)
C(24)	6125 (16)	3204 (20)	2765 (19)	334 (55)
P(3)	2576 (2)	5726 (2)	296 (2)	42 (2)
C(311)	2458 (7)	5289 (7)	−689 (6)	47 (6)
C(312)	2253 (9)	5748 (8)	−1358 (7)	88 (10)
C(313)	2206 (10)	5412 (10)	−2086 (6)	82 (10)
C(314)	2350 (8)	4648 (9)	−2177 (7)	68 (9)
C(315)	2573 (7)	4220 (8)	−1527 (7)	61 (8)
C(316)	2623 (6)	4527 (7)	−791 (6)	47 (7)
C(321)	1855 (7)	6538 (7)	229 (7)	50 (7)
C(322)	1056 (7)	6504 (7)	−227 (8)	61 (8)
C(323)	492 (8)	7110 (9)	−196 (10)	71 (10)
C(324)	698 (11)	7734 (10)	230 (11)	90 (14)
C(325)	1454 (12)	7769 (9)	720 (9)	95 (13)
C(326)	2021 (8)	7160 (8)	696 (7)	71 (9)
C(331)	3630 (7)	6174 (7)	342 (6)	52 (7)
C(332)	4338 (6)	5798 (8)	693 (8)	70 (9)
C(333)	5122 (7)	6087 (9)	702 (8)	80 (10)
C(334)	5230 (9)	6767 (9)	381 (9)	82 (10)
C(335)	4563 (8)	7181 (8)	42 (10)	87 (11)
C(336)	3765 (7)	6851 (8)	3 (8)	83 (9)
C(4)	2889 (7)	5656 (7)	2096 (6)	53 (6)
O(4)	3647 (4)	5755 (5)	2351 (4)	66 (5)
N(4)	1243 (5)	5561 (5)	1524 (4)	40 (5)
C(41)	1419 (7)	6057 (7)	2139 (5)	48 (6)
C(42)	2269 (6)	6142 (7)	2480 (6)	53 (7)
C(43)	2451 (7)	6613 (7)	3115 (7)	71 (8)
C(44)	1801 (9)	7011 (8)	3413 (8)	83 (10)
C(45)	987 (8)	6967 (8)	3046 (7)	78 (9)
C(46)	759 (7)	6483 (7)	2413 (6)	54 (7)
C(47)	−79 (7)	6371 (7)	2019 (7)	56 (8)
C(48)	−226 (7)	5871 (7)	1422 (6)	56 (7)
C(49)	456 (6)	5469 (6)	1178 (5)	49 (6)
Cl(2)	1402 (2)	2176 (2)	1631 (2)	67 (2)
C(5)	3307 (6)	2466 (6)	2079 (6)	45 (6)
O(5)	3518 (5)	2491 (5)	2775 (4)	62 (5)
N(5)	2732 (5)	2402 (5)	533 (5)	47 (5)
C(51)	3353 (6)	1865 (6)	776 (6)	48 (6)
C(52)	3667 (6)	1870 (6)	1588 (6)	50 (6)
C(53)	4303 (7)	1370 (7)	1852 (7)	71 (8)
C(54)	4600 (8)	847 (8)	1337 (9)	86 (10)
C(55)	4271 (9)	831 (8)	570 (9)	92 (11)
C(56)	3643 (8)	1352 (7)	232 (7)	67 (8)
C(57)	3272 (8)	1403 (8)	−542 (7)	71 (9)
C(58)	2664 (8)	1938 (8)	−770 (7)	65 (8)
C(59)	2398 (6)	2431 (6)	−209 (6)	50 (6)

NMR Spectra. The NMR data for **2a**–**c** are consistent with the structure of **2a**. Two sharp sets of signals for the quinoline H atoms are observed consistent with the asymmetric structure. The assignments of the peaks observed for **1a**–**c** and **2a**–**c** are based

