Journal of Organometallic Chemistry, 190 (1980) 353—361

REACTIONS OF THIOCARBAMOYL COMPOUNDS WITH VASKA COMPLEXES: MECHANISM AND STEREOCHEMISTRY

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(Received October 9th, 1979)

Summary

Bis(dimethylthiocarbamoyl)sulfide, $(Me_2NCS)_2S$, reacts with $(Ph_3P)_2MCOCl$ complexes giving ionic species $[Ph_3PM(\eta^2\text{-}CSNMe_2)(S_2CNMe_2)CO]X$ (M = Rh, Ir; X = Cl, PF_6) as kinetic products. On standing in solution, $[Ph_3PRh(\eta^2\text{-}CSNMe_2)(S_2CNMe_2)CO]Cl$ is slowly transformed into the thermodynamic product $Ph_3PRh(\eta^2\text{-}CSNMe_2)(S_2CNMe_2)Cl$. The known reactions of Vaska-type complexes with Me_2NCSCl to give $[trans\text{-}(Ph_3P)_2Ir(\eta^2\text{-}CSNMe_2)COCl]Cl$ and $trans\text{-}(Ph_3P)_2Rh(\eta^2\text{-}CSNMe_2)Cl_2$ probably follow a similar course. $(Ph_3P)_2Ru$-NOCl reacts with $(Me_2NCS)_2S$ and Me_2NCSCl in the same way as $(Ph_3P)_2Ir$-COCl, but reacts with $(Me_2NCS)_2NPh$ to give $[trans\text{-}(Ph_3P)_2Ru(\eta^2\text{-}CSNMe_2)$-NOCl]$PF_6$. The mechanism and stereochemistry of these reactions are discussed. Reactions were monitored by NMR spectroscopy in an attempt to identify intermediate η^1-thiocarboxamido complexes, but no such species could be detected.

Introduction

In metal complexes containing *N,N*-dialkylthiocarboxamido ligands C(S)-NR_2, three different modes of coordination are observed. These are: η^1 (coordination by C), η^2 (coordination by C and S to a single metal), and μ (coordination by C and S bridging two metals). Most mononuclear thiocarboxamido complexes reported have been η^2 complexes; η^1 coordination apparently predominates only in the case of square-planar d^8 species [1—3].

Most η^2-thiocarboxamido complexes have been prepared by one of two routes: displacement of chloride ion from Me_2NCSCl by a metal carbonyl anion, or oxidative addition of a Me_2NCSX species (X = Cl, S_2CNMe_2, N(Ph)CS-

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TABLE 1

MELTING POINT AND ANALYSES

		MP (°C)	Analysis found (calcd.) (%)				
			C	H	N	S	Cl
$[Ph_3PIr(\eta^2\text{-}CSNMe_2)(S_2CNMe_2)CO]PF_6$	(I-PF_6)	258—260	35.9 (35.9)	3.24 (3.26)	3.34 (3.35)	11.5 (11.5)	
$[Ph_3PRu(\eta^2\text{-}CSNMe_2)(S_2CNMe_2)NO]PF_6$	(II-PF_6)	267—270	38.6 (38.6)	3.68 (3.61)	5.52 (5.63)	14.7 (12.9)	
$[Ph_3PRh(\eta^2\text{-}CSNMe_2)(S_2CNMe_2)CO]PF_6$	(IV-PF_6)	245—250	41.4 (40.2)	3.85 (3.64)	3.81 (3.75)	13.2 (12.9)	
$[trans\text{-}(Ph_3P)_2Ir(\eta^2\text{-}CSNMe_2)COCl]PF_6$	(V-PF_6)	260—262	47.6 (47.4)	3.60 (3.58)	1.43 (1.38)	3.28 (3.16)	3.42, 3.56 [a] (3.50)
$[trans\text{-}(Ph_3P)_2Ru(\eta^2\text{-}CSNMe_2)NOCl]PF_6$	(VII-PF_6)	246—249	51.1 (50.7)	4.02 (3.92)	3.11 (3.03)	4.15 (3.47)	4.36 (3.84)

[a] For the sample prepared fronm $(Ph_3P)_2IrCOBr$; other analyses on the sample prepared from $(Ph_3P)_2IrCOCl$.

