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ACTIVATION OF THIOCYANOGEN AND SELENOCYANOGEN BY LOW OXIDATION STATE TRANSITION METAL COMPLEXES

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Summary

Thiocyanogen and selenocyanogen react with $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ to give respectively the complexes $\text{Ru}(\text{CO})_2(\text{PPh}_3)_2(\text{NCS})_2$ and $\text{Ru}(\text{CO})_2(\text{PPh}_3)_2(\text{NCSe})_2$. (M—NCS and M—SCN represent *N*- and *S*-thiocyanato groups, M—NCSe and M—SeCN represent *N*- and *Se*-selenocyanato groups respectively, while M—CNS indicates the bridging coordination mode of thiocyanate.) Only the thiocyanogen reacts with $\text{Ru}_3(\text{CO})_{12}$ giving $[\text{Ru}(\text{CO})_2(\text{CNS})_2]_n$, which dissolves in hot coordinating solvents, such as pyridine, to form $\text{Ru}(\text{CO})_2(\text{py})_2(\text{NCS})_2$. Selenocyanogen is less effective than thiocyanogen in the oxidative addition reactions with rhodium(I) and iridium(I) complexes; in fact selenocyanogen does not react with $\text{Rh}(\text{CO})(\text{PPh}_3)_2\text{Cl}$ while with $\text{Ir}(\text{CO})(\text{PPh}_3)_2\text{Cl}$ the former gives $\text{Ir}(\text{CO})(\text{PPh}_3)_2(\text{SeCN})_2\text{Cl}$ by an equilibrium reaction. The coordination number of the metal and the charge on the complex do not change the bonding mode of the thiocyanate and selenocyanate groups in the iridium(III) complexes; in the $\text{Ir}(\text{PPh}_3)_2\text{ClX}_2$ and $[\text{Ir}(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)_2\text{X}_2]^+$ (X = SCN and SeCN) complexes the pseudohalogens are S- and Se-bonded.

The complexes *trans*- $\text{M}(\text{PPh}_3)_2(\text{SeCN})_2$ (M = Pd, Pt) have been obtained by reacting $\text{M}(\text{PPh}_3)_4$ with selenocyanogen.

Introduction

Oxidative addition reactions of low oxidation state transition metal complexes have shown much variety both in the range of molecules that can be added and in the stereochemical course of the additions [1–3]. These reactions are of interest because of the novel nature of the products which can be obtained and also because of their significance in relationship to homogeneous catalytic reactions [4].

Despite the variety of molecules which have been oxidatively added to low oxidation state transition metal complexes, only a relatively small number of

pseudohalogens have been used in these reactions [5–10]. Thiocyanato and selenocyanato complexes of the transition elements have received considerable attention during recent years because of the ambidentate nature of the ligands [11,12]. Recently, thiocyanogen has been used as a thiocyanation reagent in oxidative addition reactions [7,9,13,14]. In order to determine whether this behaviour is shared by selenocyanogen, we have examined the reaction of this molecule with ruthenium(0), rhodium(I), iridium(I), palladium(0) and platinum(0) complexes. Some analogous reactions of thiocyanogen are also reported.

Experimental

The complexes $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$, $\text{Ir}(\text{CO})(\text{PPh}_3)_2\text{Cl}$, $\text{Ir}(\text{N}_2)(\text{PPh}_3)_2\text{Cl}$, $\text{Rh}(\text{CO})(\text{PPh}_3)_2\text{Cl}$, $\text{Pd}(\text{PPh}_3)_4$ and $\text{Pt}(\text{PPh}_3)_4$ were prepared by methods reported in the literature [15–20] as was $(\text{SCN})_2$ and $(\text{SeCN})_2$ [21,22]. Other chemicals were reagent grade and were used without purification. IR spectra were recorded using a Perkin–Elmer 457 spectrometer. Molecular weights were determined with a Knauer vapour-pressure osmometer. Elemental analyses were carried out by Bernhardt, Mulheim, Germany. All reactions were carried out under an atmosphere of oxygen-free nitrogen. Analytical data and pertinent IR frequencies are reported in Tables 1 and 2, respectively.