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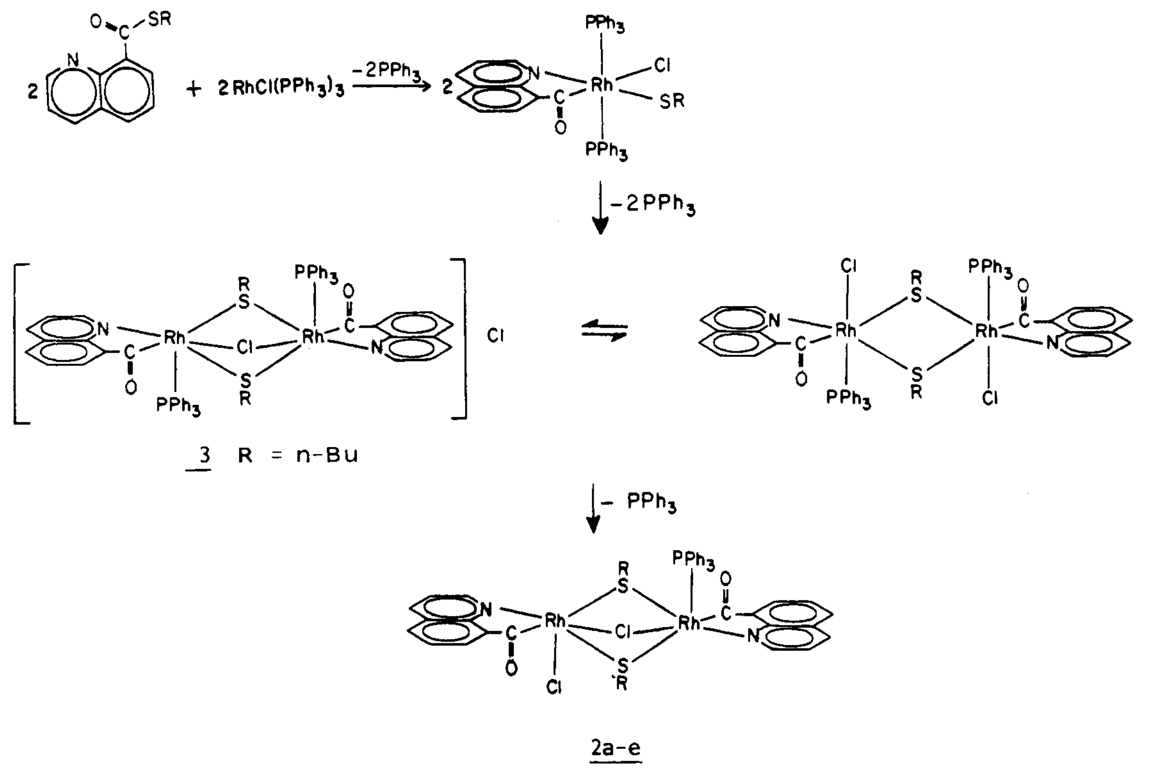
Scheme I.



on those reported for quinoline[13] and 8-substituted quinolines.[14] The NMR spectra for **2d** and **2e** were broad, and assignment was not possible. The asymmetry of **2** also leads to diastereotopism for some of the R groups. For **2a** (R = $CH_2CH_2CH_2CH_3$), three broad resonances containing fine structure are observed in the SCH_2 region while the fourth occurs above TMS (−0.41 ppm), possibly due to interaction with Rh. For **2b** (R = CH_2Ph), two resonances due to methylene hydrogens appear as broad resonances with some fine structure (~4–5 ppm). The remaining two methylene resonances occur further upfield with one signal observed as a doublet and the other as a doublet of doublets, perturbations possibly due to nearby H and P atoms. The phenyl groups are detected in the integration of the aromatic region. The four methyl resonances of **2c** appear as distinct doublets; however, one is split further possibly due to spin–spin coupling.

When R = 4-C_6H_4Me (**2e**), two pairs of methyl resonances (i.e. four peaks) were observed. The relative intensities of the two pairs were dependent on the workup/recrystallization of the sample. The close agreement between the calculated elemental analysis and that found suggests that the two complexes may be isomers. The R group in **2** can exist in either equatorial or axial positions, leading to four possible isomers (ee, ea, and two ae isomers due to the asymmetry of **2**). The NMR spectra of **2b** (R = CH_2Ph) and **2d** (R = Ph) display more signals in the quinoline region than can be attributed to only two such residues. The relative intensities of the extra peaks were dependent upon the recrystallization history of the samples. However, discrepancies in the elemental analyses of **2b** and **2d** are consistent with the presence of additional products.