TABLE 2

INFRARED [a] AND NMR [c] SPECTRA

		νCO (νNO)	$\nu(C{=}N)$	Other characteristic peaks [b]	$\tau(NMe_2)$ [d]
$[Ph_3PIr(\eta^2\text{-}CSNMe_2)(S_2CNMe_2)CO]PF_6$	(I-PF_6)	2020	1608, 1530	995, 980, 918	6.65(3), 6.63(3) 6.49(6)
$[Ph_3PRu(\eta^2\text{-}CSNMe_2)(S_2CNMe_2)NO]PF_6$	(II-PF_6)	(1790)	1606, 1525	990, 975, 920	6.55(6), 6.43(6)
$[Ph_3PRh(\eta^2\text{-}CSNMe_2)(S_2CNMe_2)CO]PF_6$	(IV-PF_6)	2030	1612, 1545	1000, 985, 925	6.67(3), 6.59(3), 6.47(3), 6.42(3)
$[trans\text{-}(Ph_3P)_2Ir(\eta^2\text{-}CSNMe_2)COCl]PF_6$	(V-PF_6)	2010	1615	995, 915	7.44(3), 7.34(3)
$[trans\text{-}(Ph_3P)_2Ru(\eta^2\text{-}CSNMe_2)NOCl]PF_6$	(VII-PF_6)	(1800)	1609	995, 918	7.48(3), 71.3(3)

[a] KBr disc. [b] An intense peak at 830 cm^{-1} due to the PF_6^- ion obscures the characteristic peak in this region. [c] Relative to TMS. Phenyl proton resonances occur as a broad multiplet in the region 2.0—2.4 τ. [d] Numbers in parentheses are the number of protons as determined by integration relative to phenyl resonances. No distinction could be made between thiocarboxamido and dithiocarbamato methyl resonances.

NMe_2, SMe) to various metal complexes. It seems reasonable to propose that the formation of such complexes takes place through a η^1-thiocarboxamido intermediate followed by closure of the M—C—S ring, but this sequence has been demonstrated in only one case [1].

In this paper I report an investigation of the reactions of the Vaska-type complexes $(Ph_3P)_2RhCOCl$, $(Ph_3P)_2IrCOCl$, and $(Ph_3P)_2RuNOCl$ with $(Me_2NCS)_2S$, Me_2NCSCl, and $(Me_2NCS)_2NPh$. One object of this study was to attempt to isolate octahedral d^6 η^1-thiocarboxamido complexes, or at least to detect their presence as intermediates in the formation of η^2 complexes. A second objective was to investigate the stereochemistry of these reactions. Finally, it was hoped that this study would lead to an explanation of a previously reported and rather puzzling difference in the behavior of $(Ph_3P)_2RhCOCl$ and $(Ph_3P)_2IrCOCl$ in their reactions with Me_2NCSCl, giving the neutral dichloro complex *trans*-$(Ph_3P)_2Rh(\eta^2\text{-}CSNMe_2)Cl_2$ * [2] and the ionic carbonyl complex [*trans*-$(Ph_3P)_2Ir(\eta^2\text{-}CSNMe_2)COCl$]Cl [1], respectively.

Experimental

Starting materials ($(Ph_3P)_2RhCOCl$ [4], $(Ph_3P)_2IrCOCl$ [4], $(Ph_3P)_2IrCOBr$ [5], $(Ph_3P)_2RuNOCl_3$ [6], $(Me_2NCS)_2S$ [7], and $(Me_2NCS)_2NPh$ [8]) were prepared by literature methods. Me_2NCSCl, obtained from the Aldrich Chemical Company, was purified by crystallization from ether and by vacuum sublimation just before use.

Reactions were carried out at room temperature under nitrogen. NMR spectra were monitored during the reactions after weighing equimolar quantities of the reactants into an NMR tube, adding solvent, and flushing with nitrogen.

Infrared spectra were measured as KBr discs using a Perkin-Elmer model 461 spectrophotometer. NMR spectra were obtained on a JEOL JNM-MH-100 instrument. Analyses were performed by Atlantic Microlab, Inc., Atlanta, GA.

Melting points and analytical data for all new compounds are given in Table 1. Spectrophotometric data are presented in Table 2.

