Organometallic Macrocycle Chemistry. 4.† Synthesis and Reactions of $[RuX(CS)(PPh_3)([9]aneS_3)]ClO_4$ (X = H, Cl, SCN, SC_6H_4Me-4; [9]$aneS_3$ = 1,4,7-Trithiacyclononane)

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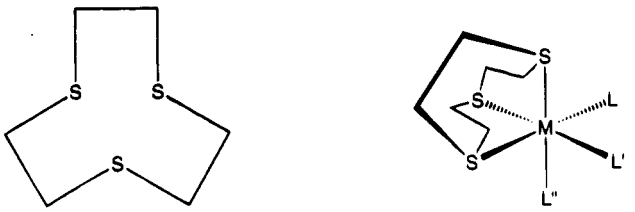
The reactions of $[RuCl_2(OH_2)(CS)(PPh_3)_2]$ and $[RuHCl(CS)(PPh_3)_3]$ with 1,4,7-trithiacyclononane ([9]$aneS_3$) provide the thiacrown complexes $[RuX(CS)(PPh_3)([9]aneS_3)]^+$ (X = Cl, H; isolated as ClO_4^- salts). $[RuCl(CS)(PPh_3)([9]aneS_3)]ClO_4$ reacts with potassium 4-toluenethiolate and potassium thiocyanate to provide the salts $[RuX(CS)(PPh_3)([9]aneS_3)]ClO_4$ (X = SC_6H_4Me-4, SCN) but with sodium azide to provide $[RuCl(NCS)(PPh_3)([9]aneS_3)]$.

Introduction

The thiacrown macrocycle 1,4,7-trithiacyclononane ([9]$aneS_3$) (Chart 1) has been observed to coordinate to divalent ruthenium in a number of complexes[1-4] consistent with its perceived primary role as a σ-donor ligand. The reactivity of such complexes is as yet ill-defined, and there is a comparative ignorance of the ligand reactions which coordination spheres bearing sulfur crown ligands might support. Of particular interest to us are organometallic complexes which might serve as models for catalytic processes[1,5,6] since it has been suggested that sulfur crowns might combine the properties of phosphine ligands with the robust nature of macrocyclic ligands.[2] The possibility that thiacrowns might also serve as π-acids under favorable circumstances has been suggested;[7] however, evidence in support of this remains scant, although this is considered an important, though controvertible, component of the bonding of phosphines to transition metal centers.

The thiocarbonyl ligand has served as an important model for the metal-mediated reactions of carbon monoxide and derived "C_1" ligands[8] due to its greater propensity to react via migratory insertion, nucleophilic attack (α to the metal), and electrophilic attack (β to the metal). We wish to report here full preparative details for a range of thiocarbonyl complexes of ruthenium(II) which are ligated by the facially tridentate macrocycle [9]$aneS_3$ for which parallels with the ubiquitous cyclopentadienyl ligand have already begun to emerge. Some aspects of this work have formed the basis of a preliminary report.[6]

Chart 1. Coordination of 1,4,7-Trithiacyclononane ([9]$aneS_3$)



Experimental Section

General Procedures. All manipulations were carried out under aerobic ambient conditions using solvents as obtained commercially. None of the new compounds showed marked air-sensitivity during workup or subsequent spectroscopic characterization. The ligand [9]$aneS_3$ was obtained commercially (Aldrich) and the precursor complexes $[RuCl_2(OH_2)(CS)(PPh_3)_2]$[9] and $[RuHCl(CS)(PPh_3)_3]$[10] were prepared according to published procedures. In general all salts were prepared as both the ClO_4 and PF_6 derivatives due to the different spectroscopic windows (IR) offered by these counteranions. $^{31}P\{^1H\}$ NMR spectra were recorded on a Jeol JNM-EX270 NMR spectrometer and calibrated against external H_3PO_4 (^{31}P). Infrared spectra were recorded using a Perkin-Elmer 1720-X FT-IR spectrometer. FAB-mass spectrometry was carried out on either a Kratos MS80 or Autospec Q instrument using 3-nitrobenzyl alcohol as a matrix.