Preparation of $\text{Ru}(\text{CO})_2(\text{PPh}_3)_2(\text{NCS})_2$

An excess of a freshly prepared benzene solution of thiocyanogen was added

TABLE 1
ANALYTICAL DATA

Compound	Colour	Analysis found (calcd.) (%)				
		C	H	N	S	Cl
$\text{Ru}(\text{CO})_2(\text{PPh}_3)_2(\text{NCS})_2$	Orange	60.12 (60.22)	3.80 (3.79)	3.50 (3.51)	— (8.04)	— (8.04)
$\text{Ru}(\text{CO})_2(\text{PPh}_3)_2(\text{NCS}_2)_2$	Red	53.85 (53.88)	3.40 (3.39)	3.10 (3.12)	—	—
$[\text{Ru}(\text{CO})_2(\text{CNS})_2]_n$	Yellow	17.64 (17.58)	—	10.31 (10.25)	23.38 (23.47)	—
$\text{Ru}(\text{CO})_2(\text{C}_5\text{H}_5\text{N})_2(\text{NCS})_2$	Yellow	29.47 (29.50)	1.38 (1.37)	15.28 (15.29)	17.35 (17.50)	—
$\text{Ir}(\text{CO})(\text{PPh}_3)_2\text{Cl}(\text{SeCN})_2$	Yellow	48.25 (47.30)	3.00 (3.05)	2.56 (2.83)	—	3.84 (3.58)
$\text{Ir}(\text{PPh}_3)_2(\text{SCN})_2\text{Cl}^a$	Yellow	52.48 (52.56)	3.42 (3.48)	3.18 (3.22)	7.46 (7.38)	4.13 (4.08)
$[\text{Ir}(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)_2(\text{SCN})_2]\text{BPh}_4$	Pale yellow	65.71 (65.77)	4.78 (4.81)	1.92 (1.96)	4.45 (4.50)	—
$[\text{Ir}(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)_2(\text{SeCN})_2]\text{BPh}_4$	Yellow	54.70 (54.77)	3.96 (4.00)	1.61 (1.64)	—	—
$\text{Pd}(\text{PPh}_3)_2(\text{SeCN})_2$	Yellow	54.22 (54.25)	3.57 (3.59)	3.30 (3.33)	—	—
$\text{Pt}(\text{PPh}_3)_2(\text{SeCN})_2$	Pale yellow	49.12 (49.09)	3.23 (3.23)	2.99 (3.01)	—	—

^a Molecular weight in dichloromethane 912 (868).

TABLE 2
PERTINENT IR STRETCHING FREQUENCIES ^a

Compound	$\nu(\text{CO})$	$\nu(\text{CN})$
$\text{Ru}(\text{CO})_2(\text{PPh}_3)_2(\text{NCS})_2$	2065vs 2010vs	2082s
$\text{Ru}(\text{CO})_2(\text{PPh}_3)_2(\text{NCSe})_2$	2068vs 2015vs	2085ms
$[\text{Ru}(\text{CO})_2(\text{NCS})_2]_n$	2080vs 2025vs	2170vs
$\text{Ru}(\text{CO})_2(\text{C}_5\text{H}_5\text{N})_2(\text{NCS})_2$	2070vs 2010vs	2095(sh) s
$\text{Ir}(\text{CO})(\text{PPh}_3)_2\text{Cl}(\text{SeCN})_2$ ^b	2078s	2122m
$\text{Ir}(\text{PPh}_3)_2(\text{SCN})_2\text{Cl}$		2135(sh) 2115ms
$\text{Ir}(\text{PPh}_3)_2(\text{SeCN})_2\text{Cl}$		2130(sh) 2105m
$[\text{Ir}(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)_2(\text{SCN})_2]\text{BPh}_4$		2108s
$[\text{Ir}(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)_2(\text{SeCN})_2]\text{BPh}_4$		2098m
$\text{Pd}(\text{PPh}_3)_2(\text{SeCN})_2$		2120m
$\text{Pt}(\text{PPh}_3)_2(\text{SeCN})_2$		2132m

^a Nujol mull. ^b $\nu(\text{Ir}-\text{Cl})$ 315 cm^{-1} .

to a solution of $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ in the same solvent. The reaction was monitored by IR spectroscopy and was allowed to proceed until the carbonyl absorption due to the starting complex had disappeared completely. The solution was filtered and the solvent evaporated to dryness. Recrystallisation from dichloromethane/hexane gave the product as orange crystals.

Preparation of $\text{Ru}(\text{CO})_2(\text{PPh}_3)_2(\text{NCSe})_2$

This product was prepared by the preceding method and was obtained as red crystals.

Preparation of $[\text{Ru}(\text{CO})_2(\text{CNS})_2]_n$

To a benzene solution of $\text{Ru}_3(\text{CO})_{12}$ was added an excess of a freshly prepared solution of thiocyanogen and the reaction mixture stirred overnight. The yellow-orange precipitate formed was isolated by filtration, washed with dichloromethane and dried in vacuo. The product is insoluble in all the common organic solvents.

Preparation of $\text{Ru}(\text{CO})_2(\text{C}_5\text{H}_5\text{N})_2(\text{NCS})_2$

$[\text{Ru}(\text{CO})_2(\text{CNS})_2]_n$ dissolved readily in boiling pyridine to give a yellow solution. The product, obtained by evaporation of the filtered solution, was washed with ether and dried.