$[Ph_3PIr(\eta^2\text{-}CSNMe_2)(S_2CNMe_2)CO]PF_6$ (I-PF_6). $(Ph_3P)_2IrCOCl$ (0.136 g, 0.174 mmol) and $(Me_2NCS)_2S$ (0.0365 g, 0.175 mmol) were stirred in 10 ml of toluene. After 18 h, 50 ml of ether were added, the mixture was stirred for two hours, and the product (I-Cl) was filtered and taken up in 10 ml of acetone. A solution of 2.0 g of NH_4PF_6 in 25 ml of acetone was added and the resulting precipitate of NH_4Cl was removed by filtration. The filtrate was added to 125 ml of cold water, and the precipitate (I-PF_6) was filtered, dried in vacuo, and recrystallized from acetone/ether. Yield, 0.130 g of white crystals (0.155 mmol, 89.1%).

$[Ph_3PRu(\eta^2\text{-}CSNMe_2)(S_2CNMe_2)NO]PF_6$ (II-PF_6). $(Ph_3P)_2RuNOCl_3$ (1.52 g, 2.00 mmol) was reduced to $(Ph_3P)_2RuNOCl$ in refluxing toluene (100 ml) by the literature method [9]. After cooling to room temperature, a solution of $(Me_2NCS)_2S$ (0.418 g, 2.01 mmol) in 10 ml of toluene was added; the solution immediately changed color from green to brown. The solution was filtered and

* In this paper, when used as part of a formula, *trans* indicates the relative positions of the two phosphine ligands.

evaporated to dryness, and the residue was treated with NH_4PF_6 as described above. The product was recrystallized three times from acetone/ether. Yield, 0.593 g of orange crystals (0.794 mmol, 39.7%).

[$Ph_3PRh(\eta^2$-$CSNMe_2)(S_2CNMe_2)CO]PF_6$ (IV-PF_6). $(Ph_3P)_2RhCOCl$ (0.171 g, 0.248 mmol) and $(Me_2NCS)_2S$ (0.0529 g, 0.254 mmol) were dissolved in 5 ml of chloroform and allowed to stand for five minutes. The solvent was then removed and the residue was treated with NH_4PF_6 as described above. The product was recrystallized from acetone/ether. Yield, 0.160 g of yellow crystals (0.214 mmol, 86.4%).

The corresponding chloride salt (IV-Cl) was isolated in 87.4% yield by adding 20 ml of ether to the chloroform solution of the reactants and chilling the solution to —20° C for two hours.

If the same reactants are allowed to react for a prolonged time, $Ph_3PRh(\eta^2$-$CSNMe_2)(S_2CNMe_2)Cl$ is obtained as the product. When 0.109 g $(Ph_3P)_2RhCOCl$ (0.157 mmol) and 0.0336 g of $(Me_2NCS)_2S$ (0.162 mmol) were stirred in 10 ml of toluene, a yellow precipitate was formed initially which redissolved on continued stirring. After 40 hours the product was precipitated with 80 ml of heptane and recrystallized from CH_2Cl_2/heptane. It was identified as $Ph_3PRh(\eta^2$-$CSNMe_2)(S_2CNMe_2)Cl \cdot CH_2Cl_2$ by comparison of its infrared spectrum with that of a sample prepared by the literature method [10]. Yield, 0.0885 g (0.128 mmol, 81.5%).

[trans-$(Ph_3P)_2Ir(\eta^2$-$CSNMe_2)COCl]PF_6$ (V-PF_6). $(Ph_3P)_2IrCOCl$ (0.102 g, 0.131 mmol) and Me_2NCSCl (0.0163 g, 0.132 mmol) were stirred in 10 ml of toluene for 18 hours and worked up as the hexafluorophosphate salt as described above. Yield, 0.114 g of white crystals (0.112 mmol, 85.5%).

The same product was obtained from the reaction of $(Ph_3P)_2IrCOBr$ (0.126 g, 0.153 mmol) with Me_2NCSCl (0.0191 g, 0.155 mmol) in the same way. The infrared spectrum and chloride analysis of the product were identical to those of an authentic sample of V-PF_6. Yield, 0.101 g (0.099 mmol, 64.8%).

