4 and 14 bridging atoms (Zr, Ge, Si), α varies nearly linearly. For group 15, only two values are plotted but the line joining these two points has the same slope.

If only elements belonging to the same period are considered, moving from group 14 to 15 (Si → P and Ge → As), variations of α, β, θ, and the X–Fe distance are as follows: $\Delta\alpha = 7°$, $\Delta\beta = -7°$, $\Delta\theta = -7°$, $\Delta d = 0.13$ Å. Smaller θ values for P and As compounds have been related to the lone pair.[27] The d distance increasing while the atomic radius slightly decreases may appear surprising. It might be explained by the repulsion of lone-pair electrons of the bridging atom with iron d electrons. For bridging atoms of a given period, the X–C and Cp–Fe distances remain fairly constant and consequently the d distance increase diminishes θ and β values as well as the ring leaning toward X; that is, α increases.

In contrast, the zirconium complex for which the d distance is the longest exhibits inverted variations: the β value is slightly increasing and the α value is highly decreasing. Consequently, the extreme values found for this case could be related to the long X–C distance, a result of the high atomic radius of the metal belonging to group 4.

It is interesting to note that the closest cyclopentadienyl–*tert*-butylcyclopentadienyl inter-ring distances are C(2)---C(11) = 3.150 (3) Å, C(2)---C(12) = 3.249 (4) Å on one side and C(1)---C(11′) = 3.339 (3) Å, C(1)---C(15′) = 3.305 (4) Å on the other side.

The structure is not exactly symmetrical, as shown in Figure 2. This figure also shows that the Cp′ rings are in a staggered situation. The shortest C---C distances between the two Cp′ rings are similar to values found for other compounds, 3.106 (3) Å for C(4)---C(4′) and 3.137 (3) Å for C(3)---C(4′). Corresponding distances are 3.17 Å for Cp'_2ZrCl_2[17] and 3.18 and 3.198 Å for $Cp'_2Zr(Se_2C_6H_4)$.[18] All cyclopentadienyl rings are planar within experimental error.

Supplementary Material Available: Tables of anisotropic thermal parameters (Table S1), fractional atomic coordinates (Table S2), bond lengths and angles (Table S3), equations of least-squares planes and distances from the plane (Table S4), and complete X-ray crystal data (Table S5) (5 pages); a table of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

Contribution from the Institut für Anorganische Chemie der Universität,
Egerlandstrasse 1, D-8520 Erlangen, Federal Republic of Germany

Transition-Metal Complexes with Sulfur Ligands. 50.[1] Sulfur Bond Cleavage in Organosulfur Ligands Induced by PPh_3/NO Substitution Reactions at $[Ru(PPh_3)_2(‘L_4’)]$ Centers ($‘L_4’$ = 1,2-Bis((2-mercaptophenyl)thio)ethanate(2–), 1,2-Bis((3,5-di-*tert*-butyl-2-mercaptophenyl)thio)ethanate(2–)). Synthesis and Reactions of Various (Vinylthio)arenethiolate and Related $[Ru(NO)(Y)(‘L_4’)]$ (Y = PPh_3, Cl) Complexes. X-ray Structure Analysis of Nitrosyl(triphenylphosphine)(1,2-benzenedithiolato)(1-(vinylthio)-2-benzenethiolato)ruthenium(III)

Dieter Sellmann,* Isabella Barth, Falk Knoch, and Matthias Moll

Received August 8, 1989

The ruthenium(II) complexes $[Ru(PPh_3)_2$(1,2-bis((2-mercaptophenyl)thio)ethanate(2–))], $[Ru(PPh_3)_2(‘S_4’)]$ (**1**), and [Ru-$(PPh_3)_2$(1,2-bis((3,5-di-*tert*-butyl-2-mercaptophenyl)thio)ethanate(2–))], $[Ru(PPh_3)_2(‘^{Bu}S_4’)]$ (**2**), react with gaseous nitrogen monoxide. The substitution of one PPh_3 by NO is coupled with S–C bond cleavage of the $‘S_4’$ and $‘^{Bu}S_4’$ ligands yielding the (vinylthio)arenethiolate complexes $[Ru(NO)(PPh_3)$(1,2-benzenedithiolate)(1-(vinylthio)-2-benzenethiolate)], $[Ru(NO)(PPh_3)(‘S_2’)(‘S_2’–CH{=}CH_2)]$ (**3**), and $[Ru(NO)(PPh_3)$(3,5-di-*tert*-butyl-1,2-benzenedithiolate)(1-(vinylthio)-3,5-di-*tert*-butyl-2-benzenethiolate)], $[Ru(NO)(PPh_3)(‘^{Bu}S_2’)(‘^{Bu}S_2’–CH{=}CH_2)]$ (**4**), respectively. A reaction mechanism via $19e^-$ intermediates is suggested. Complex **3**·CH_2Cl_2 crystallizes in space group $P\bar{1}$ with $a = 1114.0$ (2) pm, $b = 1221.9$ (3) pm, $c = 1278.3$ (3) pm, $\alpha = 83.29$ (2)°, $\beta = 80.85$ (2)°, $\gamma = 76.91$ (2)°, $d_{calcd} = 1.56$ g/cm³ ($Z = 2$), $R = 0.069$, and $R_w = 0.059$. In **3** the Ru center is pseudooctahedrally coordinated by nitrogen, phosphorus, and sulfur atoms. When complex **2** is reacted with NO^+ ($NOPF_6$), no S–C bond cleavage occurs and a complex forms being tentatively described as ionic $[Ru(NO)(PPh_3)$(1,2-bis((3,5-di-*tert*-butyl-2-mercaptophenyl)thio)ethanate(2–))](PF_6), $[Ru(NO)(PPh_3)(‘^{Bu}S_4’)](PF_6)$ (**5**). Neutral Ru(II) nitrosyl compounds with intact $‘S_4’^{2-}$ as well as $‘^{Bu}S_4’^{2-}$ ligands are obtained when $Ru(NO)Cl_3{\cdot}H_2O$ is reacted with $‘S_4’–Li_2$ or $‘^{Bu}S_4’–Li_2$, yielding [Ru(NO)-(Cl)(1,2-bis((2-mercaptophenyl)thio)ethanate(2–))], $[Ru(NO)(Cl)(‘S_4’)]$ (**6**), and [Ru(NO)(Cl)(1,2-bis((3,5-di-*tert*-butyl-2-mercaptophenyl)thio)ethanate(2–))], $[Ru(NO)(Cl)(‘^{Bu}S_4’)]$ (**7**), respectively. All new complexes were characterized by spectroscopic means and elemental analyses.

