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Cyanodithioformate Complexes of Cyclopentadientylruthenium(II). Synthesis, Spectral and Electrochemical Study

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A series of mono and binuclear cyanodithioformate (cdf) complexes with $[Ru^{II}CpL_2]$ [L=PPh_3, $AsPh_3$, $SbPh_3$, $(dppe)_{1/2}$, $(dppm)_{1/2}$], exploiting its different coordination modes have been synthesized. Various physical and electrochemical methods have been used to characterize them. cdf by virtue of its vacant π^* orbital introduces a low laying energy state in the compounds that facilitates Ru→cdf ($d\pi \rightarrow \pi^*$) MLCT transition. MLCT band, upon dimerizaion shows red shift, whose magnitude depends upon site of attachment of second ruthenium moiety [$\Delta\bar{\nu}$, 3750 cm^{-1} for $\mu(\eta^1$-S; η^1-S′) and 1010 cm^{-1} for $\mu(\eta^1$-S; η^1-N) cdf complexes]. All complexes exhibit anodic oxidation peaks except binuclear $\mu(\eta^1$-S; η^1-S′) cdf complex which exhibits reversible oxidation wave $E_{1/2}$, −0.20 V vs. SCE in acetonitrite. Their spectral and electrochemical behavior are correlated with the σ, π characterstics of cdf and ruthenium moieties.

Although the synthetic and structural chemistry of cyclopentadienylruthenium(II) complexes is well documented,[1—3] information regarding their redox parameters is considerably sparse.[4—6] Still more sparse is information about their electronic spectral data.[7,8]

Electronic spectral studies particularly MLCT transition provide a direct measure of highest occupied metal d orbital energies in a complex in relative terms, and hence also tell about their redox potentials. Several such studies on $[Ru^{II}(bpy)_2]$ system have already been carried out[9—12] but their counterpart in cyclopentadienylruthenium chemistry are rare.

As we are interested in the synthesis and study of electronic effects, of sulfur donor ligands on $[Ru^{II}Cp(PPh_3)_2]$ moiety, we have already reported mono- and binuclear cyclopentadienylruthenium(II) complexes with maleonitrile dithiolate, *N*-cyanodithiocarbimate and their dithioether analogues.[13,14] In continuation to those earlier works we report here mono- and dinuclear ruthenium complexes of cyanodithioformate with $[Ru^{II}CpL_2]$ (L=PPh_3, $AsPh_3$, $SbPn_3$, $(dppe)_{1/2}$, $(dppm)_{1/2}$).

Experimental

All of the chemicals and solvents were of either AR or GR grade and were used without further purification. The synthetic manipulations were carried out under nitrogen atmosphere for which commercially available nitrogen was used after deoxygenation. Analyses, physical and electrochemical measurements were carried out as described elsewhere.[13]

The compounds $NaS_2CCN \cdot 3dmf$,[15] $RuCp(PPh_3)_2Cl$,[16] its triphenylarsine,[17] stibine,[18] bis-1,2-(diphenylphosphino)ethane (dppe),[19] and bis(diphenylphosphino)methane (dppm)[19] analogues; were synthesized by literature methods.

Preparation of $[CpL_2Ru\{SC(S)CN\}]$ (L=PPh_3, $AsPh_3$, $SbPh_3$, $(dppe)_{1/2}$, $(dppm)_{1/2}$). A 0.6—0.8 g (ca. 1 mmol) sample of $[CpL_2\ RuCl]$ and 4.0 g (ca. 10 mmol) of $NaS_2CCN \cdot 3dmf$[20] were combined in 100 mL of methanol. The mixture was stirred under N_2 for 1 h, after which a red colored precipitate was formed. The precipitate was collected by vacuum filtration, washed repeatedly with methanol followed by diethylether and dried in air. The solid thus obtained was dissolved in CH_2Cl_2, filtered and to the filtrate added excess of petroleum ether to induce precipitation. Solid was collected by filtration washed with petroleum ether and dried at reduced pressure over $CaCl_2$. Yield: 0.48—0.8 g (ca. 80%).

Preparation of $[Cp(EPh_3)\overline{Ru(SC(S})CN]$ (E=P, As, Sb). A 0.4—0.5 g (ca. 0.5 mmol) sample of $[Cp(EPh_3)_2Ru\{SC(S)CN\}]$ in 60 mL of benzene was refluxed for 1 h and solvent was removed by evaporation. The residue was then dissolved in CH_2Cl_2 and added excess of petroleum ether to precipitate the golden yellow product. It was filtered, washed with petroleum ether and dried at reduced pressure over $CaCl_2$. Yield (0.2—0.25 g) (ca. 75%).

Reaction of $[Cp(EPh_3)_2Ru\{SC(S)CN\}]$ with $[Cp(EPh_3)_2RuCl]$ (E=P, As, Sb). A 0.3 mmol sample of $[Cp(EPh_3)_2Ru\{SC(S)CN\}]$ was stirred with one equivalent of $[Cp(EPh_3)_2RuCl]$ at room temperature in 30 mL methanol for 2—5 h upon which a blue purple solution resulted. From this the complex was precipitated by adding excess of solid NH_4PF_6. Compound thus obtained was a mixture of two compounds.

Separation of the compounds was achieved by passing through 2×60 cm column containing activated neutral alumina using 1 : 5 acetonitrile–benzene mixture as eluent. The two fractions of the major band; first purple and second blue are collected seperately. Compounds were obtained from their respective fraction by removing the solvent at low pressure and reprecipitating the residue from CH_2Cl_2/pet. ether. Yield purple complex, $[Cp(EPh_3)_2Ru\{SC(S)CN\}Ru(EPh_3)_2Cp](PF_6)$, ca. 30—50%; blue complex $[Cp(EPh_3)_2Ru\{SC(CN)S\}Ru(EPh_3)_2Cp](PF_6)$ ca. 5—20%.

Reaction of $[CP(L\text{-}L)Ru\{SC(S)CN\}]$ with $[Cp(L\text{-}L)RuCl]$ (L-L=dppe, dppm). A 0.2 g (ca. 0.3 mmol) sample of $[Cp(L\text{-}L)Ru\{SC(S)CN\}]$ and 1.8 g (ca. 0 3 mmol) $[Cp(L\text{-}L)RuCl]$ in 40 mL of methanol was refluxed for 1 h under N_2. From the resulting blue pruple solution compound is precipitated by adding excess of solid NH_4PF_6. The solid thus obtained is a mixture of two/three compounds which were separated by passing through neutral alumina column with 1 : 3 acetonitrile benzene mixture as eluent. Solid compounds were obtained by removing the solvent at low pressure and recrystallizing residues from CH_2Cl_2/pet. ether.