[trans-$(Ph_3P)_2Ru(\eta^2$-$CSNMe_2)NOCl]PF_6$ (VII-PF_6). $(Ph_2P)_2RuNOCl_3$ (1.52 g, 2.00 mmol) was reduced to $(Ph_3P)_2RuNOCl$ in refluxing toluene (100 ml), cooled to room temperature, and a solution of 0.250 g of Me_2NCSCl (2.02 mmol) in 10 ml of toluene was added. The reaction took place immediately. The solution was filtered and the product was worked up as the hexafluorophosphate salt as described above and recrystallized three times from acetone/ether. Yield, 0.273 g of red-orange crystals (0.296 mmol, 14.8%).

The same product was obtained from the reaction of 2.00 mmol of $(Ph_3P)_2$-$RuNOCl$ with 0.537 g of $(Me_2NCS)_2NPh$ (2.01 mmol) in the same way. Yield, 0.253 g (0.274 mmol, 13.6%).

Results and discussion

Reactions of $(Me_2NCS)_2S$

Bis(dimethylthiocarbamoyl)sulfide reacts with $(Ph_3P)_2IrCOCl$ to give the ionic complex $[Ph_3PIr(\eta^2$-$CSNMe_2)(S_2CNMe_2)CO]Cl$ (I-Cl), which can be converted to the hexafluorophosphate salt (I-PF_6). The crystal structure of the latter has been determined [11] and the cation has the structure shown in Fig. 1a. A similar complex $[Ph_3PRu(\eta^2$-$CSNMe_2)(S_2CNMe_2)NO]PF_6$ (II-PF_6) is

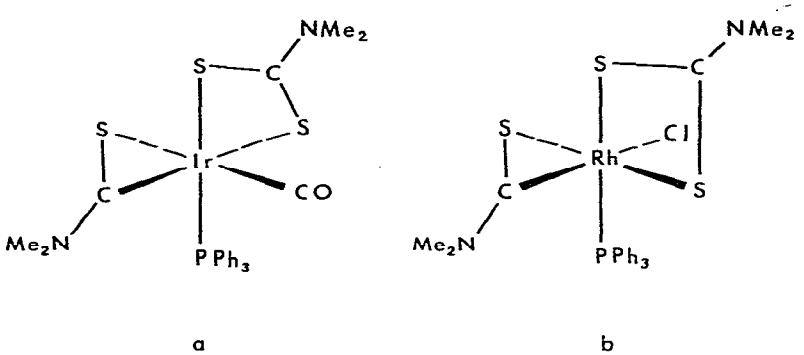


Fig. 1. The structures of the $[Ph_3PIr(\eta^2\text{-}CSNMe_2)(S_2CNMe_2)CO]^+$ ion (a) and of $Ph_3PRh(\eta^2\text{-}CSNMe_2)(S_2CNMe_2)Cl$ (b).

obtained from the reaction of $(Me_2NCS)_2S$ with $(Ph_3P)_2RuNOCl$; in this case the chloride salt was not isolated. Except for the CO and NO stretching vibrations, the infrared spectra of I-PF_6 and II-PF_6 are identical and they are presumably isostructural.

The reaction of $(Me_2NCS)_2S$ with $(Ph_3P)_2RhCOCl$, on the other hand, appears at first to follow quite a different course. When these are allowed to react for 40 hours in toluene, the neutral chloro complex $Ph_3PRh(\eta^2\text{-}CSNMe_2)(S_2CNMe_2)Cl$ (III) is formed. This complex was previously known from its preparation from $(Me_2NCS)_2S$ and $(Ph_3P)_3RhCl$ [10] and its crystal structure has also been determined (Fig. 1b) [12].

This difference in behavior between $(Ph_3P)_2IrCOCl$ and $(Ph_3P)_2RhCOCl$, giving rise to cationic carbonyl and neutral chloro complexes, respectively, has been noted previously in their reactions with Me_2NCSCl to give [*trans*-$(Ph_3P)_2Ir(\eta^2\text{-}CSNMe_2)COCl]Cl$ [1] and *trans*-$(Ph_3P)_2Rh(\eta^2\text{-}CSNMe_2)Cl_2$ [2]. This behavior has been ascribed to a difference between the metals in the relative ease of displacement (by the sulfur atom during closure of the M—C—S ring) of CO and Cl^-: for Rh, $CO > Cl^-$ and for Ir, $Cl^- > CO$ [1]. However, there seems to be no obvious reason for such a difference.