Introduction

Transition-metal nitrosyl complexes are of interest as models for elementary steps of metal-catalyzed removal of nitric oxide from waste gases,[2] for key steps in the biological nitrate–ammonia conversion,[3] as catalysts in organic syntheses,[4] and as potential precursors for the synthesis of N_2 complexes.[5] One of the characteristic features of metal nitrosyl complexes is the dependence of the MNO angle upon the electronic configuration at the metal center, and angles from 120° up to nearly 180° are found.[5]

We are interested in metal nitrosyl complexes as chemical models for oxidoreductases, whose active centers consist of sulfur-coordinated transition metals[6] that can either activate or stabilize small molecules ranging from NO via hydroxylaminyl to NH_3.

In this context we recently found that $18e^-$ NO complexes can be either reduced by one electron or by two electrons plus two protons. This is shown by the two couples $[Fe(NO)(‘N_HS_4’)]^n$ (n = 1+, 0) ($‘N_HS_4’^{2-}$ = dianion of bis(2-((2-mercaptophenyl)-

---

(1) Part 49: Sellmann, D.; Käppler, O.; Knoch, F.; Moll, M. *Z. Naturforsch.*, in press.

(2) *Ullmanns Encyklopädie der technischen Chemie*, 4th ed.; Verlag Chemie: Weinheim, West Germany, 1981, Vol. 6.

(3) Hughes, M. N. In *The Inorganic Chemistry of Biological Processes*, 2nd ed.; John Wiley & Sons: New York, 1981.

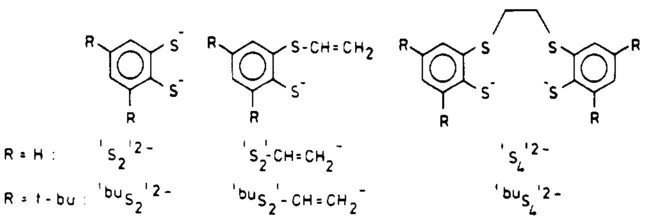
(4) Pandey, K. K. *Coord. Chem. Rev.* **1983**, *51*, 69.

(5) McCleverty, J. A. *Chem. Rev.* **1979**, *79*, 53.

(6) Lowe, D. J.; Thorneley, R. N. F.; Smith, B. E. In *Metalloproteins Part 1: Metal Proteins with Redox Roles*; Harrison, P. M., Ed.; Verlag Chemie: Weinheim, West Germany, 1985.

0020-1669/90/1329-1822$02.50/0

Chart I. Ligands and Their Abbreviations[a]



[a] Key: ‘S$_4$’$^{2-}$ = dianion of 1,2-bis((2-mercaptophenyl)thio)ethane; ‘$^{\mathrm{Bu}}$S$_4$’$^{2-}$ = dianion of 1,2-bis((3,5-di-*tert*-butyl-2-mercaptophenyl)thio)ethane; ‘S$_2$’$^{2-}$ = 1,2-benzenedithiolate; ‘$^{\mathrm{Bu}}$S$_2$’$^{2-}$ = 3,5-di-*tert*-butyl-1,2-benzenedithiolate; ‘S$_2$’–CH=CH$_2^-$ = 1-(vinylthio)-2-benzenethiolate; ‘$^{\mathrm{Bu}}$S$_2$’–CH=CH$_2^-$ = 1-(vinylthio)-3,5-di-*tert*-butyl-2-benzenethiolate.

thio)ethyl)amine)[7] and [Mo(NO)$_2$(‘S$_4$’)]/[Mo(NH$_2$O)(NO)(‘S$_4$’)] (‘S$_4$’$^{2-}$ = dianion of 1,2-bis((2-mercaptophenyl)thio)ethane).[8] In these complexes, the metal centers have soft Lewis acid character, as it is also found for the Ru center in [Ru(PPh$_3$)$_2$(‘S$_4$’)]. The latter has one labile PPh$_3$, which can be replaced by 2e$^-$ donors, e.g. CO,[9] N$_2$H$_2$,[9] N$_2$H$_4$,[10] or PMe$_3$.[10] Quite a different reaction takes place when [Ru(PPh$_3$)$_2$(‘S$_4$’)] is reacted with the 3e$^-$ donor NO. If an excess of NO was applied, the formation of NO complexes was indicated by IR spectroscopy, but the products were obviously a mixture of complexes that could neither be separated nor characterized.[9] Uncertain was also the degree of PPh$_3$ substitution. We have now reinvestigated these reactions and, by applying exactly stoichiometric conditions, could observe a new type of ligand substitution by NO that includes simultaneous S–C bond cleavage of the core ligand. Our aim was also the synthesis of related NO complexes in order to investigate the relative stability of 19e$^-$ and 18e$^-$ nitrosyl complexes. The results leading to Ru complexes with the ‘S$_2$’$^{2-}$, ‘S$_2$’–CH=CH$_2^-$, ‘S$_4$’$^{2-}$, and the related *tert*-butyl ligands ‘$^{\mathrm{Bu}}$S$_2$’$^{2-}$, ‘$^{\mathrm{Bu}}$S$_2$’–CH=CH$_2^-$, and ‘$^{\mathrm{Bu}}$S$_4$’$^{2-}$ will be described here.

The ligands and their abbreviations are shown in Chart I.

Experimental Section

General Procedures. Unless otherwise noted, all reactions were carried out at room temperature under nitrogen, the Schlenk technique being used. Solvents were dried and distilled under nitrogen before use. Spectra were recorded on the following instruments: Perkin-Elmer 983 infrared spectrophotometer (solutions in CaF$_2$ cuvettes with compensation of solvent bands; solids in KBr); JEOL JNM-GX 270 FT-NMR spectrometer; Varian Mat 212 mass spectrometer.