For infrared spectroscopic purposes, both the hexafluorophosphate and perchlorate derivatives of salts were prepared. ***Caution:*** Under the conditions and *reaction scales* indicated no problems were encountered in manipulating perchlorate salts; however, these should be treated as potentially explosive and shock-sensitive. A safety shield is therefore strongly recommended. Alternatively the tetrafluoroborate derivatives may be prepared which offer the same spectroscopic window but are less easily crystallized and therefore obtained in slightly reduced yield.

Synthesis of $[RuCl(CS)(PPh_3)([9]aneS_3)]PF_6$. A suspension of $[RuCl_2(OH_2)(CS)(PPh_3)_2]$ (0.20 g, 0.26 mmol) and [9]$aneS_3$ (0.043 g, 0.24 mmol) in dichloromethane (20 cm^3) was treated with a solution of $[NH_4][PF_6]$ (0.16 g, 0.95 mmol, excess) in water (4 cm^3) and ethanol (15 cm^3). If necessary, further ethanol was added to maintain homogeneity. The mixture was heated under reflux for 1 h and then allowed to cool to room temperature whereupon yellow crystals formed. The suspension was concentrated under reduced pressure (rotary

† For part 3 of this series, see ref 1.

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evaporator) to ca. 10 cm^3. The yellow precipitate was isolated by filtration, washed with water (5 cm^3), ethanol (2 × 5 cm^3), and diethyl ether (20 cm^3), and dried in vacuo. Yield: 0.12 g (70%). The crude product, thus isolated, was of sufficient purity for subsequent spectroscopic and synthetic purposes; however, an analytically pure sample was obtained by recrystallization from a a mixture of dichloromethane and ethanol. Anal. Found: C, 38.7; H, 3.2. Calcd for $C_{25}H_{27}ClF_6P_2RuS_4$: C, 39.1; H, 3.5. The perchlorate salt (***Caution:*** see above) was prepared, in a similar manner and yield for spectroscopic purposes, by replacing $[NH_4][PF_6]$ with $Li[ClO_4]$. IR (Nujol): 1298 vs ($\nu_{C=S}$), 937 w, 906 m, 835 w, 827 m, 813 w cm^{-1} ([9]aneS$_3$). NMR ($CDCl_3$, 25 °C): ^1H, δ 2.34, 2.46, 3.02, 3.17, 3.32, 3.49 [m × 6, 12 H, [9]aneS$_3$], 7.2−7.9 [m, 15 H, C_6H_5] ppm; $^{31}P\{^1H\}$ 55.0 ppm. FAB-MS: m/z = 622, $[M + 1]^+$.

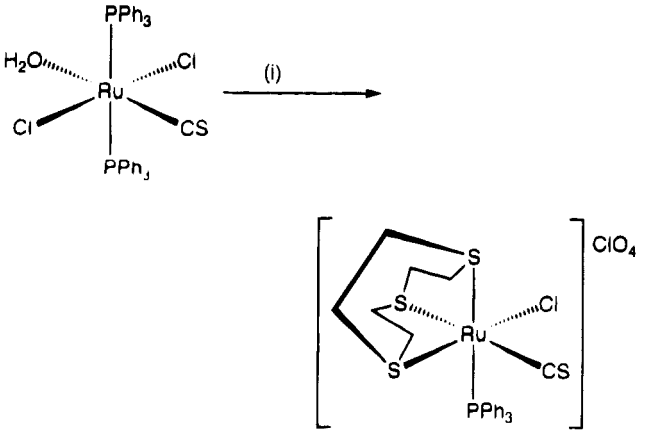
Synthesis of [RuH(CS)(PPh$_3$)([9]aneS$_3$)]PF$_6$. A solution of [RuHCl(CS)(PPh$_3$)$_3$] (0.10 g, 0.10 mmol) and [9]aneS$_3$ (0.023 g, 0.12 mmol) in dichloromethane (20 cm^3) was treated with a solution of $[NH_4][PF_6]$ (0.075 g, 0.46 mmol, excess) in water (4 cm^3) and ethanol (20 cm^3). The solution was stirred at room temperature for 3 h and then concentrated (rotary evaporator) to ca. 10 cm^3. The yellow precipitate was isolated by filtration and washed with water (5 cm^3), cold ethanol (2 × 5 cm^3), and diethyl ether (20 cm^3). The crude product was crystallized from a mixture of dichloromethane and ethanol. Yield: 0.057 g (72%). Anal. Found: C, 41.2; H, 3.9. Calcd for $C_{25}H_{28}F_6P_2RuS_4$: C, 40.9; H, 3.9. IR (Nujol): 1913 (ν_{RuH}) 1281 vs ($\nu_{C=S}$), 933 w, 903 m, 821 w cm^{-1} ([9]aneS$_3$). NMR ($CDCl_3$, 25 °C): ^1H, δ −7.64 [d, 1 H, RuH, J(PH) = 21.2 Hz], 1.75, 2.03, 2.61, 2.81, 3.04, 3.30 [m × 6, 12 H, [9]aneS$_3$], 7.47, 7.61 [m × 2, 15 H, C_6H_5] ppm; $^{31}P\{^1H\}$ 48.4 ppm. FAB-MS: m/z = 588, $[M - 1]^+$.