Isolation of a Precursor to 2a. If the reaction between **1a** and Rh(PPh$_3$)$_3$Cl in refluxing toluene is allowed to proceed for only 15 min, complex **3** was isolated from the mother liquors of the recrystallization of the major product **2a**. It was not possible to isolate a sample of **3** free of **2a**, but conversion to its PF_6 salt, **4**, gave the analytical sample. Refluxing **3** in toluene overnight gave **2a** and free PPh$_3$. The NMR spectra of **3** and **4** were generally broad and ill-defined, but two signals of equal intensity were observed for the H_7 protons of the quinoline residues. Integration indicated the presence of one PPh$_3$ ligand for each quinoline ligand. The results suggest that **3** is a precursor to **2a** which contains an additional PPh$_3$ ligand such that its structure is either a dichloro dimer bridged by two thiolato groups or a chloride salt with two thiolato and one chloro bridge.

Discussion

The formation of **2a–e** is consistent with oxidative addition of the C–S bond in **1** to the Rh(I) center and loss of PPh$_3$ leading to dimerization. A reasonable sequence that includes **3** as an intermediate is shown in Scheme I. It might be expected that reaction under milder conditions would give a monomeric product. However, in refluxing CH_2Cl_2 (40 °C) the products were the starting thioester, PPh$_3$, and an unidentified material that could not be isolated. It has been shown[15] that the initial monomeric product from the reaction of 8-(methylthio)quinoline and Rh(PPh$_3$)$_3$Cl dimerized upon heating. Further aggregation may account for the additional products detected in association with **2b** and **2d**. Elimination of quinoline has been observed[1f] upon heating similar systems in refluxing xylene.

Model systems incorporating C–S bond fission are of interest with respect to hydrodesulfurization. Coordination via the sulfur atom occurs prior to C–S bond cleavage,[16] but the actual bond breaking appears to be unfavorable[17] and must be driven by other factors. One factor is the further reaction of the organic fragment with a nearby hydride species, leading to elimination of the hydrocarbon.[18,19] The release of the organic group probably plays an important role in driving industrial hydrodesulfurization. Another factor may be the formation of additional M–S bonds (bridging) by the thiolato fragment.[18,20,21] Complexes **2** are

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interesting examples where both the hydrocarbon and the thiolato fragments from the C–S cleavage remain attached to the metal(s) in the final product.

Experimental Section

General Experimental Considerations. The reactions were carried out under a nitrogen atmosphere in appropriately sized three-necked round-bottomed flasks. One neck was equipped with a gas inlet, the middle neck was fitted with a condenser having a gas inlet at its top, and the remaining neck was stoppered. Solvents were transferred by means of 50-mL syringes. All manipulations of the reaction products were performed in air. Chromatography was performed using Merck silica gel (70–230 mesh ASTM). Thin-layer chromatography was performed on 13179 silica gel chromatogram sheets (Eastman).

Toluene and tetrahydrofuran (THF) were refluxed over sodium/benzophenone and distilled just prior to use. Reagent grade thionyl chloride was distilled from triphenyl phosphite twice before use.[22] All other solvents were reagent grade unless otherwise stated and were used without further purification. Thionyl chloride, benzyl mercaptan, 2-propanethiol, 1-butanethiol, thiophenol, and thiocresol were obtained from Aldrich. These and pyridine (Anachemia), triethylamine (Anachemia), and $RhCl_3 \cdot 3H_2O$ (Strem) were used as received. 8-Quinolinecarboxylic acid[23] and $RhCl(PPh_3)_3$[24] were prepared as reported; the former was purified by chromatography on silica gel (mp 184.5–185.0 °C, ethanol).