Starting materials were prepared as described in the literature: [Ru(PPh$_3$)$_2$(‘S$_4$’)];[9] [Ru(PPh$_3$)$_2$(‘$^{\mathrm{Bu}}$S$_4$’)].[11] Ru(NO)Cl$_3$·H$_2$O was prepared by a modified literature procedure.[12] A stream of NO gas was bubbled through a solution of RuCl$_3$·H$_2$O in MeOH for 6 h, and formed Ru(NO)Cl$_3$·H$_2$O was used in situ.

Syntheses. (a) [Ru(NO)(PPh$_3$)(‘S$_2$’)(‘S$_2$’–CH=CH$_2$)]·CH$_2$Cl$_2$ (3·CH$_2$Cl$_2$). To a suspension of 934 mg (1 mmol) of [Ru(PPh$_3$)$_2$(‘S$_4$’)] (**1**) in 200 mL of THF is added 22.4 mL (1 mmol) of NO gas. When stirring for 1 day, the yellow suspension turns into a deep red solution. The volume of the reaction mixture is reduced to ca. 30 mL, and the remaining solution is filtered. Upon addition of 200 mL of Et$_2$O, **3** precipitates as a red powder. It is separated, washed with 30 mL of Et$_2$O, and recrystallized from CH$_2$Cl$_2$ (+20 °C/+5 °C) to give dark red prisms of **3**·CH$_2$Cl$_2$. They are collected, washed with 15 mL of Et$_2$O, and dried in vacuo for 1 day. Yield: 479 mg (68%). Anal. Calcd for C$_{33}$H$_{28}$Cl$_2$NOPRuS$_4$ (M_r = 785.78): C, 50.44; H, 3.59; N, 1.78. Found: C, 50.31; H, 3.49; N, 1.65.

(b) [Ru(NO)(PPh$_3$)(‘$^{\mathrm{Bu}}$S$_2$’)(‘$^{\mathrm{Bu}}$S$_2$’–CH=CH$_2$)]·CH$_2$Cl$_2$ (4·CH$_2$Cl$_2$). Into a solution of 235 mg (0.2 mmol) of [Ru(PPh$_3$)$_2$(‘$^{\mathrm{Bu}}$S$_4$’)] (**2**), in 30 mL of THF is introduced 4.5 mL (0.2 mmol) of NO gas whereupon the color turns from yellow to dark red. The solution is stirred for 1 day, the solvent is evaporated, and the dry residue is recrystallized from CH$_2$Cl$_2$ (+20 °C/+5 °C) to give deep red prisms of **4**·CH$_2$Cl$_2$. They were separated, washed with 20 mL of *n*-hexane, and dried in high vacuum for 1 day. Yield: 105 mg (57%). Despite several purifications, no satisfactory elemental analyses could be obtained because of wide scatter among consecutive analyses. Anal. Calcd for C$_{49}$H$_{60}$Cl$_2$NOPRuS$_4$ (M_r = 1010.21): C, 58.26; H, 5.99; N, 1.39. Found: C, 61.79; H, 6.99; N, 0.84.

Table I. Summary of Crystallographic Data for [Ru(NO)(PPh$_3$)(‘S$_2$’)(‘S$_2$’–CH=CH$_2$)]·CH$_2$Cl$_2$ (3·CH$_2$Cl$_2$)

formula	C$_{33}$Cl$_2$H$_{28}$NOPRuS$_4$	V, nm^3	1.667 (1)
mol	785.80	Z	2
space group	$P\bar{1}$	d_{calcd}, g/cm^3	1.56
cell dimens		diffractometer	Nicolet R3m/V
a, pm	1114.0 (2)	radiation	Mo Kα/graphite monochr
b, pm	1221.9 (3)		
c, pm	1278.3 (3)	wavelength, pm	71.073
α, deg	83.29 (2)	temp of measmt, K	200
β, deg	80.85 (2)		
γ, deg	76.91 (2)	R	0.069
		R_w	0.059

(c) “[Ru(NO)(PPh$_3$)(‘$^{\mathrm{Bu}}$S$_4$’)](PF$_6$)·CH$_2$Cl$_2$” (5·CH$_2$Cl$_2$). To a suspension of 280 mg (0.24 mmol) of [Ru(PPh$_3$)$_2$(‘$^{\mathrm{Bu}}$S$_4$’)] (**2**) in 15 mL of CH$_2$Cl$_2$ is added 91.55 mg (0.52 mmol) of NOPF$_6$ in small portions. A clear solution forms, and the color turns from yellow to dark brown. The solution is reduced to a volume of ca. 5 mL, filtered, and evaporated to dryness, yielding a dark brown powder that is recrystallized from CH$_2$Cl$_2$ (+20 °C/+5 °C). Yield: 115 mg (44%). Anal. Calcd for C$_{49}$H$_{61}$Cl$_2$F$_6$NOPRuS$_4$ (M_r = 1071.25): C, 50.90; H, 5.32; N, 1.21. Found: C, 51.15; H, 5.42; N, 1.23.

(d) [Ru(NO)(Cl)(‘S$_4$’)]·THF (6·THF). Through a red-brown solution of 500 mg (1.91 mmol) of RuCl$_3$·H$_2$O in 150 mL of MeOH is bubbled a gentle stream of NO gas for 6 h. A clear blue-violet solution forms, which is evaporated to dryness. The residue is redissolved in 10 mL of THF, and the solution is saturated with NO gas for 1 h more. To this solution is added dropwise a solution of ‘S$_4$’–Li$_2$, which was prepared by treating 539 mg (1.91 mmol) of ‘S$_4$’–H$_2$ in 10 mL of THF with 2.4 mL (3.82 mmol) of *n*-BuLi (1.6 m in *n*-hexane) at –78 °C. The color immediately turns dark brown, and **6**·THF precipitates. After 1 day the solution is filtered, and the solid residue is washed with 45 mL of THF and dried under high vacuum for 2 days. Because of its poor solubility, **6**·THF could not be recrystallized. Yield: 495 mg (55%). Anal. Calcd for C$_{18}$H$_{20}$ClNORuS$_4$ (M_r = 547.13): C, 39.51; H, 3.68; N, 2.56. Found: C, 38.73; H, 3.68; N, 2.35.