Synthesis of [Ru(SC$_6$H$_4$Me-4)(CS)(PPh$_3$)([9]aneS$_3$)]PF$_6$. A mixture of [RuCl(CS)(PPh$_3$)([9]aneS$_3$)]PF$_6$ (0.20 g, 0.24 mmol), 4-thiocresol (0.10 g, 0.81 mmol, excess), and triethylamine (0.10 g, 1.0 mmol, excess) in ethanol (10 cm^3) was stirred for 2 h and then filtered. The filtrate was treated with petroleum ether (bp 40−60 °C, 30 cm^3) to precipitate the crude orange product which was isolated by filtration and washed with water (10 cm^3), cold ethanol (5 cm^3), and diethyl ether (20 cm^3). The crude product was then recrystallized from a mixture of dichloromethane and ethanol. Yield: 0.14 g (63%). Anal. Found: C, 44.4; H, 4.2. Calcd for $C_{32}H_{34}F_6P_2RuS_5$: C, 44.9; H, 4.0. IR (Nujol): 1278 vs ($\nu_{C=S}$), 1168, 940 w, 906 m, 823 w ([9]aneS$_3$), 808 m ($\delta_{C_6H_4}$) cm^{-1}. NMR ($CDCl_3$, 25 °C): ^1H, δ 1.63, 1.98, 2.62, 2.89, 3.05−3.18 [m × 5 12 H, [9]aneS$_3$], 2.28 [s, 3 H, CH_3], 6.94, 7.43 [(**AB**)$_2$, 4 H, SC_6H_4, J(**AB**) = 7.9 Hz], 7.47, 7.71 [m × 2, 15 H, C_6H_5] ppm; $^{31}P\{^1H\}$ 32.0 ppm.

Synthesis of [Ru(SCN)(CS)(PPh$_3$)([9]aneS$_3$)]PF$_6$. A mixture of [RuCl(CS)(PPh$_3$)([9]aneS$_3$)]PF$_6$ (0.10 g, 0.12 mmol) and $[NH_4]SCN$ (0.023 g, 0.42 mmol, excess) was suspended in ethanol (10 cm^3), and the suspension was stirred for 18 h. The solvent was removed under reduced pressure. The residue was triturated ultrasonically with water (10 cm^3) and isolated by filtration. The crude product was then crystallized from a mixture of dichloromethane and ethanol to yield a microcrystalline yellow powder which was dried in vacuo. Yield: 0.090 g (93%). Anal. Found: C, 39.9; H, 4.1. Calcd for $C_{26}H_{27}F_6NP_2RuS_5$: C, 39.5; H, 3.4. IR (Nujol): 2059 m, 2047 m (ν_{NCS}), 1305 vs ($\nu_{C=S}$), 937 w, 907 m, 841 w, 831 w ([9]aneS$_3$) cm^{-1}. NMR ($CDCl_3$, 25 °C): ^1H, δ 2.43, 3.08, 3.24, 3.48 [m × 4 12 H, [9]aneS$_3$], 7.43, 7.73 [m × 2, 15 H, C_6H_5] ppm; $^{31}P\{^1H\}$ 32.1 ppm.