Proton NMR spectra were obtained on a Varian XL-200 FT-NMR spectrometer. Tetramethylsilane (TMS) was used as the internal standard, and the data are reported in δ units (ppm) ± 0.02. Infrared spectra were determined with a Perkin-Elmer 257 spectrophotometer and were calibrated with the polystyrene peak at 1601 cm^{-1}. The values are accurate to within ± 4 cm^{-1}. Melting points were obtained by using a Thomas-Hoover Uni-melt apparatus and are uncorrected. Mass spectra were performed on a Du Pont 21-492B mass spectrometer by direct inlet, in the electron impact mode with the ion source at 60 °C. Spectra are reported as m/z (assignment, relative intensity). Elemental analyses were carried out by Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada.

1. Butyl 8-Quinolinecarbothioate, C_9H_6N-8-$C(O)SCH_2CH_2CH_2CH_3$ (1a). The preparation of **1a** is typical of that used to prepare **1b–d**. 8-Quinolinecarboxylic acid (5.0 g, 28.7 mmol) was refluxed in a large excess of thionyl chloride (17 mL, 236 mmol) for 1 h.[23] The unreacted thionyl chloride was removed under vacuum. The acid chloride was not isolated but reacted further with *n*-butyl mercaptan (2.8 mL, 25.9 mmol) and pyridine (3 mL, 37.2 mmol) in toluene (200 mL) at 70 °C for 2 h. The solution was filtered to remove pyridine hydrochloride. The filtrate was washed with aqueous saturated sodium carbonate solution (4 × 35 mL) and water (4 × 35 mL) and then dried over magnesium sulfate. The solution was evaporated to dryness and the residue chromatographed on a 25 mm diameter column containing 43 g of silica gel with a 1:5 ethyl acetate/hexanes solution as eluent. The product was collected, dried, and recrystallized from ethanol to give orange flakes (3.6 g, 56%), mp 50.5–51.0 °C (CH_2Cl_2/hexane). Anal. Calcd for $C_{14}H_{15}NOS$: C, 68.53; H, 6.17; N, 5.71. Found: C, 68.59; H, 6.24; N, 5.52. IR (KBr): $\nu(CO)$ 1660 cm^{-1}. ^1H NMR ($CDCl_3$; δ, ppm (multiplicity and assignment)): 9.04 (dd, H_2), 8.18 (dd, H_4), 8.04 (dd, H_7), 7.94 (dd, H_5), 7.57 (dd, H_6), 7.45 (dd, H_3), 3.19 (t, SCH_2, $J = 7.3$ Hz), 1.73 (m, β-CH_2), 1.49 (sextet, γ-CH_2, $J = 7.1$ Hz), 0.97 (t, CH_3, $J = 7.2$ Hz). $J(H_n–H_m)$ (Hz) 2–3, 4.2; 2–4, 1.8; 3–4, 8.4; 6–7, 7.1; 5–7, 1.5; 5–6, 8.3. Mass spectrum: 245 ($M^{\bullet +}$, 4); 188 ($M^{\bullet +} - (CH_2)_3CH_3^{\bullet}$, 31); 156 ($M^{\bullet +} - S(CH_2)_3CH_3^{\bullet}$, 100); 128 ($M^{\bullet +} - C(O)S(CH_2)_3CH_3^{\bullet}$, 49).