(e) [Ru(NO)(Cl)(‘$^{\mathrm{Bu}}$S$_4$’)] (7). To 292 mg (1 mmol) of Ru(NO)Cl$_3$·H$_2$O in 100 mL of THF, which was prepared as described before, is added dropwise a solution of 547 mg (1 mmol) of ‘$^{\mathrm{Bu}}$S$_4$’–Li$_2$. The solution, which turns from blue-violet to dark red-brown, is stirred for 1 day, and the solvent is removed. The red-brown solid residue is redissolved in 100 mL of CH$_2$Cl$_2$, and the solution is dried over Na$_2$SO$_4$ for 1 day and filtered. After reduction of the volume to ca. 10 mL, the solution is cooled to –78 °C when **7** precipitates. It is separated, washed with 5 mL of *n*-hexane, and dried under high vacuum for 1 day. Yield: 275 mg (41%). Anal. Calcd for C$_{30}$H$_{44}$ClNORuS$_4$ (M_r = 699.45): C, 51.51; H, 6.34; N, 2.00. Found: C, 51.95; H, 6.68; N, 1.65.

X-ray Structure Determination of [Ru(NO)(PPh$_3$)(‘S$_2$’)(‘S$_2$’–CH=CH$_2$)]·CH$_2$Cl$_2$ (3·CH$_2$Cl$_2$). Single crystals (0.60 × 0.30 × 0.10 mm^3) of **3**·CH$_2$Cl$_2$ were obtained by slow cooling of a CH$_2$Cl$_2$ solution from +20 to +5 °C and sealed in a glass capillary without drying. The non-hydrogen atoms were refined anisotropically, and the solvent molecule was refined isotropically. The hydrogen atoms of the vinyl and phenyl groups were calculated for ideal geometry and fixed during refinement. Hydrogen atoms were refined with a common temperature factor. Relevant data are summarized in Table I; Table II lists the fractional atomic coordinates and thermal parameters.

Results

Sulfur–Carbon Bond Cleavage. When gaseous nitrogen monoxide is introduced into a yellow suspension of [Ru(PPh$_3$)$_2$(‘S$_4$’)] (**1**) according to eq 1, a clear dark red solution results within 1 day and **3** forms. **3** is well soluble in CH$_2$Cl$_2$ and THF, slightly soluble in toluene and acetone, and insoluble in *n*-hexane and Et$_2$O.

$$\mathbf{1} + \mathrm{NO} \xrightarrow{\mathrm{THF}/20\ ^{\circ}\mathrm{C}/1\ \mathrm{day}} \underset{\mathbf{3}}{[\mathrm{Ru(NO)(PPh_3)(‘S_2’)(‘S_2’–CH{=}CH_2)}]} + \text{other products} \qquad (1)$$

---

(7) Sellmann, D.; Kunstmann, H.; Moll, M.; Knoch, F. *Inorg. Chim. Acta* **1988**, *154*, 157.

(8) Sellmann, D.; Seubert, B.; Moll, M.; Knoch, F. *Angew. Chem.* **1988**, *100*, 1221; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1164.

(9) (a) Sellmann, D.; Boehlen, E. *Z. Naturforsch.* **1982**, *37B*, 1026. (b) Sellmann, D.; Boehlen, E.; Waeber, M.; Huttner, G.; Zsolnai, L. *Angew. Chem.* **1985**, *97*, 984.

(10) (a) Boehlen, E. Dissertation, Universität Erlangen-Nürnberg, 1982. (b) Waeber, M. Dissertation, Universität Erlangen-Nürnberg, 1985.

(11) Sellmann, D.; Barth, I. *Z. Anorg. Allg. Chem.* **1989**, *577*, 234.

(12) Fenske, D.; Demant, U.; Dehnicke, K. *Z. Naturforsch.* **1985**, *40B*, 1672.

Table II. Fractional Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($pm^2 \times 10^{-1}$) of the Non-Hydrogen Atoms of $[Ru(NO)(PPh_3)('S_2')('S_2'-CH{=}CH_2)]\cdot CH_2Cl_2$ ($3\cdot CH_2Cl_2$)

	x	y	z	U_{eq}[a]
Ru(1)	3792 (1)	7971 (1)	3264 (1)	28 (1)
N(1)	3066 (6)	9026 (5)	2379 (5)	39 (2)
O(1)	2579 (7)	9736 (5)	1826 (5)	76 (3)
S(1)	1946 (2)	7408 (2)	4124 (2)	41 (1)
S(2)	3493 (2)	9214 (2)	4685 (2)	38 (1)
S(3)	5841 (2)	8380 (2)	2804 (2)	35 (1)
S(4)	4654 (2)	6633 (2)	4559 (1)	31 (1)
C(15)	2167 (8)	8909 (7)	5528 (6)	43 (3)
C(14)	1784 (10)	9449 (8)	6484 (7)	58 (4)
C(13)	773 (10)	9247 (9)	7152 (7)	73 (5)
C(12)	115 (9)	8493 (8)	6900 (7)	62 (4)
C(11)	490 (8)	7939 (7)	5974 (6)	50 (4)
C(10)	1522 (8)	8136 (7)	5272 (6)	40 (3)
C(16)	2860 (9)	10613 (6)	4206 (7)	53 (4)
C(17)	3534 (10)	11362 (7)	3974 (7)	64 (4)
C(25)	6750 (7)	7397 (6)	3627 (5)	29 (3)
C(24)	8033 (7)	7360 (6)	3530 (6)	38 (3)
C(23)	8779 (8)	6597 (7)	4179 (6)	43 (3)
C(22)	8282 (8)	5848 (7)	4909 (6)	41 (3)
C(21)	7005 (7)	5878 (6)	5016 (6)	35 (3)
C(20)	6244 (7)	6644 (6)	4390 (5)	29 (3)
P(1)	4318 (2)	6623 (2)	1952 (2)	30 (1)
C(35)	4890 (8)	8215 (6)	307 (6)	39 (3)
C(34)	4800 (9)	8822 (6)	−677 (6)	47 (3)
C(33)	4043 (9)	8617 (7)	−1341 (6)	51 (4)
C(32)	3402 (9)	7776 (7)	−1030 (6)	51 (4)
C(31)	3471 (8)	7155 (6)	−46 (6)	42 (3)
C(30)	4230 (7)	7368 (6)	634 (5)	30 (3)
C(45)	3737 (8)	4505 (6)	1904 (6)	36 (3)
C(44)	2911 (9)	3798 (7)	1929 (6)	45 (3)
C(43)	1658 (9)	4213 (7)	2061 (6)	49 (4)
C(42)	1188 (8)	5361 (8)	2153 (6)	49 (4)
C(41)	2008 (8)	6059 (7)	2132 (6)	41 (3)
C(40)	3283 (7)	5639 (6)	2026 (5)	29 (3)
C(55)	6153 (8)	4938 (6)	2732 (6)	38 (3)
C(54)	7326 (8)	4246 (7)	2706 (7)	45 (3)
C(53)	8196 (8)	4317 (7)	1830 (8)	54 (4)
C(52)	7936 (8)	5092 (7)	982 (7)	52 (4)
C(51)	6751 (8)	5804 (6)	1016 (6)	41 (3)
C(50)	5869 (7)	5732 (6)	1881 (6)	30 (3)
C(1)	−1582 (15)	9029 (12)	555 (12)	147 (6)
Cl(1)	−1584 (4)	7920 (3)	−325 (3)	147 (2)
Cl(2)	86 (5)	8519 (4)	772 (4)	173 (2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