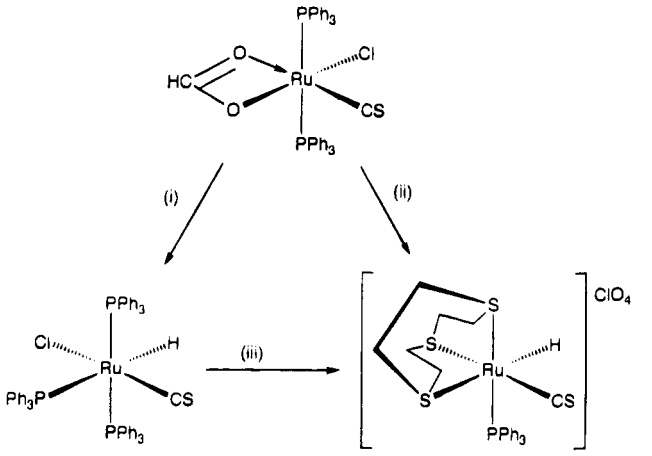
Reaction of [RuCl(CS)(PPh$_3$)([9]aneS$_3$)]PF$_6$ with NaN$_3$. ***Caution:*** Sodium azide and azido derivatives in general are potentially explosive and shock sensitive. We experienced no difficulties with the following scale of reaction; however, precautions (safety shield) should be taken. A mixture of [RuCl(CS)(PPh$_3$)([9]aneS$_3$)]PF$_6$ (0.100 g, 0.12 mmol) and sodium azide (0.020 g, 0.31 mmol, excess—dispensed with a ***plastic*** spatula) was suspended in ethanol (5 cm^3) and stirred for 3 h. The crude product was isolated by filtration and washed with water (5 cm^3), ethanol (2 × 5 cm^3), and petroleum ether (bp 40−60 °C, 10 cm^3). The crude product formulated as [Ru(NCS)Cl(PPh$_3$)([9]aneS$_3$)] was recrystallized from a mixture of dichloromethane and ethanol but was not obtained in analytically pure form. IR (Nujol): 2099 m, 2048 m (ν_{SCN}), 905 ([9]aneS$_3$), 842 (δ_{NCS}), 829 m, 800 w ([9]aneS$_3$) cm^{-1}. NMR ($CDCl_3$, 25 °C): $^{31}P\{^1H\}$ 36.2 ppm.

Scheme 1. Synthesis of [RuCl(CS)(PPh$_3$)([9]aneS$_3$)]ClO$_4$[a]



[a] (i) [9]aneS$_3$, $LiClO_4$, −PPh_3, −LiCl, −H_2O.

Scheme 2. Synthesis of [RuH(CS)(PPh$_3$)([9]aneS$_3$)]ClO$_4$[a]



[a] (i) Δ, PPh_3, −CO_2; (ii) [9]aneS$_3$, $LiClO_4$, −PPh_3, −CO_2, −LiCl; (III) [9]aneS$_3$, $LiClO_4$, −PPh_3, −LiCl.