A more satisfactory explanation suggested itself when the reaction of $(Me_2NCS)_2S$ with $(Ph_3P)_2RhCOCl$ was studied more closely. When this reaction was monitored by NMR spectroscopy, the spectra shown in Fig. 2 were obtained. It was found that within a few minutes at room temperature, the starting materials were completely consumed and the spectrum of a new species appeared. This species then disappeared much more slowly and was replaced by the final product III.

The intermediate species was easily isolated by a slight modification of the reaction conditions. The reactants were dissolved in chloroform and after five minutes ether was added. The intermediate separated as a yellow precipitate which was shown to be $[Ph_3PRh(\eta^2\text{-}CSNMe_2)(S_2CNMe_2)CO]Cl$ (IV-Cl). This complex was easily converted to the hexafluorophosphate salt (IV-PF_6). The infrared spectra of these two complexes are identical with those of their iridium analogs and the complex cations presumably have the same structure.

IV-PF_6 is stable indefinitely in acetone solution, but on addition of chloride

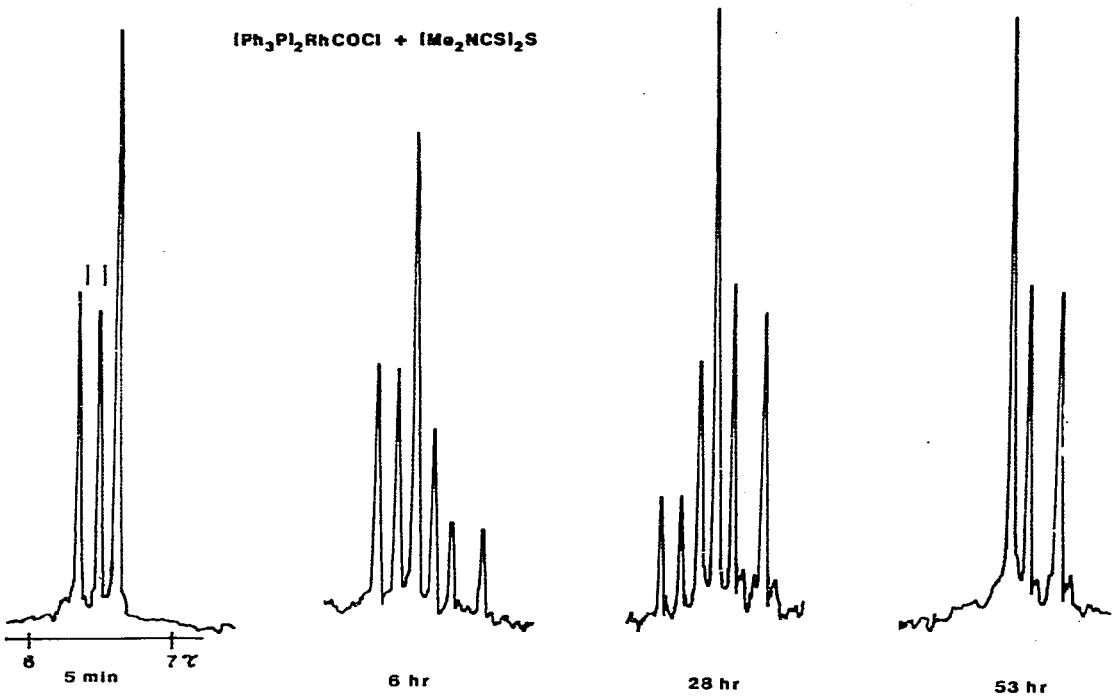
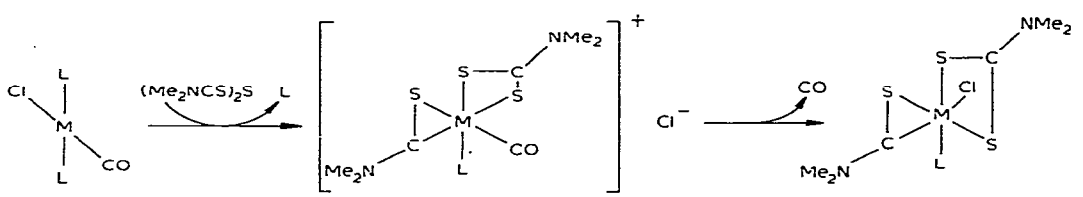