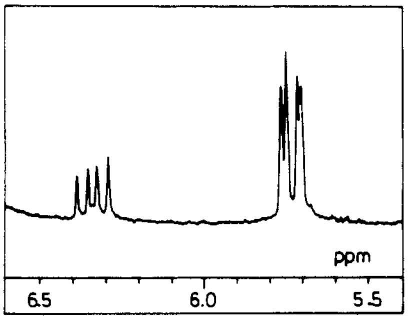


Figure 1. Vinyl section of the ^1H NMR spectrum of $[Ru(NO)(PPh_3)('S_2')('S_2'-CH{=}CH_2)]$ (**3**) in CD_2Cl_2.

The characteristic $\nu(NO)$ absorption of **3** in the KBr IR spectrum appears at 1775 cm^{-1}, 75 cm^{-1} lower than the $\nu(NO)$ of the cationic $18e^-$ complex $[Ru(NO)(PPh_3)('S_4')](PF_6)$ (1850 cm^{-1}).[13] In the ^1H spectrum of **3** in CD_2Cl_2 the pseudodoublets of the C_2H_4 protons at 3.56 and 1.95 ppm of **1** have disappeared and the typical pattern of a vinyl group at 6.34, 5.76, and 5.71 ppm is to be seen (Figure 1).

This observation suggested that the $'S_4'^{2-}$ ligand was cleaved in the course of the reaction (eq 1) and yielded a vinyl thioether thiolate ligand. This could be confirmed by X-ray structure analysis.

Table III. Selected Bond Distances (pm) and Angles (deg) of $[Ru(NO)(PPh_3)('S_2')('S_2'-CH{=}CH_2)]\cdot CH_2Cl_2$ ($3\cdot CH_2Cl_2$)

Ru(1)–N(1)	175.4 (6)	S(1)–C(10)	175.0 (8)
Ru(1)–S(1)	237.8 (2)	S(2)–C(15)	177.1 (9)
Ru(1)–S(2)	243.7 (2)	S(2)–C(16)	177.2 (8)
Ru(1)–S(3)	241.5 (2)	S(3)–C(25)	175.2 (7)
Ru(1)–S(4)	234.4 (2)	S(4)–C(20)	175.3 (8)
Ru(1)–P(1)	240.1 (2)	C(16)–C(17)	129.1 (14)
N(1)–O(1)	114.5 (8)		
N(1)–Ru(1)–S(1)	96.3 (2)	S(1)–Ru(1)–S(3)	166.0 (1)
N(1)–Ru(1)–S(2)	94.0 (2)	S(2)–Ru(1)–S(3)	86.4 (1)
N(1)–Ru(1)–S(3)	96.1 (2)	S(2)–Ru(1)–S(4)	82.0 (1)
N(1)–Ru(1)–S(4)	175.4 (2)	Ru(1)–S(2)–C(15)	103.8 (3)
Ru(1)–N(1)–O(1)	177.9 (6)	Ru(1)–S(2)–C(16)	109.4 (3)
N(1)–Ru(1)–P(1)	92.1 (2)	S(2)–C(16)–C(17)	121.6 (8)
S(1)–Ru(1)–S(2)	86.3 (1)	S(3)–Ru(1)–S(4)	86.1 (1)

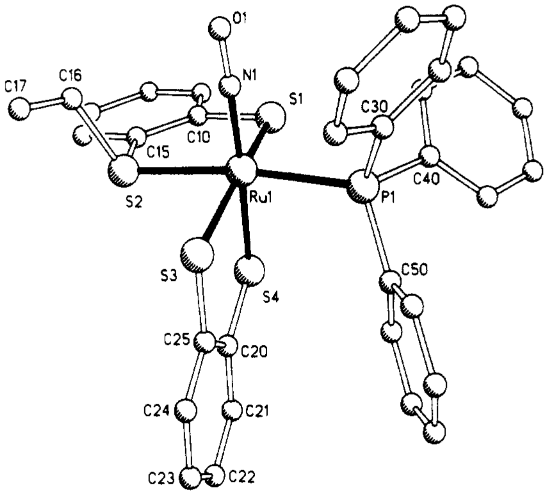


Figure 2. Molecular structure of $[Ru(NO)(PPh_3)('S_2')('S_2'-CH{=}CH_2)]\cdot CH_2Cl_2$ ($3\cdot CH_2Cl_2$) (H atoms omitted).

Figure 2 shows the molecular structure of $3\cdot CH_2Cl_2$; Table III lists selected bond distances and angles.

The Ru center of **3** is surrounded pseudooctahedrally by one nitrogen and three thiolate S atoms lying approximately in a plane, the thioether S and phosphorous atom occupying the remaining trans positions. The bond lengths of all Ru–S bonds differ. This is certainly due to the different chemical character of the S atoms as well as the respective trans ligands. Ru(II/III)–S bond distances in the range 234–244 pm, however, are quite normal. They are also found in the related $[Ru(PMe_3)_4('S_2')]$ (242–243 pm),[14] $(NBu_4)[Ru(PMe_3)_2('S_2')_2]$ (233–236 pm),[14] and $[(\mu\text{-}N_2H_2)\{Ru(PPh_3)('S_4')\}_2]$ (228–238 pm).[9] The bond angles show no anomalies. Deviations from 180° or right angles are plausibly explained by steric repulsion, e.g. of the bulky PPh_3, or by the bidenticity of the S ligands. The RuNO entity with an angle of 177.9 (6)° is nearly linear, indicating an electronic configuration close to $[Ru^{II}-NO^+]$. On the other hand, the $\nu(NO)$ of **3** (1775 cm^{-1}) shows that the electron density in π^* NO orbitals is larger than in $[Ru(NO)(PPh_3)('S_4')](PF_6)$ ($\nu(NO)$ = 1850 cm^{-1}).[13] The C=C bond distance of 129.1 (14) pm lies in the typical range of vinyl groups.[15] The structure determination unambiguously proves that substituting PPh_3 in **1** by NO leads to S–C bond cleavage and formation of a vinyl thioether thiolate ligand.