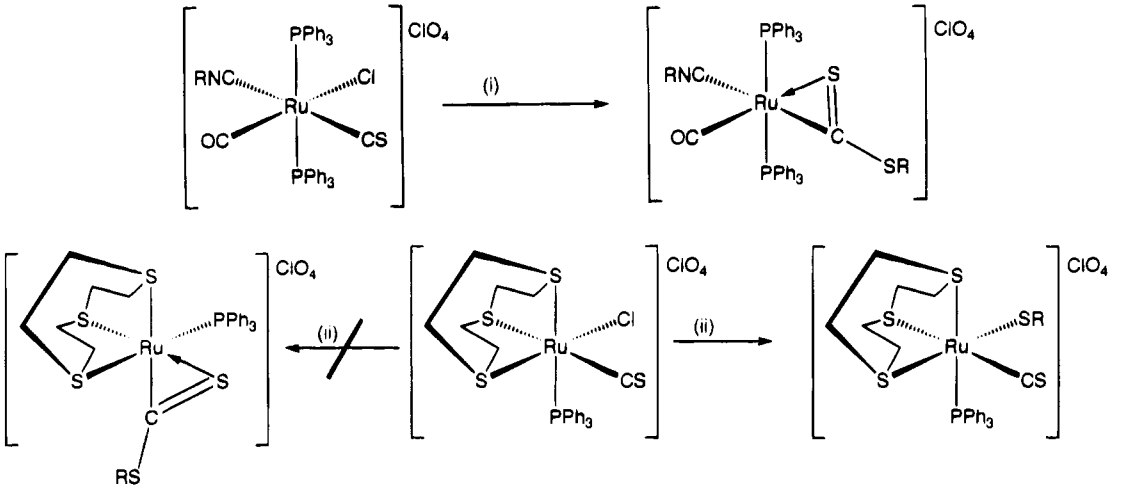
Results and Discussion

The complex $[RuCl_2(OH_2)(CS)(PPh_3)_2]$,[9] prepared from $[RuCl_2(PPh_3)_3]$ and moist carbon disulfide, features both labile chloride and water ligands and appeared therefore to be a suitable starting complex for the introduction of sulfur crown macrocycles into a ruthenium(II) coordination sphere. Indeed reaction of this complex with [9]aneS$_3$ in refluxing ethanol or tetrahydrofuran in the presence of lithium perchlorate or ammonium hexafluorophosphate leads to the smooth and high-yielding formation of a salt formulated as [RuCl(CS)(PPh$_3$)([9]aneS$_3$)]ClO$_4$ (Scheme 1) on the basis of spectroscopic data: The appearance of an isotope cluster centerd at m/z = 823 ($[M + 1]^+$) in the FAB-mass spectrum attests to the gross composition of the cationic complex while the complexity of the patterns associated with the ^1H NMR signals attributable to the macrocyclic ligand is consistent with its coordination to a chiral $RuL_1L_2L_3$ unit.[5] The infrared absorption observed at 1298 cm^{-1} indicates that the thiocarbonyl ligand has retained its integrity in the reaction and is coordinated to an electron-poor ruthenium(II) center. This is in contrast to our recent observation that similar treatment of σ-vinyl thiocarbonyl complexes leads to subsequent reactions involving the thiocarbonyl ligand.[5]

In situations where a hydride ligand coordinates *cis* to a thiocarbonyl ligand, there is a strong tendency for migratory insertion reactions to ensue leading to thioformyl complexes.[11] We anticipated that any attempt to prepare the hydrido analogue

(11) Collins, T. J.; Roper, W. R. *J. Organomet. Chem.* **1978**, *159*, 73.

Scheme 3. Reaction of Ruthenium(II) Thiocarbonyls with Toluenethiolate[a]



[a] R = C_6H_4Me-4: (i) KSR, −KCl; (ii) HSR, Et_3N, −[Et_3NH]Cl.