In case of dppe complex band one contained two fractions the first fraction, purple compound [Cp(dppe)Ru{SC(S)-

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$\mathrm{CN\}Ru(dppe)Cp]\,(PF_6)}$ (Yield: ca. 20%) and the second fraction of blue compound $\mathrm{[Cp(dppe)Ru\{SC(CN)S\}Ru(dppe)Cp](PF_6)}$ (Yield: ca. 20%); whereas the second band consisted of only single green compound $\mathrm{[\{Cp(dppe)Ru\}_2(S_2CCN)](PF_6)_2}$ (Yield: ca. 10%).

In case of dppm complex two bands were obtained the first major blue band $\mathrm{[Cp(dppm)Ru\{SC(CN)S\}Ru(dppm)Cp](PF_6)}$ (Yield: ca. 30%); and second small green band $\mathrm{[\{Cp(dppm)Ru\}_2(S_2CCN)](PF_6)_2}$ (Yield: ca. 10%).

Preparation of $\mathbf{(Cp(EPh_3)Ru\{SC(S)CN\}Ru(EPh_3)Cp](PF_6)_2}$ (E=P, As, Sb). A 0.21—0.25 g (0.4 mmol) sample of $\mathrm{[Cp(EPh_3)Ru\{SC(S)CN\}]}$ and 0.29—0.36 g (0.4 mmol, 1 equiv) of $\mathrm{[Cp(EPh_3)_2RuCl]}$ in 50 mL of methanol was refluxed for 1.5 h. To the resulting orange solution added excess of solid $\mathrm{NH_4PF_6}$ to precipitate out the cation. It was reprecipitated from $\mathrm{CH_2Cl_2}$/pet. ether and purified by passing through activated neutral alumina column as described above. Yield: 0.4—0.5 g (75%).

Results and Discussion

Cyanodithioformate (cdf) complexes of ruthenium prepared are characterized by (1) the method of preparation and their further reactions, (2) physical data (color, mp, and conductance) and satisfactory elemental analyses (Table 1), (3) IR, and ^{1}H NMR spectra of representative complexes (Table 2), (4) visible spectra and cyclic voltammetric parameters of representative complexes (Table 3), (5) ESR spectra. Following five types of cdf ($\mathrm{S_2CCN}$) coordination modes have been observed.