Fig. 2. Time-dependent NMR spectrum of the reaction between $(Me_2NCS)_2S$ and $(Ph_3P)_2RhCOCl$. The two tick marks on the left-hand spectrum show the location of the peaks in the spectrum of $(Me_2NCS)_2S$.

ion (as Ph_4AsCl) conversion to III takes place. However, neither I-PF_6 nor II-PF_6 react with chloride ion, even on prolonged (seven days) reflux in acetone.

The reaction of $(Me_2NCS)_2S$ with $(Ph_3P)_2MCOCl$ complexes thus apparently follows the course shown below:



(L = Ph_3P ; M = Rh, Ir) (M = Rh only)

The carbonyl cations, then, are kinetic products, while the neutral chloro complex (formed in the case of rhodium only) is the thermodynamic product. Since the initial product is the same for both metals, it is not necessary to invoke any difference between them other than the expected difference in the rate of displacement of CO by chloride ion. (Displacement of the nitrosyl ligand in II-PF_6 by Cl^- is of course not expected to take place).

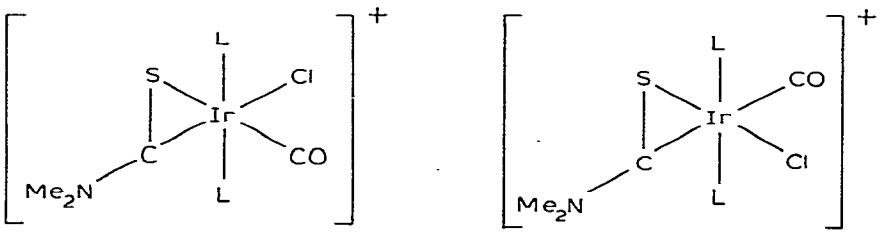
Reaction of Me_2NCSCl

The known reactions of Me_2NCSCl with $(Ph_3P)_2IrCOCl$ and $(Ph_3P)_2RhCOCl$ to give [*trans*-$(Ph_3P)_2Ir(\eta^2$-$CSNMe_2)COCl$]Cl (V-Cl) and *trans*-$(Ph_3P)_2Rh(\eta^2$-$CSNMe_2)Cl_2$ (VI) respectively have already been noted. The hexafluoro-

phosphate salt of the iridium complex (V-PF_6) and its isostructural ruthenium nitrosyl analog, [*trans*-$(Ph_3P)_2Ru(\eta^2$-$CSNMe_2)NOCl]PF_6$ (VII-PF_6), can also be prepared and are reported here. V-PF_6 and VII-PF_6 fail to react with chloride ion in refluxing acetone.

It seems probable that, as with the reactions of $(Me_2NCS)_2S$, the initial product formed in the reaction of Me_2NCSCl with $(Ph_3P)_2RhCOCl$ is also an ionic complex (the rhodium analog of V) which reacts to give VI by chloride ion displacement of CO. However, in this case direct evidence is lacking. When the NMR spectrum of the reaction was monitored, only the disappearance of Me_2NCSCl and the appearance of VI were seen (see Fig. 3), and no intermediate species could be detected. Presumably the oxidative addition of the less reactive Me_2NCSCl is slow compared to displacement of CO by Cl^-, making the detection of the intermediate complex [*trans*-$(Ph_3P)_2Rh(\eta^2$-$CSNMe_2)COCl]Cl$ impossible.