2. μ,μ'-Bis(1-butanethiolato)bis(η^2-8-carbonylquinolinato)(μ-chloro)chloro(triphenylphosphine)dirhodium(III), $Rh_2(\eta^2$-8-$C_9H_6NC(O))_2(\mu$-$Cl)(Cl)$-μ,μ'-$(SCH_2CH_2CH_2CH_3)_2(PPh_3)$ (2a). Method A. Toluene (40 mL) was added to a reaction flask containing Wilkinson's catalyst (0.400 g, 0.43 mmol) and butyl 8-quinolinecarbothioate (0.157 g, 0.64 mmol). The mixture was refluxed for 5 h. The solution was decanted from a small amount of residue, concentrated, and cooled to −15 °C. The solvent was removed by means of a syringe, and the precipitate was washed with ether (3 × 10 mL). The crude product was recrystallized from CH_2Cl_2–ether (0.18 g, 81%). A second recrystallization from CH_2Cl_2–ether was performed (0.11 g, 49%); mp 263–267 °C. Anal. Calcd for $C_{46}H_{45}N_2O_2S_2PCl_2Rh_2$: C, 53.65; H, 4.41; N, 2.72. Found: C, 52.45; H, 4.43; N, 2.65. IR (KBr): $\nu(CO)$ 1675, 1680 cm^{-1}. ^1H NMR ($CDCl_3$); δ, ppm (multiplicity and assignment)): 9.98 (d, H_2), 9.76 (d, $H_{2'}$), 8.40 (dd, H_4), 8.24 (dd, $H_{4'}$), 8.24 (dd, H_7), 8.00 (dd, $H_{7'}$), 7.97 (dd, H_5), 7.86 (dd, $H_{5'}$), 7.71 (dd, H_3), 7.63 (dd, H_6), 7.56 (dd, $H_{6'}$), 7.39 (dd, $H_{3'}$), 7.37–7.03 (m, Ph), 3.24–3.04 (m, SCH_2), 2.96–2.73 (m, SCH'_2), 2.67–2.55 (m, SCH''_2), 1.4–0.5 (m, β-CH_2), 1.17 (septet, γ-CH_2, $J = 7.1$ Hz); 0.88 (m, γ-CH'_2), 0.63 (t, CH_3, $J = 7.3$ Hz), 0.26 (t, CH''_3, $J = 7.0$ Hz), −0.1 to −0.3 (m, SCH'''_2). $J(H_n–H_m)$ (Hz): 2–3, 4.9; 2′–3′, 5.2; 3–4, 8.3; 2–4, 1.3; 3′–4′, 8.3; 2′–4′, 1.2; 6–7, 7.1; 5–7, 1.2; 6′–7′, 7.1; 5′–7′, 1.1; 5–6, 8.0; 5′–6′, 8.2; 3–4, 8.4.

Method B. A suspension of $RhCl(PPh_3)_3$ (0.399 g, 0.43 mmol) and butyl 8-quinolinecarbothioate (0.110 g, 0.45 mmol) was refluxed in toluene (40 mL) for 15 min. The reaction product was stripped of solvent and washed with ether (3 × 10 mL). The precipitate was recrystallized from CH_2Cl_2/ethanol, and yellow crystals were obtained. The mother liquors were retained for further analysis; mp 254–255 °C. Anal. Calcd for $C_{46}H_{45}N_2O_2S_2Cl_2Rh_2$: C, 53.65; H, 4.41; N, 2.72; Cl, 6.89. Found: C, 53.24; H, 4.43; N, 2.39; Cl, 5.62. ^1H NMR: same as above.

3. μ,μ'-Bis(1-butanethiolato)bis(η^2-8-carbonylquinolinato)bis(triphenylphosphine)(μ-chloro)dirhodium(III) Chloride and Hexafluorophosphate, $[Rh_2(\eta^2$-8-$C_9H_6NC(O))_2(\mu$-$Cl)$-μ,μ'-$(SCH_2CH_2CH_2CH_3)_2(PPh_3)_2][X]$ (X = Cl (3a), PF_6 (4a)). The mother liquors from the preparation of **2a** via procedure 2B were treated by using either of two methods.

Method A. The mother liquors were stripped to dryness, and the residue was then recrystallized from benzene. Yellow crystals of **3a** were obtained. IR (KBr): $\nu(CO)$ 1680, 1550 cm^{-1}. ^1H NMR ($CDCl_3$; δ, ppm (multiplicity and assignment)): 9.92 (dd, H_2), 9.87 (dd, $H_{2'}$) 8.47 (dd, H_4), 8.34 (dd, $H_{4'}$), 8.25 (dd, H_7), 8.06–7.93 (m, $H_{7'} + H_5 + H_{5'}$), 7.82 (dd, H_3), 7.67–7.46 (m, $H_{3'} + H_6 + H_{6'}$), 7.40–7.00 (m, Ph), 0.91 (m, SCH_2), 0.43 (t, CH_3, $J = 7.2$ Hz), 0.28 (t, $CH_{3'}$, $J = 7.2$ Hz). $J(H_n–H_m)$ (Hz): 2–3, 4.4; 2′–3′, 5.4; 3–4, 8.1; 3′–4′, 8.8; 6–7, 7.0; 5–7, 1.0; 3–4, 8.0.