All of the synthetic manipulations were carried out in

Table 1. Physical and Microanalytical Data

	Complex	Mp	Analyses [Found (Calculated)]/%				Λ_M [a)]
		%	C	H	N	S	$\Omega^{-1}\,\mathrm{cm^2\,mol^{-1}}$
1	$\mathrm{[RuCp(PPh_3)_2\{SC(S)CN\}]}$	152	65.2 (65.2)	4.5 (4.4)	1.8 (1.8)	8.1 (8.1)	4
2	$\mathrm{[RuCp(AsPh_3)_2\{SC(S)CN\}]}$	150	58.6 (58.6)	3.8 (4.0)	1.5 (1.6)	7.3 (7.3)	6
3	$\mathrm{[RuCp(SbPh_3)_2\{SC(S)CN\}]}$	149	53.2 (53.0)	3.8 (3.6)	1.5 (1.4)	6.4 (6.6)	2
4	$\mathrm{[RuCp(dppe)\{SC(S)CN\}]}$	175	59.3 (59.5)	4.4 (4.4)	2.0 (2.1)	9.5 (9.6)	3
5	$\mathrm{[RuCp(dppm)\{SC(S)CN\}]}$	173	59.0 (58.9)	4.2 (4.1)	2.1 (2.2)	9.7 (9.8)	2
6	$\mathrm{Cp(PPh_3)Ru(SC(S)CN)}$	175	56.5 (56.6)	3.7 (3.8)	2.6 (2.6)	12.2 (12.1)	4
7	$\mathrm{Cp(AsPh_3)Ru(SC(S)CN)}$	175	52.1 (52.3)	3.6 (3.5)	2.5 (2.4)	11.3 (11.2)	5
8	$\mathrm{Cp(SbPh_3)Ru(SC(S)CN)}$	175	48.3 (48.3)	3.2 (3.2)	2.1 (2.3)	10.3 (10.3)	3
9	$\mathrm{[Cp(PPh_3)_2Ru\{SC(S)CN\}Ru(PPh_3)_2Cp](PF_6)}$	132	61.8 (62.0)	4.3 (4.3)	0.8 (0.9)	3.7 (3.9)	160
10	$\mathrm{[Cp(PPh_3)_2Ru\{SC(S)CN\}Ru(AsPh_3)_2Cp](PF_6)}$	132	58.8 (58.8)	4.2 (4.1)	0.8 (0.8)	3.5 (3.7)	160
11	$\mathrm{[Cp(PPh_3)_2Ru\{SC(S)CN\}Ru(SbPh_3)_2Cp](PF_6)}$	133	55.7 (55.7)	3.9 (3.9)	0.8 (0.8)	3.7 (3.5)	158
12	$\mathrm{[Cp(AsPh_3)_2Ru\{SC(S)CN\}Ru(PPh_3)_2Cp](PF_6)}$	132	58.9 (58.8)	4.3 (4.1)	0.9 (0.8)	3.6 (3.7)	159
13	$\mathrm{[Cp(AsPh_3)_2Ru\{SC(S)CN\}Ru(AsPh_3)_2Cp](PF_6)}$	135	55.9 (55.9)	4.0 (3.9)	0.7 (0.8)	3.6 (3.6)	162
14	$\mathrm{[Cp(AsPh_3)_2Ru\{SC(S)CN\}Ru(SbPh_3)_2Cp](PF_6)}$	133	53.3 (53.2)	3.5 (3.7)	0.7 (0.7)	3.3 (3.4)	159
15	$\mathrm{[Cp(SbPh_3)_2Ru\{SC(S)CN\}Ru(PPh_3)_2Cp](PF_6)}$	133	55.7 (55.7)	3.8 (3.9)	0.8 (0.8)	3.4 (3.5)	158
16	$\mathrm{[Cp(SbPh_3)_2Ru\{SC(S)CN\}Ru(AsPh_3)_2Cp](PF_6)}$	135	53.1 (53.2)	3.6 (3.7)	0.7 (0.7)	3.3 (3.4)	160
17	$\mathrm{[Cp(SbPh_3)_2Ru\{SC(S)CN\}Ru(SbPh_3)_2Cp](PF_6)}$	134	50.7 (50.7)	3.4 (3.5)	0.7 (0.7)	3.1 (3.2)	163
18	$\mathrm{[Cp(dppe)Ru\{SC(S)CN\}Ru(dppe)Cp](PF_6)}$	155	55.9 (55.9)	4.2 (4.2)	1.1 (1.0)	4.6 (4.7)	157
19	$\mathrm{[Cp(PPh_3)_2Ru\{SC(CN)S\}Ru(PPh_3)_2Cp](PF_6)}$	132	61.5 (62.0)	4.3 (4.3)	0.8 (0.9)	3.9 (3.9)	142
20	$\mathrm{[Cp(PPh_3)_2Ru\{SC(CN)S\}Ru(AsPh_3)_2Cp](PF_6)}$	132	58.6 (58.8)	4.0 (4.1)	0.8 (0.8)	3.8 (3.7)	144
21	$\mathrm{[Cp(PPh_3)_2Ru\{SC(CN)S\}Ru(SbPh_3)_2Cp](PF_6)}$	133	55.5 (55.7)	3.8 (3.9)	0.7 (0.8)	3.5 (3.5)	140
22	$\mathrm{[Cp(AsPh_3)_2Ru\{SC(CN)S\}Ru(AsPh_3)_2Cp](PF_6)}$	134	55.7 (55.9)	3.7 (3.9)	0.7 (0.8)	3.5 (3.6)	143
23	$\mathrm{[Cp(dppe)Ru\{SC(CN)S\}Ru(dppe)Cp](PF_6)}$	155	55.6 (55.9)	4.1 (4.2)	1.0 (1.0)	4.8 (4.7)	133
24	$\mathrm{[Cp(dppm)Ru\{SC(CN)S\}Ru(dppm)Cp](PF_6)}$	158	55.2 (55.2)	3.9 (4.0)	1.0 (1.0)	4.9 (4.8)	148
25	$\mathrm{[Cp(PPh_3)Ru\{SC(S)CN\}Ru(PPh_3)_2Cp](PF_6)}$	186	58.1 (58.0)	4.1 (4.0)	1.1 (1.0)	4.9 (4.7)	139
26	$\mathrm{[Cp(PPh_3)Ru\{SC(S)CN\}Ru(AsPh_3)_2Cp](PF_6)}$	186	54.4 (54.5)	3.6 (3.8)	1.0 (1.0)	4.5 (4.4)	142
27	$\mathrm{[Cp(PPh_3)Ru\{SC(S)CN\}Ru(SbPh_3)_2Cp](PF_6)}$	186	51.2 (51.2)	3.5 (3.6)	0.9 (0.9)	4.3 (4.1)	140
28	$\mathrm{[Cp(AsPh_3)Ru\{SC(S)CN\}Ru(PPh_3)_2Cp](PF_6)}$	186	56.2 (56.2)	3.9 (3.9)	1.0 (1.0)	4.7 (4.5)	140
29	$\mathrm{[Cp(AsPh_3)Ru\{SC(S)CN\}Ru(AsPh_3)_2Cp](PF_6)}$	187	53.0 (52.9)	3.7 (3.7)	1.0 (0.9)	4.1 (4.3)	140
30	$\mathrm{[Cp(AsPh_3)Ru\{SC(S)CN\}Ru(SbPh_3)_2Cp](PF_6)}$	187	49.8 (49.8)	3.2 (3.5)	0.9 (0.9)	4.1 (4.0)	142
31	$\mathrm{[Cp(SbPh_3)Ru\{SC(S)CN\}Ru(PPh_3)_2Cp](PF_6)}$	186	54.6 (54.4)	3.7 (3.8)	0.9 (1.0)	4.5 (4.4)	139
32	$\mathrm{[Cp(SbPh_3)Ru\{SC(S)CN\}Ru(AsPh_3)_2Cp](PF_6)}$	187	51.5 (51.3)	3.7 (3.6)	0.9 (0.9)	4.1 (4.2)	138
33	$\mathrm{[Cp(SbPh_3)Ru\{SC(S)CN\}Ru(SbPh_3)_2Cp](PF_6)}$	188	48.6 (48.4)	3.4 (3.4)	0.9 (0.9)	4.0 (3.9)	139
34	$\mathrm{[Cp(dppe)Ru\{SC(CN)S\}Ru(dppe)Cp](PF_6)_2}$	196	50.3 (50.5)	3.8 (3.8)	0.9 (0.9)	4.1 (4.2)	260
35	$\mathrm{[Cp(dppm)Ru\{SC(CN)S\}Ru(dppm)Cp](PF_6)_2}$	196	50.0 (49.9)	3.9 (3.6)	0.9 (0.9)	4.1 (4.3)	272

a) Measured for 1×10^{-4} M acetone solution at room temperature (1 M=1 mol dm^{-3}). Color: 1—5, Red; 6—8 Golden Yellow; 9—18 Purple; 19—24 Blue; 25—33 Orange-Red; 34, 35 Green.

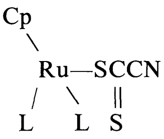
Table 2. IR and NMR Spectral Data of Some Selected Complexes