Synthesis of Further NO Complexes. An analogous reaction as for **1** was observed for $[Ru(PPh_3)_2('^{Bu}S_4')]$ (**2**), which contains the sterically demanding ligand $'^{Bu}S_4'^{2-}$. $[Ru(NO)(PPh_3)('^{Bu}S_2')('^{Bu}S_2'-CH{=}CH_2)]$ (**4**) forms according to eq 2.

$$2 + NO \xrightarrow{\text{THF/20 °C/1 day}} 4 + \text{other products} \qquad (2)$$

---

(13) Sellmann, D.; Waeber, M. *Z. Naturforsch.* **1986**, *41B*, 877.

(14) Sellmann, D.; Binker, G.; Knoch, F. *Z. Naturforsch.* **1987**, *42B*, 1298.

(15) Staab, H. A. *Einführung in die theoretische Organische Chemie*, 3rd ed.; Verlag Chemie: Weinheim, West Germany, 1962.

Table IV. Selected Spectroscopic Data for the New Nitrosyl Complexes

compd	IR: ν, cm^{-1}	^{1}H NMR:[a] δ, ppm	^{31}P NMR:[b] δ, ppm	^{14}N NMR:[c] δ, ppm	MS: *m/e*
[Ru(NO)(PPh$_3$)(‘S$_2$’)(‘S$_2$’–CH=CH$_2$)] (**3**)	1775 (ν(NO)),[d] 1790 (ν(NO))[e]	7.73–6.67 (m) (23; C$_6$H$_2$, PPh$_3$), 6.34 (m) (1; –CH=), 5.76 (d) (1; =CH$_2$), 5.71 (d) (1; =CH$_2$)	24.4	35.0	701 ([M]$^+$)[f]
[Ru(NO)(PPh$_3$)(‘^{Bu}S$_2$’)(‘^{Bu}S$_2$’–CH=CH$_2$)] (**4**)	1775 (ν(NO)),[d] 1780 (ν(NO))[e]	7.78–6.52 (m) (19; C$_6$H$_2$, PPh$_3$), 6.36 (m) (1; –CH=), 5.79 (d) (1; =CH$_2$), 5.63 (d) (1; =CH$_2$), 1.75–1.20 (m) (36; C(CH$_3$)$_3$)	26.0	38.4	925 ([M]$^+$)[f]
[Ru(NO)(PPh$_3$)(‘^{Bu}S$_4$’)](PF$_6$)	1825 (ν(NO)),[d] 840 (ν(PF$_6$)), 1838 (ν(NO))[e]	7.22–6.43 (m) (19; C$_6$H$_2$, PPh$_3$), 3.68–2.89 (m) (4; C$_2$H$_4$), 1.60 (s) (9; C(CH$_3$)$_3$), 1.53 (s) (9; C(CH$_3$)$_3$), 1.34 (s) (9; C(CH$_3$)$_3$), 1.23 (s) (9; C(CH$_3$)$_3$)	*g*	49.0	926 ([M]$^+$)[h]
[Ru(NO)(CL)(‘S$_4$’)] (**6**)	1852 (ν(NO)),[d] 1848 (ν(NO))[k]	8.31–6.82 (m) (8; C$_6$H$_4$),[i] 3.28–2.03 (m) (4; C$_2$H$_4$)		*j*	475 ([M]$^+$)[f]
[Ru(NO)(Cl)(‘^{Bu}S$_4$’)] (**7**)	1828 (ν(NO)),[d] 1841 (ν(NO))[l]	7.55–7.13 (m) (4; C$_6$H$_2$), 3.46–2.98 (m) (4; C$_2$H$_4$), 1.70 (s) (9; C(CH$_3$)$_3$), 1.69 (s) (9; C(CH$_3$)$_3$), 1.34 (s) (9; C(CH$_3$)$_3$), 1.30 (s) (9; C(CH$_3$)$_3$)		42.0	699 ([M]$^+$),[h] 669 ([M – NO]$^+$), 641 ([M – NO – C$_2$H$_4$]$^+$), 606 ([M – NO – C$_2$H$_4$ – Cl]$^+$)

[a] In CD$_2$Cl$_2$, relative to TMS; m = multiplet, t = triplet, d = doublet, and s = singlet. [b] In CD$_2$Cl$_2$, relative to external H$_3$*P*O$_4$. [c] In CD$_2$Cl$_2$, relative to external NH$_4$*N*O$_3$. [d] In KBr. [e] In THF. [f] FD-MS. [g] See text. [h] EI-MS. [i] In DMSO-d_6. [j] Because of poor solubility, no ^{14}N NMR spectrum was accessible. [k] In DMF. [l] In CH$_2$Cl$_2$.

4 is very soluble in CH$_2$Cl$_2$, THF, acetone, and toluene and was characterized spectroscopically and by elemental analysis (Table IV).

A different reaction takes place when **2** is reacted with NO$^+$. According to eq 3 a product forms that we tentatively describe

$$\mathbf{2} + \mathrm{NOPF_6} \xrightarrow[-\mathrm{PPh_3}]{\mathrm{CH_2Cl_2/20\ ^\circ C/1\ day}} \mathbf{5} \tag{3}$$

as the ionic complex [Ru(NO)(PPh$_3$)(‘^{Bu}S$_4$’)](PF$_6$) (**5**). **5** has an intact ‘^{Bu}S$_4$’ ligand and would be the analogue of [Ru(NO)(PPh$_3$)(‘S$_4$’)](PF$_6$).[13] This follows from the ^{1}H NMR spectrum of **5**, showing four *tert*-butyl signals and also the typical pattern of the C$_2$H$_4$ bridge due to the C_1 symmetry of **5** (Figure 3). The PF$_6^-$ anion has been detected in the IR spectrum.