of $[RuCl(CS)(PPh_3)([9]aneS_3)]ClO_4$ would also lead to the formation of a thioformyl derivative, i.e., $[Ru(\eta^2\text{-}SCH)(PPh_3)([9]aneS_3)]ClO_4$ by analogy with the formation of the complexes $[Ru(\eta^2\text{-}SCR)(PPh_3)([9]aneS_3)]ClO_4$.[5] This appears, however, not to be the case: The hydrido−thiocarbonyl complex $[RuHCl(CS)(PPh_3)_3]$[10] reacts with $[9]aneS_3$ in a mixture of dichloromethane, water, and ethanol to provide the complex $[RuH(CS)(PPh_3)([9]aneS_3)]^+$ isolated as either the perchlorate or hexafluorophosphate salt. The tris(phosphine) precursor complex is prepared by thermal decarboxylation of the bidentate formato complex $[Ru(\kappa^2\text{-}O_2CH)Cl(CS)(PPh_3)_2]$,[10] and this reaction is sufficiently clean that the $[9]aneS_3$ derivative may be prepared directly in a one-pot procedure from this complex, although yields are somewhat reduced (40−50%) making the two-step procedure preferable (Scheme 2). Despite the constraint that the hydride and thiocarbonyl ligands are mutually cis-coordinated due to the facial ligation requirements of the macrocycle, there is no evidence for the operation of even reversible thioformyl formation. The ^1H NMR spectrum of $[RuH(CS)(PPh_3)([9]aneS_3)]ClO_4$ features a doublet at δ −7.63 ppm showing a typical cis coupling to the phosphorus atom of one phosphine ligand [J(HP) = 21.2 Hz]. Once again the complexity of the ^1H NMR resonances due to the macrocyclic ligand indicate coordination to a chiral ruthenium center, and this is confirmed by the appearance of an isotope cluster centerd at m/z = 588 in the FAB-mass spectrum corresponding to $[M - 1]^+$ for the complex. The infrared activity due to the thiocarbonyl ligand (1281 cm^{-1}) while indicating a comparatively electron-poor metal center, comes to lower energy than that observed for the chloro derivative. A weak absorption at 1913 cm^{-1} is tentatively assigned to ν_{RuH} although no confirmation by deuteration studies was attempted.

Reactions of $[RuCl(CS)(PPh_3)([9]aneS_3)]ClO_4$. On the basis of a moderately high value for ν_{CS} in the infrared spectrum, it could be expected that the thiocarbonyl ligand in this complex would be prone to nucleophilic attack.[8] Treatment of $[RuCl(CS)(PPh_3)([9]aneS_3)]ClO_4$ with an ethanolic solution of potassium 4-toluenethiolate, or a mixture of 4-thiocresol and triethylamine, leads however, to the isolation of a salt formulated as $[Ru(SC_6H_4Me\text{-}4)(CS)(PPh_3)([9]aneS_3)]ClO_4$ in which the integrity of the thiocarbonyl group is retained. This is somewhat surprising in view of the related reaction of $[RuCl(CO)(CNR)(CS)(PPh_3)_2]ClO_4$ (R = C_6H_4Me-4) with toluenethiolate, in which an η^2-dithioester ligand is produced in the complex $[Ru(\eta^2\text{-}SCSR)(CO)(CNR)(PPh_3)_2]^+$ (Scheme 3).[12] The mutual cis coordination of thiolate and thiocarbonyl ligands is unusual, especially since we have established the stability of the related thiocinnamoyl complexes $[Ru(\eta^2\text{-}SCCR{=}CHPh)(PPh_3)([9]aneS_3)]ClO_4$ (R = H, Ph) which result from the addition of $[9]aneS_3$ to $[Ru(CR{=}CHPh)Cl(CS)(PPh_3)_2]$.[5]

Given the unexpected failure of the thiolate anion to attack the α-carbon of the thicarbonyl ligand, we have investigated other nucleophiles which have been shown previously to attack thiocarbonyl ligands. Busetto has reported the reactions of the electrophilic thiocarbonyl complex cation $[Fe(CS)(CO)_2(\eta\text{-}C_5H_5)]^+$ with thiocyanate and azide[13] sources to provide the neutral complexes $[Fe(CN)(CO)_2(\eta\text{-}C_5H_5)]$ and $[Fe(NCS)(CO)_2(\eta\text{-}C_5H_5)]$, respectively (Scheme 4). The complexes $[RuCl(CS)(PPh_3)([9]aneS_3)]^+$ and $[Fe(CS)(CO)_2(\eta\text{-}C_5H_5)]^+$ are formally isoelectronic [18 valence electron, d^6-ML_6, cationic] although the presence of two strong π-acidic carbonyl coligands in the latter presumably further activates the thiocarbonyl ligand toward nucleophilic attack. $[RuCl(CS)(PPh_3)([9]aneS_3)]PF_6$ reacts smoothly with potassium thiocyanate; however, rather than the thiocarbonyl being the site of attack, "simple" chloride/thiocyanate metathesis occurs to provide $[Ru(SCN)(CS)(PPh_3)([9]aneS_3)]PF_6$. The precursor complex is coordinatively saturated and would be unlikely to react via an associative process. Initial dissociation of the chloride ligand to provide the dicationic complex $[Ru(CS)(PPh_3)([9]aneS_3)]^{2+}$ which is subsequently attacked by SCN^- is possible, especially given the comparatively polar solvent mixture employed; however, an alternative route involving dissociation of one sulfur donor to provide the required vacant coordination site should perhaps also be considered as an alternative which avoids excessive charge buildup.