Complex	IR $\bar{\nu}$/cm^{-1}			^{1}H NMR δ/ppm (area)	
	CN	$\mathrm{C{-}C}\begin{smallmatrix}\mathrm{S}\\ \mathrm{S}\end{smallmatrix}$		Cp-H	Ar-H
$[\mathrm{RuCp(PPh_3)_2\{SC(S)CN\}}]$	2203 s	1055 s(sh),	1000 s	4.85(5H)	6.7—7.7(30H)
$[\mathrm{RuCp(dppe)\{SC(S)CN\}}]$	2200 s	1065 vs,	1010 s	4.90(5H) 2.0—3.0; broad; 4H; $\mathrm{CH_2}$	6.7—7.8(20H)
$[\mathrm{Cp(PPh_3)Ru\{SC(S)CN\}}]$	2200 s	1000 s		4.92(5H)	6.7—7.7(15H)
$[\mathrm{Cp(PPh_3)_2Ru\{SC(S)CN\}Ru(PPh_3)_2Cp](PF_6)}$	2200 w	1050 vw,	1000 s	4.86(5H-SRu) 4.32(5H-NRu)	6.7—7.7(60H)
$[\mathrm{Cp(PPh_3)_2Ru\{SC(CN)S\}Ru(PPh_3)_2Cp](PF_6)}$	2080 vw	1000 vs		4.50(10H)	6.7—7.7(60H)
$[\mathrm{Cp(dppe)Ru\{SC(S)CN\}Ru(dppe)Cp](PF_6)}$	2200	1065 s(sh),	1000 s	4.86(5H) 4.66(5H) 2.0—3.0; broad; 4H; $\mathrm{CH_2}$	6.8—8.0(40H)
$[\mathrm{Cp(dppe)Ru\{SC(CN)S\}Ru(dppe)Cp](PF_6)}$	2200	1000 s		4.50(10H) 2.0—3.0; 4H; $\mathrm{CH_2}$	6.8—8.0(40H)
$[\mathrm{Cp(dppe)Ru\{SC(CN)S\}Ru(dppe)Cp](PF_6)_2}$	2100	$\underline{\text{1380 vs}}$,	1000 s	5.00(10H) 2.0—3.0; broad; 4H; $\mathrm{CH_2}$	6.8—8.0(40H)
$[\mathrm{Cp(PPh_3)_2Ru\{SC(S)CN\}Ru(PPh_3)_2Cp](PF_6)}$	2185	1003 s		4.81(5H,SRu) 4.41(5H,NRu)	6.7—7.7(45H)
$[\mathrm{Cp(dppm)Ru\{SC(S)CN\}}]$	2190	1055 vs,	1000 s	4.95(5H) 2.0—3.0; broad; 2H; $\mathrm{CH_2}$	6.7—7.8(20H)
$[\mathrm{Cp(dppm)Ru\{SC(CN)S\}Ru(dppm)Cp](PF_6)}$	2200	1000 vs		4.45(10H) 2.0—3.0; broad; 2H; $\mathrm{CH_2}$	6.7—7.8(40H)
$[\mathrm{Cp(dppm)Ru\{SC(CN)S\}Ru(dppm)Cp](PF_6)_2}$	2100	$\underline{\text{1385 vs}}$,	1000 vs	5.25(10H) 2.0—3.0; broad, 2H; $\mathrm{CH_2}$	6.7—7.8(40H)

Table 3. Visible Spectral and Cyclic-Voltammetry Data of Some Selected Complexes

Complex	$\lambda_{\max}$/nm	($\varepsilon_{\max}$/M^{-1} cm^{-1})$^{a)}$	$E^{\mathrm{ox}}_{1/2}$/V$^{b)}$
$[\mathrm{RuCp(PPh_3)_2\{SC(S)CN\}}]$	503(10000)	364(3700)	0.30(rev)
$[\mathrm{Cp(PPh_3)Ru\{SC(S)CN\}}]$	470(1450)	360(sh)	0.78(q.r.)
$[\mathrm{Cp(PPh_3)_2Ru\{SC(S)CN\}Ru(PPh_3)_2Cp](PF_6)}$	530(9700)	376(7600)	0.57(q.r.)
$[\mathrm{Cp(PPh_3)_2Ru\{SC(CN)S\}Ru(PPh_3)_2Cp](PF_6)}$	620(12000)	380(4400)	−0.20(rev) 0.31(q.r.)
$[\mathrm{Cp(PPh_3)_2Ru\{SC(S)CN\}Ru(PPh_3)_2Cp](PF_6)}$	510(3600)	378(6900)	—
$[\mathrm{Cp(dppe)Ru\{SC(S)CN\}Ru(dppe)Cp](PF_6)}$	530(9700)	378(7600)	—
$[\mathrm{Cp(dppe)Ru\{SC(CN)S\}Ru(dppe)Cp](PF_6)}$	620(12000)	382(4500)	−0.22(rev) 0.31(q.r.)
$[\mathrm{Cp(dppe)Ru\{SC(CN)S\}Ru(dppe)Cp](PF_6)_2}$	862(7200)	668(12000) 340(11600)	0.31(i.r.)

a) In acetonitrile. b) Condition: 0.1 M TEAP in acetonitrile at glassy carbon electrode vs. SCE reference electrode.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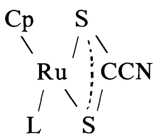
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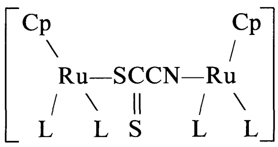
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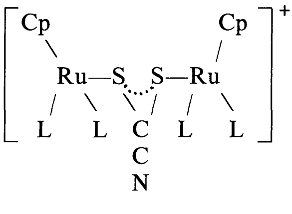
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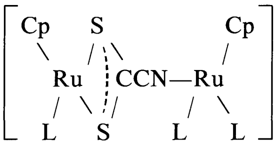

(V)

L=$\mathrm{PPh_3}$, $\mathrm{AsPh_3}$, $\mathrm{SbPh_3}$, $\mathrm{(dppe)^{1/2}}$, $\mathrm{(dppm)^{1/2}}$

methanol at either room temperature, elevated temperature or under refluxing conditions. The conversion of $[Cp(EPh_3)_2Ru\{SC(S)CN\}]$ into $[Cp(EPh_3)Ru\{SC(S)CN\}]$ (E=P, As, Sb) was achieved by refluxing the former in benzene. In the reactions of sodium cyanodithioformate (NaS_2CCN) with $[CpL_2RuCl]$ yielded only the η^1-S coordinated products. Effect seems rather kinetic as because of the low solubility and consequent precipitation of the products from reaction medium (methanol), cdf was prevented to become bidentate chelate; otherwise bidentacy is common with other dithioacid ligands.21—23) In more solubilizing solvents or under drastic conditions $NCCS_2^-$ ion has been found to become bidentate chelate.

$$(EPh_3)\ Ru\text{-}SC(S)CN \xrightarrow[\text{reflux}]{\text{Benzene}} \overline{Ru\text{-}SC(S)}CN + EPh_3 \qquad (1)$$

$[Cp(EPh_3)_2Ru\{SC(S)CN\}]$ undergoes above reaction only in benzene but not in methanol even after prolonged refluxion, probably because the former serves as better solvating agent for reactant-product complexes and the departing ligand, all three.

The dimerizations were achieved by reacting the mono cyanodithioformate precursor complexes with one molar equivalent of corresponding chloro or solvated precursors. Mononuclear bidentate chelate cdf, (Type II) complexes gave smooth reactions leading to desired dinuclear complexes. The reactions of Type I cdf complexes lead to two/three products as a consequence of availablity of two nucleophilic coordination sites viz. S and N atoms and also due to partial oxidation of the products leading to mixed valence species.