Compatible with the proposed structure are also the ^{14}N NMR spectrum, the mass spectrum displaying the cation at *m/e* = 926, and the elemental analysis. ν(NO) of **5** at 1825 cm^{-1} in the KBr IR spectrum, however, is 25 cm^{-1} lower than in the analogous ‘S$_4$’ complex, although ν(CO) and ν(NO) in analogous ‘S$_4$’ and ‘^{Bu}S$_4$’ complexes usually do not differ, and despite repeated recrystallizations, the ^{31}P NMR spectrum showed more ^{31}P signals than to be expected. Neutral Ru(II) nitrosyl compounds with intact [Ru(‘L$_4$’)] cores (‘L$_4$’ = ‘S$_4$’$^{2-}$, ‘^{Bu}S$_4$’$^{2-}$) were obtained according to eq 4. **6** is only poorly soluble in DMSO and insoluble in all

$$\mathrm{Ru(NO)Cl_3{\cdot}}x\mathrm{H_2O} + \text{‘L}_4\text{’–Li}_2 \xrightarrow[-2\mathrm{LiCl},\ -x\mathrm{H_2O}]{\mathrm{THF/20\ ^\circ C/1\ day}} [\mathrm{Ru(NO)(Cl)(‘L_4’)}] \tag{4}$$
$$\text{‘L}_4\text{’} = \text{‘S}_4\text{’}^{2-}\ (\mathbf{6}), \text{‘}^{\mathrm{Bu}}\mathrm{S}_4\text{’}^{2-}\ (\mathbf{7})$$

other common solvents. The much more soluble **7** dissolves also in CH$_2$Cl$_2$, THF, acetone, and toluene; it is easily characterized by its ^{1}H NMR spectrum showing the typical pattern of the ‘^{Bu}S$_4$’$^{2-}$ ligand protons in complexes of C_1 symmetry;[11] particularly characteristic are the four singlets of the *tert*-butyl groups.

Selected spectroscopic data of the new complexes are summarized in Table IV.

Discussion and Conclusion

[Ru(PPh$_3$)$_2$(‘S$_4$’)] (**1**) and [Ru(PPh$_3$)$_2$(‘^{Bu}S$_4$’)] (**2**), in which the 18e$^-$-configurated Ru(II) centers are ligated by the tetradentate thioether thiolate ligands, react with 2e$^-$ donors, e.g. CO,[9,11] as well as with the 3e$^-$ donor NO. In the former case, only a substitution of the 2e$^-$ ligand PPh$_3$ takes place and the sulfur ligand remains intact. In the second case, when the 2e$^-$ donor PPh$_3$ is substituted by the 3e$^-$ donor NO, the resulting primary species is obviously highly reactive and undergoes secondary reactions. They lead to cleavage of S–C bonds in the core ligand and the formation of **3** and **4**, respectively, in which dithiolate and vinyl thioether thiolate ligands are coordinating the Ru centers. We explain this by assuming 19e$^-$-configurated species as primary products (eq 5). 19e$^-$ complexes of this kind are usually highly reactive because the odd electron occupies antibonding orbitals.[16] These orbitals can have mainly NO π^* or metal–ligand character.[17] In either case, 19e$^-$ species could be isolated and structurally

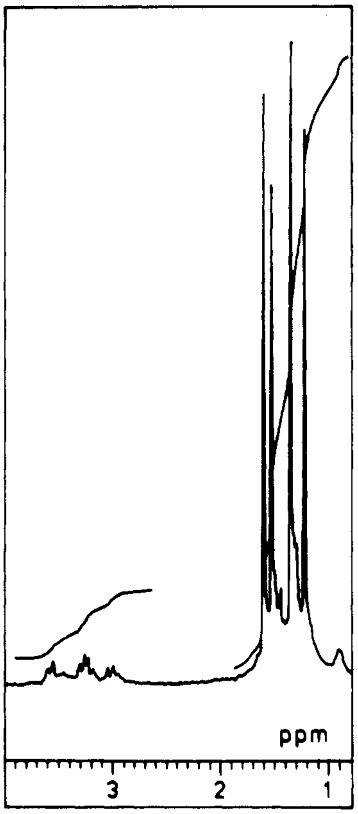
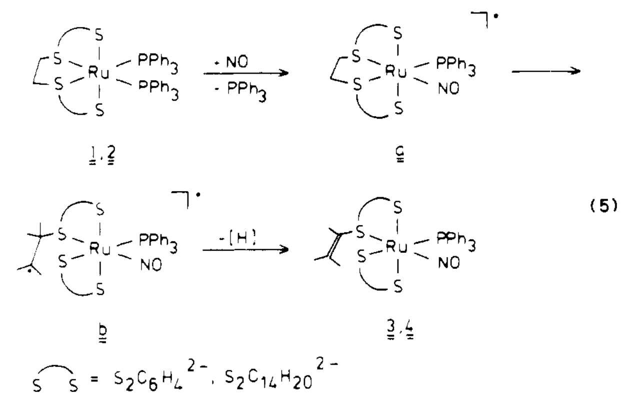


Figure 3. ^{1}H NMR spectrum of **5** in CD$_2$Cl$_2$.

---

(16) Astruc, D. *Chem. Rev.* **1988**, *88*, 1189.

(17) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; John Wiley & Sons: New York, 1985.



(5)

characterized only in a very few cases;[18] one example is $[Fe(NO)('N_HS_4')]$ ($'N_HS_4'^{2-}$ = dianion of bis(2-((2-mercaptophenyl)thio)ethyl)amine).[7] Its X-ray structure analysis shows that the odd electron causes a bending of the FeNO group and a dramatic lengthening of all core distances in comparison with the analogous 18e$^-$ species.[19] This obviously relieves the electronic strain. The 19e$^-$ species a (eq 5) takes another route: S–C bond cleavage occurs (b) followed by H elimination such that the $S-C_2H_4$ group becomes a vinyl thioether, leading to **3** and **4**, respectively. S–C bond cleavage in organosulfur ligands[20] and formation of vinyl thioethers from alkyl thioethers[21] has been previously observed in several cases, but here the conversion of *S*-alkyl into *S*-vinyl groups is clearly induced in an unprecedented way by single electron transfer from NO via the Ru center and S atoms.