Preparation of $[\text{Ir}(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)_2(\text{SCN})_2]\text{BPh}_4$

To a solution of $[\text{Ir}(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)_2]\text{Cl}$ in deoxygenated benzene was added dropwise a freshly prepared solution of thiocyanogen in deoxygenated benzene. The progress of the reaction was followed by IR spectroscopy. The reaction mixture was filtered and the solvent evaporated to dryness. The yellow-orange crude product was dissolved in methanol, filtered and precipitated by adding a solution of NaBPh_4 in the same solvent.

Preparation of $[\text{Ir}(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)_2(\text{SeCN})_2]\text{BPh}_4$

This yellow compound was prepared by the preceding method.

Preparation of Ir(PPh₃)₂(SCN)₂Cl

Ir(N₂)(PPh₃)₂Cl was dissolved in deoxygenated benzene and a solution of thiocyanogen in the same solvent was added until the nitrogen stretching frequency in the IR spectrum of the starting compound disappeared (about 2 min). The yellow reaction mixture was filtered and after partial evaporation of the solvent, a solid was obtained by addition of ether. The analytically pure product was obtained after several recrystallisations from dichloromethane/ether.

Preparation of Ir(PPh₃)₂(SeCN)₂Cl

This product was prepared in a similar manner to that described in the preceding method, but was not obtained in an analytically pure form.

Preparation of Ir(CO)(PPh₃)₂Cl(SeCN)₂

To a solution of *trans*-Ir(CO)(PPh₃)₂Cl in deoxygenated benzene was added, with stirring, a large excess of a freshly prepared solution of selenocyanogen in deoxygenated benzene. The reaction was carried out until no change was observed in the IR spectrum of the reaction mixture. A small amount of selenocyanogen was then added and the stirring continued for an additional hour. Addition of hexane to the solution gave a yellow solid which was shown to be a mixture of Ir(CO)(PPh₃)₂Cl(SeCN)₂ and *trans*-Ir(CO)(PPh₃)₂Cl. The yellow solid was finally extracted with diethyl ether, however, the resulting product was not pure, owing to the presence of a small quantity of the starting material.

Preparation of trans-Pd(PPh₃)₂(SeCN)₂

Equimolar amounts of Pd(PPh₃)₄ and selenocyanogen in a benzene solution were stirred for 3 h. The reaction mixture was filtered and the resulting yellow solution concentrated at reduced pressure. On addition of hexane a yellow solid precipitated, which was collected by filtration and recrystallised from dichloromethane/hexane.

Preparation of trans-Pt(PPh₃)₂(SeCN)₂

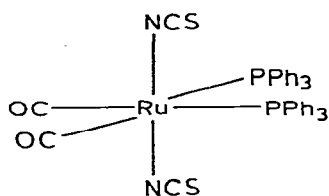
To a benzene solution of Pt(PPh₃)₄ was added an excess of selenocyanogen in the same solvent. The reaction mixture was then stirred for 4 h. During this time a pale yellow solid precipitated from the yellow solution, which was separated by filtration, washed with benzene and dried.

Results and discussion

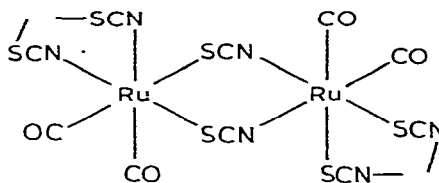
Despite the existence of a wide variety of metal thiocyanate and selenocyanate complexes, only a relatively small number contain ruthenium as the transition metal [23]. We have found the reaction of thiocyanogen with ruthenium(0) compounds Ru(CO)₃(PPh₃)₂ or Ru₃(CO)₁₂ to be a useful method for preparing thiocyanate and selenocyanate complexes.

Thiocyanogen, (SCN)₂, and selenocyanogen, (SeCN)₂, react smoothly, by oxidative addition, with Ru(CO)₃(PPh₃)₂ to give N-bonded dithiocyanate and diselenocyanate complexes Ru(CO)₂(PPh₃)₂(NCS)₂ and Ru(CO)₂(PPh₃)₂(NCSe)₂, respectively. In the IR spectra of these complexes the CN stretching vibrations

appear in the range 2080–2090 cm^{-1} , while CS and CSe stretching bands appear at 838 and 595 cm^{-1} , respectively. The positions of these bands suggest the existence of N-bonded thiocyanate and selenocyanate groups [11,12]. Further, the non-splitting of the CN stretching band is indicative of a *trans* disposition of the thiocyanate and selenocyanate groups in the complexes [24]. The assignments of the bands due to the thiocyanate and selenocyanate groups were made by comparing their IR spectra with that of the analogous chloro-complex. The IR spectra of the complexes exhibit two strong $\nu(\text{CO})$ bands in the 2000–2070 cm^{-1} region indicating also that the two carbonyl groups are in a *cis* arrangement. We assign to the new complexes the structure I (for the thiocyanate complex) which has the carbonyl groups *cis* and the pseudohalogens *trans* to each other.