Method B. Addition of excess NH_4PF_6 in ethanol to a solution of the mother liquors in ethanol resulted in the immediate formation of a precipitate. The solvent was concentrated by evaporation, and the precipitate was collected on a fritted-glass funnel. It was recrystallized twice from CH_2Cl_2/ethanol to give yellow crystals of **4a** (0.030 g), mp 220–221 °C. Anal. Calcd for $C_{64}H_{60}N_2O_2S_2P_3Rh_2ClF_6 \cdot {}^1/_2CH_2Cl_2$: C, 53.64; H, 4.27; N, 1.94; Cl, 4.91. Found: C, 53.62; H, 4.67; N, 1.85; Cl, 4.50. IR (Nujol): $\nu(CO)$ 1680, 1550 cm^{-1}. ^1H NMR ($CDCl_3$; δ, ppm (multiplicity and assignment)): the only well-defined peaks were 10.09 (1 H, d, H_7), 9.64 (1 H, d, H_7), and 1.27 (3 H, t, CH_3).

X-ray Structural Analysis of 2a. Crystal data: $C_{46}H_{45}Cl_2N_2O_2PRh_2S_2$, $M_r = 1029.70$, monoclinic, space group $P2_1/c$, $a = 15.929$ (3) Å, $b = 17.218$ (3) Å, $c = 17.214$ (3) Å, $\beta = 98.793$ (14)°, $V = 4666$ Å^3, $D_c = 1.466$ Mg m^{-3}, $Z = 4$, $F(000) = 2088$, Mo Kα radiation, $\lambda = 0.71069$ Å, μ(Mo Kα) = 0.968 mm^{-1}.

Suitable crystals were obtained by recrystallization from hot ethanol. Unit cell dimensions were determined (25 reflections, $8.56 < \theta < 13.31°$) and intensity data were measured at 295 ± 1 K on an Enraf-Nonius CAD4F diffractometer using graphite-crystal-monochromatized Mo Kα radiation. The intensities of 8470 reflections in the range $3 < \theta < 25°$ (h 0–18, k 0–20, l −20 to +20) were measured by using the $\omega/2\theta$ scan mode with a scan width of $(0.58 + 0.10 \tan \theta)°$ in ω, a variable scan speed (maximum speed 3.30° min^{-1} in ω, maximum scan time 60 s per reflection), and a fixed detector aperture of 4.0 mm (vertical) × 2.5 mm (horizontal). Three standard reflections, measured every 1 h, showed an approximately linear reduction in intensity with time totalling 23.2% (0.203% per h^{-1}). The data were corrected for this intensity loss. The data were also corrected for absorption[25] by using an 8 × 8 × 8 Gaussian grid (crystal, irregular hexagonal prism, 0.22 × 0.15 × 0.12 mm bounded by the (100), $(\bar{1}00)$, (011), $(0\bar{1}1)$, $(01\bar{1})$, $(0\bar{1}\bar{1})$, (001), and $(00\bar{1})$ faces, volume 0.00292 mm^3; corrections, minimum 1.000, maximum 1.141, average 1.063).

The structure was solved by normal heavy-atom (Patterson and difference Fourier) methods and was refined by blocked-matrix least squares ($\sum w(\Delta F^2)$ minimized, $w = \sigma^{-2}(F_o)$) using SHELX.[26] Anisotropic temperature factors were used for all non-hydrogen atoms. Atom C(323) of the triphenylphosphine ligand could not be refined anisotropically to give reasonable off-diagonal temperature tensor elements. The large temperature factors for C(23) and C(24) of one of the butyl groups indicate possible disorder, which was not resolved. All hydrogen atoms were placed in calculated positions ($d_{C-H} = 0.95$ Å). Refinement con-

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verged with $R = 0.0540$ and $R_w = 0.487$ for 3763 unique reflections with $F_o > 4\sigma(F_o)$. The largest shift/esd in the final cycles was 0.415. A final difference synthesis showed no significant residual features (maximum and minimum electron densities 0.71 and −0.49 e Å^{-3}, respectively). Complex neutral-atom scattering factors[27] were used for all atoms.