The reaction of $[RuCl(CS)(PPh_3)([9]aneS_3)]PF_6$ with azide is not as clean, and the major product of this reaction has not been obtained as an analytically pure compound. Spectroscopic data for the compound, however, suggest that it is the neutral thiocyanato-*N* derivative $[RuCl(NCS)(PPh_3)([9]aneS_3)]$ arising from direct attack at the thiocarbonyl ligand followed by a pseudo-Curtius rearrangement to eliminate dinitrogen. This process would be completely analogous to the result obtained for $[Fe(CS)(CO)_2(\eta\text{-}C_5H_5)]^+$.

Concluding Remarks. While debate continues as to the importance of π-acid effects for sulfur donor ligands and

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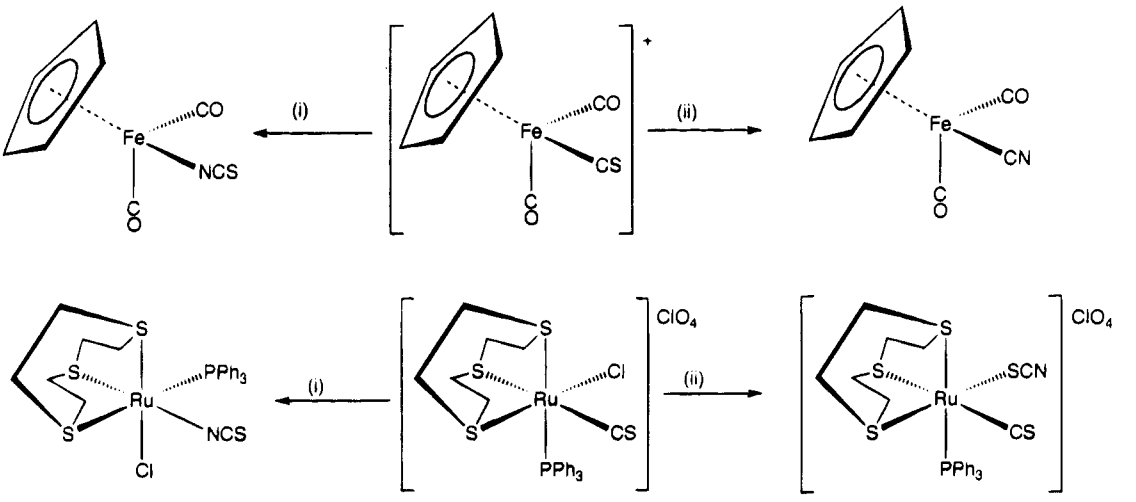
(13) Busetto, L.; Graziani, M.; Belluco, U. *Inorg. Chem.* **1971**, *10*, 78.

Scheme 4. Reactions of d^6-$[L_5MCS]^+$ Complexes with Nucleophiles[a]



[a] (i) N_3^-, $-N_2$; (ii) KSCN.

macrocycles, it is clear from the above results that the [Ru(PPh$_3$)([9]aneS$_3$)] fragment does not appear to promote either migratory coupling of hydride and thiocarbonyl ligands or nucleophilic attack at the thiocarbonyl ligand. These are both reaction classes which are recognized as being encouraged by π-acid coligands. The above results are however in contrast to those obtained for the reaction of related σ-vinyl/thiocarbonyl complexes with [9]aneS$_3$, which lead to rapid migratory insertion and formation of thiocinnamoyl complexes.[5] Clearly the effect of sulfur crown coligands on ligand-coupling processes will require further study to assess the suitability of these ligands in catalyst design.

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