Table 4. Percentage Yield of Formation for Type III and Type IV Dinuclear Complexes $[(RuCpL_2)_2\ (S_2CCN)]^+$

Ligand	Type III	Type IV
PPh_3	35	18
$AsPh_3$	45	10
$SbPh_3$	50	5
$(dppe)_{1/2}$[a]	20	20
$(dppm)_{1/2}$[a]	—	30

[a] Product contained one more green compound with yield ca. 10%.

In all these metallation reactions Ru^{II} ion being a soft acid prefers the nucleophilic attack through soft base S than N; but the steric factor has opposit effect. As the cone angle of the tertiaryaryl group-five-donor ligands increases on descending the periodic table from P to As and to Sb, the effect is distinctly manifested in the formation ratio (Table 4) of the two complexes with Type III and Type IV linkages in the reaction (2) below,

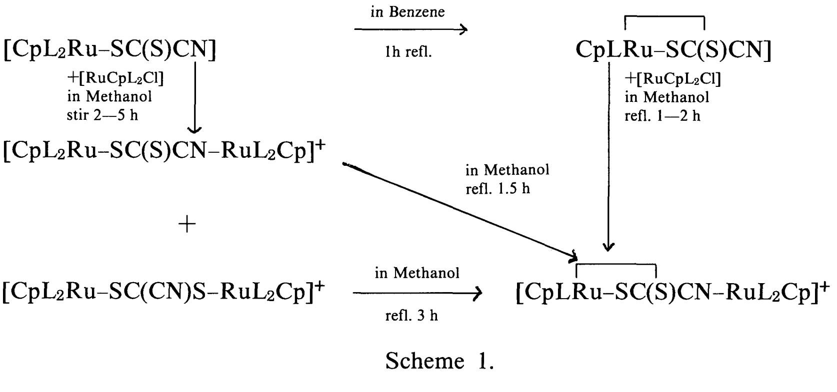
$$[RuCpL_2\{SC(S)CN\}] + [RuCpL_2Cl] \longrightarrow$$
$$\underset{\text{purple (Type III)}}{[CpL_2Ru\{SC(S)CN\}RuL_2Cp]^+} + \underset{\text{blue (Type IV)}}{[CpL_2Ru\{SC(CN)S\}RuL_2Cp]^+} \qquad (2)$$

With $L=PPh_3$ the amount of blue complex formed, which results due to the attack by the second S atom of mono-cdf complex, Type I on the second ruthenium moiety, was nearly half of that of purple complex, which results due to the nucleophilic attack by the N atom, on the second ruthenium moiety. But with $L=SbPh_3$ the purple dinuclear complex is formed almost exclusively; (amount of blue complex formed was even less than 10% of that of pruple complex). Furthermore on going to shorter cone angles (less crowding) in L_2=dppe, than in PPh_3 complex the formation of blue dinuclear complex predominates and with still shorter cone angle in L_2=dppm only blue dinuclear complex is formed exclusively.

In case of dppe, dppm ligands, reaction (2) upon refluxing in methanol yielded one more green compounds besides the red and blue ones. Based on their physico-chemical (IR, ^1H NMR, ESR spectra, and cyclic voltammetry) and microanalytical data we propose it to be mixed valence analogue of blue complexes; $[CpL_2Ru\{SC(CN)S\}RuL_2Cp]^{2+}$. 17 electron Iron(III) organometallic compounds possessing crowded coordination sphere24) are already known.

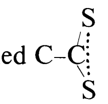
The η^1-S coordinated complexes undergo transformation into η^2S,S′ coordinated bidentate chelate complexes according to Scheme 1.

IR Spectra. The infrared data for representative complexes are listed in Table 2. Literature reported medium/strong intensity bands of Na cdf·3dmf are 2185, 1115, 1105, 1043, and 1021 cm^{-1}.25) As certain of these bands are obscured by other spectator ligand bands in these complexes; bands listed are only those

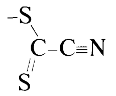


Scheme 1.

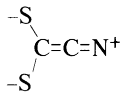
distinct bands other than that present in precursor complexes [$\mathrm{CpL_2RuCl}$].

IR bands observed in the region between 2000—2200 $\mathrm{cm^{-1}}$ are assigned to ν(CN) and those observed between 1000—1400 $\mathrm{cm^{-1}}$ in conformity with spectral assignments for xanthates, dithiocarbamates and dithioacids are assigned  $\mathrm{C{-}C\genfrac{}{}{0pt}{}{S}{S}}$ group vibrations.[23,26—30] Type I cdf complexes possess two ν(C–S) bands because binding with metal ion renders two carbon sulfur bonds unequal. However in the (η^2-S,S′)cdf, Type II complexes possess only one band due to $\nu_{as}(\mathrm{CS_2})$.

All of the cdf bands shift upon coordination depending upon (a) the extent of contribution from resonance structure VI or VII and (b) the extent of Ru→cdf π back bonding.



VI



VII

In the η^1-S coordinated complexes of the Type I the ν(CN) band is shifted to 20 $\mathrm{cm^{-1}}$ towards higher wavenumber side. But this is still lower when compared to the ν(CN) band in corresponding methylcyanodithioformate (2220 $\mathrm{cm^{-1}}$).[25] This could be understood if we consider that ruthenium(II) moiety having π basic capacity places electron density in the π* orbital of cdf consequently reducing the ν(CN) stretching frequency; which is not possible with $\mathrm{CH_3}$cdf. Upon attachment of second ruthenium(II) moiety to N end of cdf in the complexes of the Type III ν(CN) does not show any significant shift because the force field strengthening (consequent upon N coordination) is balanced by synergistic weakening due to Ru(II)–NC π back bonding. Similarly η^2-S,S′ bidentate chelation in the complexes of Type II and its dinuclear derivatives μ(η^2-S,S′; η^1-N), Type V do not cause any significant shift in the ν(CN) frequency compared to that in η^1-S cdf complex.

In μ(η^2-S; η^1-S′) cdf binuclear Type IV complexes ν(CN) band appeared at considerably lower frequency. It seems that the binding of the two ruthenium moieties through sulfurs require increased contribution from resonance structure VII. This requirement in one electron oxidized μ(η^1-S; η^1-S) cdf complexes it is still greater and hence there is significant lowering of ν(CN) (ca. 100 $\mathrm{cm^{-1}}$) and appearance of a new band at ca. 1385 $\mathrm{cm^{-1}}$ due to $\mathrm{C{\overset{...}{-}}CS_2}$ bond acquiring partial double bond character.