Acknowledgment. These investigations were supported by the Deutsche Forschungsgemeinschaft, by the Fonds der Chemischen Industrie, and by a donation of $RuCl_3 \cdot xH_2O$ by Degussa AG, Hanau, West Germany. We gratefully acknowledge this support.

Supplementary Material Available: Listings of crystallographic data and data collection parameters, anisotropic thermal parameters, all bond distances and bond angles, and fractional coordinates of hydrogen atoms (8 pages); a listing of F_o and F_c values (22 pages). Ordering information is given on any current masthead page. Further details of the X-ray crystal structure analysis have been deposited with the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen 2, West Germany, and can be obtained by quoting deposition no. CSD-320096, the authors' names, and the reference.

---

(18) (a) Yu, J. S.; Jacobson, A.; Angelici, R. J. *Inorg. Chem.* **1982**, *21*, 3106. (b) Aoyagi, K.; Mukaida, M.; Kakihana, H.; Shimuzu, K. *J. Chem. Soc., Dalton Trans.* **1985**, 1733. (c) Callahan, R. W.; Meyer, T. J. *Inorg. Chem.* **1977**, *16*, 574. (d) Callahan, R. W.; Brown, G. M.; Meyer, J. M. *J. Am. Chem. Soc.* **1975**, *97*, 894. (e) Silverthorn, W.; Feltham, R. D. *Inorg. Chem.* **1967**, *6*, 1662. (f) Scheidt, W. A.; Brinegar, A. Ch.; Ferro, E. B.; Kirner, J. F. *J. Am. Chem. Soc.* **1977**, *99*, 7315.

(19) Sellmann, D.; Kunstmann, H.; Knoch, F.; Moll, M. *Inorg. Chem.* **1988**, *27*, 4183.

(20) (a) Tatsumi, K.; Sekiguchi, Y.; Nakamura, A. *J. Am. Chem. Soc.* **1986**, *108*, 1358. (b) Sellmann, D.; Reisser, W. *Z. Naturforsch.* **1984**, *39B*, 1268.

(21) Huxtable, R. J. In *Biochemistry of Sulfur*; Plenum Press: New York, 1986.

Contribution from the Departments of Chemistry, McGill University,
801 Sherbrooke Street West, Montreal, Quebec H3A 2K6, Canada,
and Concordia University, 1455 de Maisonneuve Boulevard West, Montreal, Quebec H3G 1M8, Canada

Preparation of (η-C_5H_5)Ru(PPh_3)(L)SR (R = 1-C_3H_7, $CHMe_2$, 4-C_6H_4Me; L = PPh_3, CO) and Insertion of CS_2 into the Ru–SR Bond To Give the Thioxanthates (η-C_5H_5)Ru(PPh_3)S_2CSR (R = 1-C_3H_7, $CHMe_2$, 4-C_6H_4Me). Crystal Structure of (η-C_5H_5)Ru(PPh_3)S_2CS-1-C_3H_7

Alan Shaver,*[1a] Pierre-Yves Plouffe,[1a] Peter Bird,[1b] and Edward Livingstone[1b]

Received July 28, 1989

The reactive thiolato complexes (η-C_5H_5)Ru(PPh_3)$_2$SR, where R = 1-C_3H_7, $CHMe_2$, and 4-C_6H_4Me were prepared by briefly heating (η-C_5H_5)Ru(PPh_3)$_2$Cl and the appropriate alkali-metal thiolate in refluxing tetrahydrofuran. Treatment of the thiolates with CO gave (η-C_5H_5)Ru(PPh_3)(CO)SR. Treatment with CS_2 gave the thioxanthate complexes (η-C_5H_5)Ru(PPh_3)S_2CSR, where R = 1-C_3H_7, $CHMe_2$, and 4-C_6H_4Me, wherein the CS_2 has inserted into the Ru–SR bond. The structure of (η-C_5H_5)Ru(PPh_3)S_2CS-1-C_3H_7 was determined: space group $P\bar{1}$, a = 10.88 (1) Å, b = 10.06 (1) Å, c = 12.82 (2) Å, α = 105.05 (12)°, β = 95.00 (11)°, γ = 101.17 (9)°, V = 1314.9 Å^3, and Z = 2. The rate of CS_2 insertion is accelerated by increasing the CS_2 concentration and depressed by adding free ligand (PPh_3 or CO). The implications with respect to the mechanism of CS_2 insertion are discussed.

Introduction

Organoruthenium–sulfur chemistry is a topic of current interest. Angelici et al.[2] have developed the chemistry of π-bonded CpRu–thiophene cations as a model for hydrodesulfurization. Rauchfuss et al.[3] have reported several CpRu–polysulfide complexes with unusual structures and reactivity. We are interested in preparing complexes containing linear catenated polysulfur ligands[4] of the type RS_x^-, where $x > 1$. Such species are analogues of the ubiquitous organic polysulfanes yet are themselves surprisingly rare. To that end, we investigated the synthesis of complexes of the type CpRu(PPh_3)$_2$SR. The complexes $CpRuL_2SPh$, where L = CO, PMe_3, P(OMe)$_3$, P(OMe)$_2$Ph, and P(OPr)$_3$ and L_2 = $Ph_2PCH_2CH_2PPh_2$ have been reported.[5] A

---

* To whom correspondence should be addressed.

(1) (a) McGill University. (b) Concordia University.

(2) Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387.

(3) (a) Amarasekera, J.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **1987**, *26*, 3328. (b) Amarasekera, J.; Rauchfuss, T. B.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 2017. (c) Ogilvy, A. E.; Rauchfuss, T. B. *Organometallics* **1988**, *7*, 1884. (d) Rauchfuss, T. B.; Rodgers, D. P. S.; Wilson, S. R. *J. Am. Chem. Soc.* **1986**, *108*, 3114.

(4) (a) Shaver, A.; Lai, R. D. *Inorg. Chem.* **1988**, *27*, 2664. (b) Shaver, A.; Hartgerink, J. *Can. J. Chem.* **1987**, *65*, 1190. (c) Shaver, A.; McCall, J. M.; Bird, P. H.; Ansari, N. *Organometallics* **1983**, *2*, 1894.

0020-1669/90/1329-1826$02.50/0