Acknowledgments are made to the Natural Sciences and Engineering Research Council of Canada (NSERCC) and the Quebec Department of Education for financial support.

Supplementary Material Available: Fractional atomic coordinates and isotropic temperature factors of the calculated H atom positions (Table III), anisotropic temperature factors (Table IV), bond lengths and angles (Table V), a diagram of the structure of **2a** (Figure S1), a diagram of the unit cell (Figure S2), a description of product yields, elemental analyses, melting points, mass spectra, and IR and ^{1}H NMR data for 8-quinolinecarboxylic acid, **1b–e**, and **2b–e**, and NMR spectra of **1a**, **1c**, **2a**, and **2c** (Figures S3–6) (21 pages); observed and calculated structure factors (Table VI) (16 pages). Ordering information is given on any current masthead page.

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Temperature, Pressure, and Viscosity Dependence of Outer-Sphere Electron-Transfer Processes. Reduction of Aquapentaamminecobalt(III) by Hexacyanoferrate(II)

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Received June 3, 1988

The outer-sphere electron-transfer reaction between $Co(NH_3)_5H_2O^{3+}$ and $Fe(CN)_6^{4-}$ was studied as a function of temperature (20–35 °C), pressure (0.1–100 MPa), and solvent composition (water–glycerol mixtures up to 57 wt % glycerol). The experimental rate data were corrected for changes in viscosity with changes in temperature and pressure, and the resulting activation parameters were interpreted in terms of medium effects on the electron-transfer process. Both ΔH^* and ΔS^* increase significantly with increasing glycerol concentration, whereas ΔV^* remains constant within the experimental error limits. The results point to the importance of solvent rearrangement and collisional contributions in determining the rate of the electron-transfer process.

Introduction

Our general interest in the application of high-pressure techniques in the mechanistic analysis of inorganic and organometallic reactions[1] has led to some investigations involving typical outer-sphere electron-transfer (OSET) processes.[2-5] Earlier theoretical predictions revealed an apparently close correlation with experimentally observed volumes of activation,[6] but later work showed this to be wrong,[7] and the correlation is more complicated than originally predicted.[2,8] In an effort to gain more information on the intimate nature of the electron-transfer process itself, within the concepts of an outer-sphere mechanism, we have extended our earlier work to include an additional kinetic parameter, namely viscosity. This parameter should provide more information on the dynamic effect of the solvent on the electron-transfer process.

The role of solvent dynamics in electron-transfer processes has been realized for many years,[9-11] and the extensive theoretical treatments by Marcus[12-15] have quantified the solvent reorganization contribution toward the energy required for the electron-transfer process. Only a few studies have investigated the solvent dependence of such reactions.[16-20] The observed trends call for rather complex analyses since solvent variation affects a wide range of physical and chemical parameters that may affect the kinetics of the process in different ways. For this reason we prefer in the present study to examine the effect of viscosity on the process by varying the solvent composition of a water–glycerol mixture.

The reduction of $Co(NH_3)_5OH_2^{3+}$ by $Fe(CN)_6^{4-}$ follows an outer-sphere electron-transfer mechanism, and electron transfer occurs within the precursor ion pair.[3] The ion-pair-formation and electron-transfer rate constants can be determined kinetically and studied as a function of temperature, pressure, and viscosity. The kinetic separation of these constants enables a direct estimate of the electron-transfer rate constant within the ion pair, something that is not always possible. In cases where electron transfer is characterized by a second-order rate constant, it is usually a composite quantity and a detailed interpretation of the activation parameters is impossible. In addition, the results of this study allow us to comment on the adiabaticity versus nonadiabaticity of the OSET process.

Experimental Section

Materials. The complex $[Co(NH_3)_5H_2O](ClO_4)_3$ was prepared according to the method described in the literature.[21,22] Chemical analysis[23] and UV–vis spectral data were in agreement with the theoretically

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