NMR Spectra. ^{1}H NMR spectra have been much helpful in the characterization of these complexes. These spectra can be considered in two parts. One the complex pattern of singnals in the range δ=6.3—10.0 arising due to aromatic protons of phenyl and/or bipyridine rings, and the second the cyclopentadienyl proton signals which appear between δ=4—5. These Cp proton signals have marked variation in their position depending upon coordination of the ligand with CpRu through its S or N sites. Relevant data are listed in Table 2. The S coordinated CpRu proton signals are much downfield shifted compared to the N coordinated one. The relative ordering of shifts for Cp proton signals could be given by following series (δ values).

$$\mathrm{CpRu^{2.5}{-}SCS{-}Ru^{2.5}Cp > Cp\overline{Ru{-}SCS} > CpRu{-}SC(S) > CpRu{-}SCS{-}RuCp > CpRu{-}NC{-}}$$

Which reflects the increase in the electron density on CpRu in reverse order.

Visible Spectra. Visible spectral data of some selected complexes is listed in Table 3. The complex [$\mathrm{RuCp(PPh_3)_2\{SC(S)CN\}}$] shows two absorption maxima at 503 ($\varepsilon_{\max}$ 10000) and 374 nm ($\varepsilon_{\max}$ 3700). From comparison of intensity and position of the band at 374 nm with that in ruthenocene[31] it is assigned to π(Cp)→dπ(Ru) ligand to metal charge transfer transition. The intense lowest energy band at 503 nm undergoes bathochromic shift upon dimerization, whereupon a second [$\mathrm{Ru^{II}Cp(PPh_3)_2}$] moiety is binded through N or the second S of the (η^1-S) cdf mononuclear complex. It is a normal trend for such MLCT transitions that involve vacant orbitals of bridging ligand[10,14,32] and thus the band is tentatively assigned to dπ(Ru)→π*(cdf) MLCT transition. Magnitude of red shift depends upon the site of coordination of second $\mathrm{Ru^{II}}$ moiety in (η^1-S) cdf complex (Fig. 1), is nearly four times greater in [$\mathrm{Cp(PPh_3)_2Ru\{SC(CN)S\}Ru(PPh_3)_2Cp}$]($\mathrm{PF_6}$) 3750 $\mathrm{cm^{-1}}$ than in [{$\mathrm{Cp(PPh_3)_2Ru\{SC(S)CN\}Ru(PPh_3)_2Cp}$]($\mathrm{PF_6}$) 1010 $\mathrm{cm^{-1}}$. This could be rationalized from the fact that sulfur p orbitals participating in the ligand π system are more diffuse and thus are more favorable for

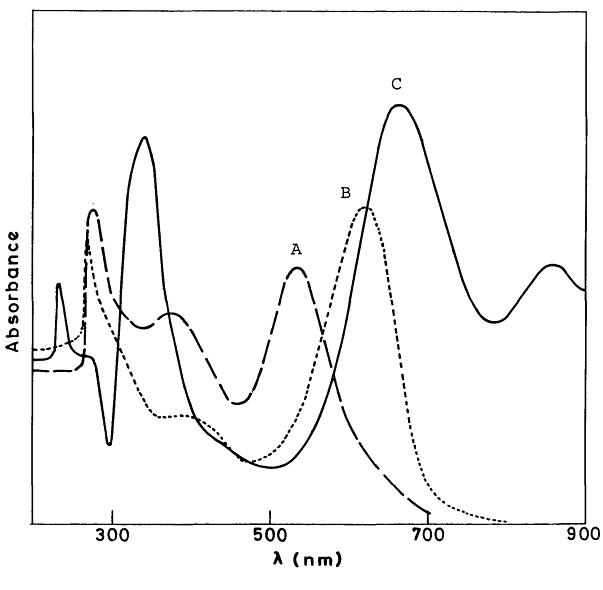


Fig. 1. Electronic spectra for (A) [Cp(dppe)Ru-SC(S)CN-Ru(dppe)Cp]($\mathrm{PF_6}$), (B) [Cp(dppe)Ru-SC(CN)S-Ru(dppe)Cp]($\mathrm{PF_6}$), and (C) [Cp(dppe)Ru-SC(CN)S-Ru(dppe)Cp]($\mathrm{PF_6}$)$_2$ in dimethylformamide.

interaction with ruthenium dπ orbitals than the nitrogen pπ orbitals. The weak d-d and n→π* (ligand centered) transitions are seemingly obscured by the strong charges transfer bands.

The MLCT band upon cdf becoming bidentate chelate in [Cp(PPh$_3$)Ru{SC(S)CN}], shifts towards higher energy (λ_{max} 470 nm) with a markedly reduced intensity (ε_{max} 1450). Two possible reasons could be given for this shift (a) in (η^2-S,S′) cdf coordination there is increased contribution from gem dithiloate resonance form $^+N=C=CS_2{}^{2-}$ (VII) and thus the energy of acceptor orbital is raised and (b) ruthenium dπ orbital getting stablilized because of stronger π back bonding interaction of the cdf involving its vacant π* MO. The M–PR$_3$ π interaction being weaker than metal-dithiolate interation,[33] the latter view (b) seems more plausible. This is further vindicated from the fact that upon binding of second [Cp(PPh$_3$)$_2$Ru^{II}] moiety at nitrile nitrogen of [Cp(PPh$_3$)Ru{SC(S)CN}] in Type V binuclear cdf complex greater perturbation ($\Delta\nu$=1670 cm^{-1}) of MLCT transition energy is introduced compared to that of [Cp(PPh$_3$)$_2$Ru{SC(S)CN}] in Type III dinuclear cdf complex ($\Delta\nu$=1010 cm^{-1}).

One electron oxidized bimetallic cyanodithioformate complex [Cp(dppe)Ru–SC(CN)S–Ru(dppe)Cp]$^{2+}$ shows three intense absorptions at λ_{max} 862 (ε_{max} 7200), 668 (12000), and 340 nm (11600) (Fig. 1). Since neither of these intense bands are present in ligand (cdf) or in [Cp(dppe)Ru^{II}] moiety they could tentatively be assigned to intervalance charge transfer (IT) dπ(Ru^{II}) →dπ(Ru^{III}), LMCT pπ(S)→dπ(Ru$^{III/II}$) and MLCT dπ(Ru$^{III/II}$)→π* (–CSS–) respectively.