(I)



(II)

When thiocyanogen was added to a benzene solution of $\text{Ru}_3(\text{CO})_{12}$, carbon monoxide was evolved and a dark yellow precipitate slowly formed. This compound was formulated, on the basis of analytical data, as $\text{Ru}(\text{CO})_2(\text{SCN})_2$ and the structure is now discussed by considering its chemical properties and infrared spectrum. Since the compound is insoluble in the common organic solvents such as benzene, dichloromethane and carbon tetrachloride but dissolves in solvents with strong coordinating ability, such as pyridine, to give adducts with two molecules of ligand, it seems fairly certain that it must be a polymeric product. Thus, the compound clearly resembles $\text{Ru}(\text{CO})_2\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) [25,26], the analogous $\text{Fe}(\text{CO})_2(\text{SCN})_2$ [13] and related complexes [27]. The IR spectrum of the compound shows 3 very strong bands in the region 2000–2200 cm^{-1} . For two CO groups *trans* to each other only a strong or medium-strong band in the $\nu(\text{CO})$ stretching region should be expected, therefore we assign the bands at 2080 and 2020 cm^{-1} to the stretching vibration of two CO groups in a *cis* arrangement and the band at 2170 cm^{-1} to CN stretching in the bridging thiocyanates [11,12]. Polymerisation must occur so that each SCN group forms a bridge between two metal atoms, in order to obtain an octahedral configuration. II represents one of several possible structures for $[\text{Ru}(\text{CO})_2(\text{CNS})_2]_n$.

No reaction was observed at room temperature when $\text{Ru}_3(\text{CO})_{12}$ was treated with a large excess of selenocyanogen.

The oxidative addition reactions of thiocyanogen with the complexes *trans*- $\text{M}(\text{CO})\text{L}_2\text{X}$ ($\text{M} = \text{Rh}, \text{Ir}$; $\text{L} = \text{PPh}_3$; $\text{X} = \text{Cl}, \text{NCO}, \text{NCS}$) have been studied by Burmeister et al. [9] in order to verify the effect of increasing the oxidation state of the metal on the bonding mode adopted by the thiocyanate groups.

The reactions reported here were carried out in order to show whether coordination number of the metal or the charge on the complex affects the bonding

mode of pseudohalogen groups in iridium(III) complexes, and to compare the ability of $(\text{SeCN})_2$ with that of $(\text{SCN})_2$ in oxidative addition to rhodium(I) and iridium(I) complexes.

Selenocyanogen is less effective than thiocyanogen in promoting oxidative addition reactions with rhodium(I) and iridium(I) complexes; selenocyanogen does not react with *trans*-Rh(CO)(PPh₃)₂Cl and in the reaction with *trans*-Ir(CO)(PPh₃)₂Cl an equilibrium is established. Using a large excess of the ligand and a long reaction time, a mixture of starting material and Ir(CO)(PPh₃)₂(SeCN)₂Cl was obtained. The IR spectrum of the new complex shows a $\nu(\text{CO})$ band at 2078 cm⁻¹ and a weak-medium band due to $\nu(\text{CN})$ at 2122 cm⁻¹, which are indicative of a Se-bonded selenocyanate iridium(III) complex.

The coordination number of the metal and the charge on the complex do not change the bonding mode of the thiocyanate and selenocyanate groups in iridium(III) complexes. Thiocyanogen and selenocyanogen promote oxidative addition reactions with [Ir(Ph₂PC₂H₄PPh₂)₂]Cl giving the cationic six-coordinated species [Ir(Ph₂PC₂H₄PPh₂)₂(SCN)₂]⁺ and [Ir(Ph₂PC₂H₄PPh₂)₂(SeCN)₂]⁺ in which pseudohalogen groups are S- and Se-bonded in a *trans* arrangement.

Thiocyanogen reacts with Ir(PPh₃)₂(N₂)Cl giving the five-coordinated iridium(III) complex Ir(PPh₃)₂(SCN)₂Cl; selenocyanogen reacts in like manner but the product was not obtained in an analytically pure form.

Selenocyanogen reacts with Pd(PPh₃)₄ and Pt(PPh₃)₄ giving *trans*-Pd(PPh₃)₂(SeCN)₂ [28] and *trans*-Pt(PPh₃)₂(SeCN)₂. As neutral selenocyanate complexes of platinum(II) can be obtained only with difficulty by metathetical replacements [29], the method reported here is more suitable for the preparation of selenocyanate complexes. The reaction of palladium(0) and platinum(0) triphenylphosphine complexes with thiocyanogen has been previously reported [14].

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