Cyclic Voltammetry. Oxidative cyclic voltammetry of some selected compounds was investigated in acetonitrile and the results obtained are recorded in Table 3. Most of the oxidation processes appear to be of irreversible type some typical CV scans are shown in Fig. 2.

(η^1-S) cdf complex [RuCp(PPh$_3$)$_2${SC(S)CN}] exhibits an anodic oxidation peak at 0.30 V vs. SCE which shifts significantly towards more positive potential side, (difficult to oxidize) at 0.78 V upon displacement of one PPh$_3$ by the second S of the cdf in [Cp(PPh$_3$)Ru(SC(S)CN)]. Considering the MO associated with the electron transfer process having more metal dπ character, i.e. Ru(II)/Ru(III) process, this reflects marked stabilization of the HOMO, which is in agreement with the electronic spectral data, (vide supra). The ease of oxidation is considerably reduced upon its dimerization in μ(η^1-S; η^1-N) cdf complex [Cp(PPh$_3$)$_2$Ru–SC(S)CN–Ru(PPh$_3$)$_2$Cp]$^+$, Type III which possesses corresponding oxidation anodic peak at 0.57 V vs. SCE. Since association of second [Cp(PPh$_3$)$_2$Ru^{II}] moiety at the N end of the ligand in Type I monomer should have a destabilizing effect on the dπ(Ru) (HOMO) of the latter; hence the shift of the anodic peak towards more positive potential side in this complex seems to be due to the positive charge on the whole species and also due to the second sphere solvation effect.

The μ(η^1-S; η^1-S′) cdf binuclear complex, [Cp(PPh$_3$)$_2$Ru–SC(CN)S–Ru(PPh$_3$)$_2$Cp]$^+$, Type IV exhibits two oxidations, first reversible $E_{1/2}$ −0.20 V and second anodic peak at 0.31 V vs. SCE. Compared to corresponding Type I mononuclear and Type III dinuclear complexes the first oxidation peak position is significantly lower. There are two mutually opposing factors that decide the position of the oxidation peaks, (a) increased positive charge on the species, (b) competition between the two Ru^{II} dπ orbitals for the same ligand π MO for π back bonding and their consequent destabilization. It seems that due to the predominance of factor (b) the peak position results as given above. Also there is an additional possibility of this new low potential

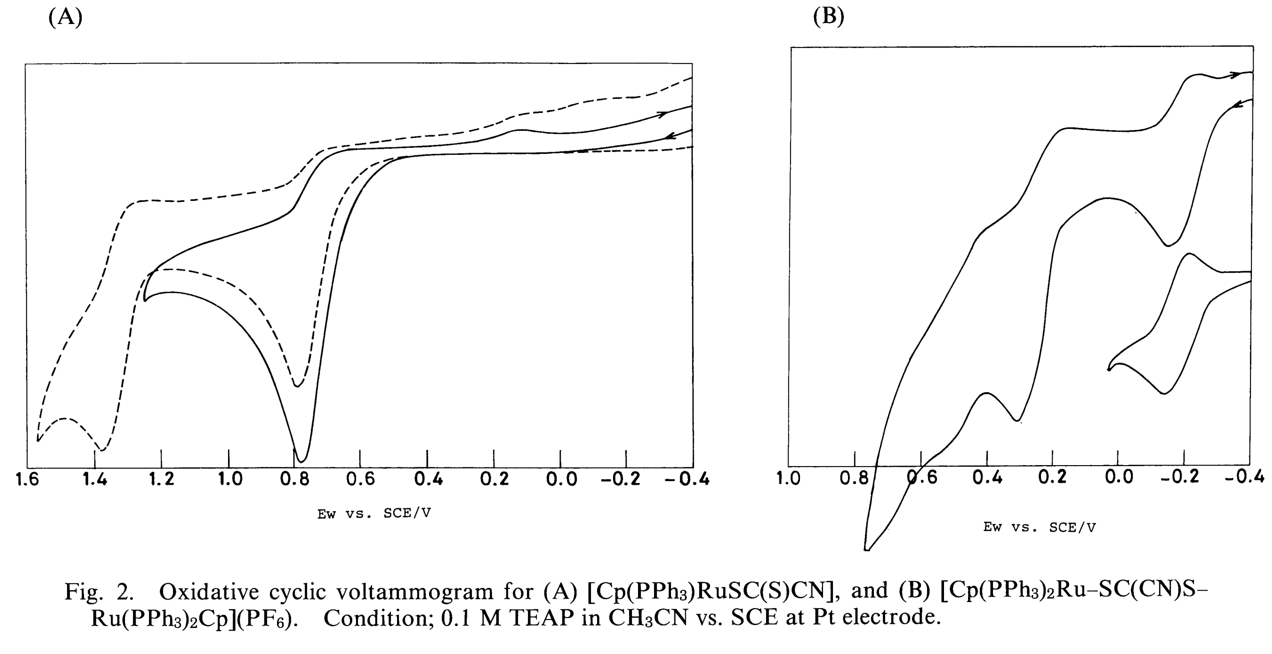


Fig. 2. Oxidative cyclic voltammogram for (A) [Cp(PPh$_3$)RuSC(S)CN], and (B) [Cp(PPh$_3$)$_2$Ru–SC(CN)S–Ru(PPh$_3$)$_2$Cp](PF$_6$). Condition; 0.1 M TEAP in CH$_3$CN vs. SCE at Pt electrode.

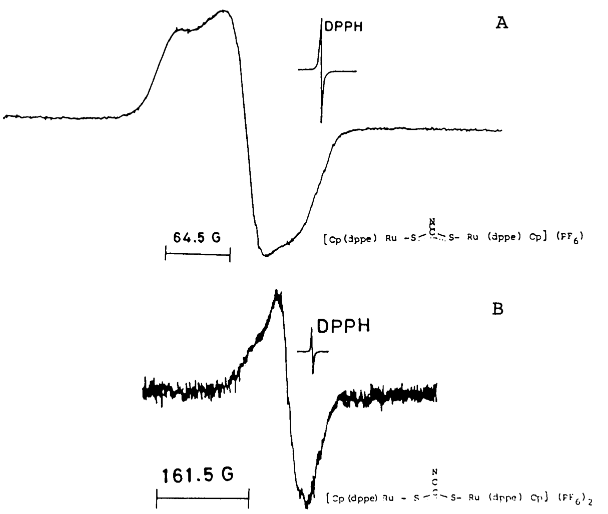


Fig. 3. ESR Spectra for (A) [Cp(dppe)Ru–SC(CN)S–Ru(dppe)Cp](PF$_6$), and (B) [CP(dppe)Ru–SC(CN)S–Ru(dppe)Cp](PF$_6$)$_2$ in solid state at room temperature.

oxidizable center arising from Ru–Ru axis as the two ruthenium centers lie at a close distance.

The green dinuclear complex [Cp(dppe)Ru–SC(CN)S–Ru(dppe)Cp]$^{2+}$ shows only one peak at 0.31 V vs. SCE which supports that it is one electron oxidized analogue of the blue complex.

ESR Spectra. One electron oxidized dinuclear $\mu(\eta^1$–S; η^1–S′) cdf complex [Cp(dppe)Ru–SC(CN)S–Ru(dppe)Cp]$^{2+}$ gives ESR signal (g=2.0649) at room temperature (Fig. 3). The corresponding dinuclear blue complex [Cp(dppe)Ru–SC(CN)S–Ru(dppe)Cp]$^+$ although in the mixture does not give any ESR signal but after passing through alumina column has given a strong triplet singal (g=2.0489) possibly due to the formation of dithioformate radical.[34]

$$[\mathrm{Cp(dppe)Ru{-}SC(CN)S{-}Ru(dppe)Cp}]^+ \xrightarrow[\mathrm{CH_3CN+Benzene}]{\mathrm{Eluent}} 2[\mathrm{Cp(dppe)Ru(NCCH_3)}]^+ + \mathrm{NCCS_2}$$

Contamination with NCCS$_2\cdot$ radical broadens Cp proton NMR resonance signal which otherwise was sharp in the mixture.

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References

1) S. G. Davies, J. P. McNally, and A. J. Smallridge, *Adv. Organomet. Chem.*, **30**, 1 (1990).

2) E. A. Seddon and K. R. Seddon, "The Chemistry of Ruthenium, (Monograph 19)," Elsevier Science Publishers, Amsterdam (1984), p. 797.

3) M. A. Bennet, M. I. Bruce, and T. W. Matheson, in "Comprehensive Organometallic Chemistry," ed by G. Wilkinson, Pergamon Press, Oxford (1982), Vol. 4 , p. 691.

4) N. G. Connelly, *Chem. Soc. Rev.*, **18**, 153 (1989).

5) N. G. Connelly and W. E. Geiger, *Adv. Organomet. Chem.*, **23**, 1 (1984).

6) H. B. Abrahansen, M. C. Palagotto, C. L. Reichel, and M. S. Wrighton, *J. Am. Chem. Soc.*, **101**, 4123 (1979).

7) K. E. Howard, T. B. Rauchfus, and A. L. Reingold, *J. Am. Chem. Soc.*, **108**, 297 (1986).

8) Y. Wakatsuki, H. Yamazaki, and C. Cheng, *J. Organomet. Chem.*, **372**, 437 (1989).

9) M. A. Greaney, C. L. Coyle, M. A. Harmar, A. Jordan, and E. I. Stiefel, *Inorg. Chem.*, **28**, 912 (1989).

10) Y. Fuchs, S. Lofters, T. Dieter, W. Shi, R. Morgan, T. C. Streckas, H. D. Gafney, and A. D. Baker, *J. Am. Chem. Soc.*, **109**, 2691 (1987).

11) J. A. Conner, T. J. Meyer, and B. P. Sullivan, *Inorg. Chem.*, **18**, 1388 (1979).

12) B. P. Sullivan, D. J. Salmon, and T. J. Meyer, *Inorg. Chem.*, **17**, 3334 (1978).

13) R. Prasad and U. C. Agarwala, *Polyhedron*, **11**, 1117 (1992).

14) R. Prasad and U. C. Agarwala, *Aust. J. Chem.*, communicated.

15) M. A. Davison and R. H. Holm, *Inorg. Synth.*, **10**, 8 (1967).

16) M. I. Bruce and N. J. Windsor, *Aust. J. Chem.*, **30**, 1601 (1977).

17) K. M. Rao, L. Mishra, and U. C. Agarwala, *Polyhedron*, **5**, 1491 (1986).

18) K. M. Rao, L. Mishra, and U. C. Agarwala, *Indian J. Chem., Sect. A*, **26**, 755 (1987).

19) M. I. Bruce, M. G. Humphrey, A. G. Swincer, and R. C. Wallis, *Aust. J. Chem.*, **37**, 1747 (1984).

20) NaS$_2$CCN·3dmf was freshly prepared which was used after filtration and washing with butanol-1 in the wet condition as such without further attempt to dry.

21) L. B. Reventos and A. G. Alonso, *J. Organomet. Chem.*, **309**, 179 (1986).

22) T. Wilczewski, M. Bochenska, and J. F. Biernat, *J. Organomet. Chem.*, **215**, 87 (1981).

23) D. Coucouvans, *Prog. Inorg. Chem.*, **11**, 233 (1970) and **26**, 301 (1979).

24) M. C. Baird, *Chem. Rev.*, **88**, 1217 (1988).

25) V. M. Drager and G. Gattow, *Z. Anorg. Allg. Chem.*, **387**, 281 (1972).

26) J. M. Burke and J. P. Fackler, Jr., *Inorg. Chem.*, **11**, 3000 (1972).

27) M. Maltese, *J. Chem. Soc., Dalton Trans.*, **1972**, 2664.

28) C. Furlani and M. L. Luciani, *Inorg. Chem.*, **7**, 1586 (1968).

29) F. Bonati and R. Ugo, *J. Organomet. Chem.*, **10**, 257 (1967).

30) R. Kellner, G. S. Nikolov, and N. Trendafilova, *Inorg. Chim. Acta*, **84**, 233 (1984).

31) Y. S. Sohn, D. N. Hendrickson, and H. B. Gray, *J. Am. Chem. Soc.*, **93**, 3603 (1971).

32) R. Prasad and U. C. Agarwala, *Inorg. Chim. Acta*, communicated.

33) R. Eisenberg, *Prog. Inorg. Chem.*, **12**, 294 (1970).

34) N. S. Garifyanov, B. M. Kozyrev, and E. I. Semenova, *Dokl. Akad. Nauk SSSR*, **170**, 1324 (1966).