The structure of VI is fully determined by the fact that the phosphine ligands are mutually *trans* [1]. There are, however, two possible structures for the cation V, since the chloride ligand may be *trans* either to the carbon atom (Va) or to the sulfur atom (Vb) of the thiocarboxamido ligand:



(Va) (Vb)

One indication of the structure of V is provided by the observation that when Me_2NCSCl reacts with $(Ph_3P)_2IrCOBr$, the only product (as the PF_6^- salt) is a chloro complex identical to that obtained from the reaction of $(Ph_3P)_2IrCOCl$. (This reaction was carried out in a nonpolar solvent (toluene) and worked up quickly at 0°C to minimize the possibility of halide exchange.) Thus

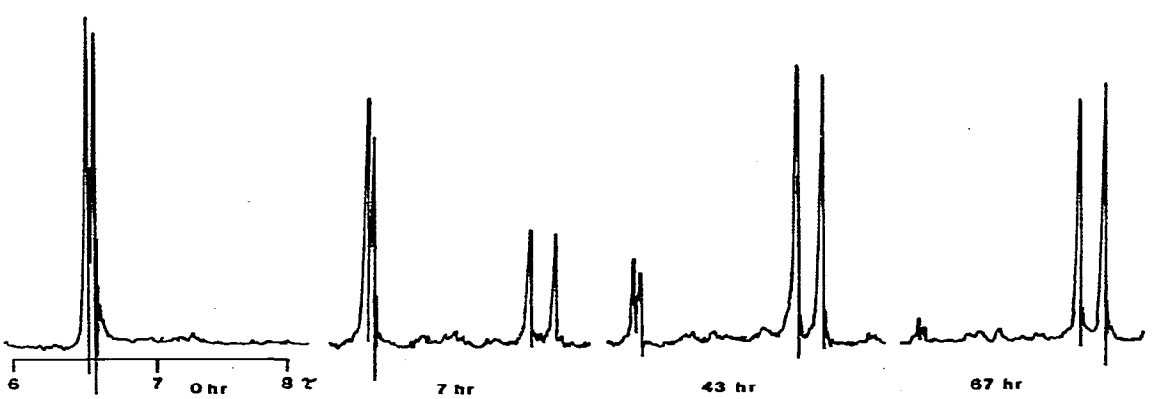
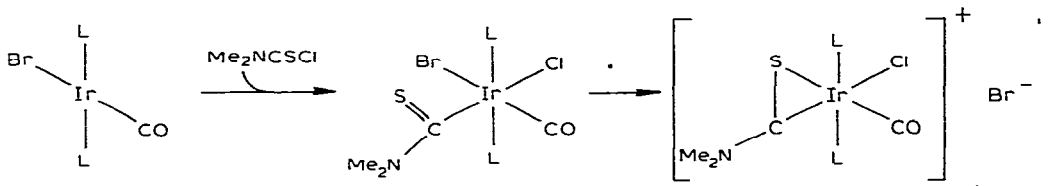


Fig. 3. Time-dependent NMR spectrum of the reaction between Me_2NCSCl and $(Ph_3P)_2RhCOCl$.

the halide initially attached to the iridium is lost, while the chloride from Me_2NCSCl is retained in the coordination sphere in the final product.

(It would be satisfying to show that the converse reaction (i.e. Me_2NCSBr with $(Ph_3P)_2IrCOCl$) gives [*trans*-$(Ph_3P)_2Ir(\eta^2$-$CSNMe_2)COBr]Cl$ as the only product. Unfortunately, Me_2NCSBr appears to be unstable; a number of attempts to synthesize this compound by several routes gave no identifiable product.)

This result suggests that the product has the structure Va, in which the chloride ligand, being *trans* to the thiocarboxamido carbon, is out of reach of displacement by the sulfur atom during the formation of the Ir—C—S ring. This structure could arise straightforwardly via *trans* addition of Me_2NCSCl to $(Ph_3P)_2IrCOBr$:



(Va-Br)

This suggestion of Va as the most likely structure of V leaves unexplained the fact that the infrared spectrum [1] of V-Cl shows ν(Ir—Cl) at 290 cm^{-1}, whereas all rhodium complexes [2,10] known to have a Cl *trans* to a thiocarboxamido carbon have ν(Rh—Cl) near 250 cm^{-1}. However, it may also be noted that for *trans*-$(Ph_3P)_2Ir(\eta^2$-$CSNMe_2)Cl_2$, ν(Ir—Cl) is reported at 305 cm^{-1} only [1].

Ideally, the structure of V should be confirmed by an X-ray structure determination. Suitable crystals of V-PF_6 have not yet been obtained, but the ruthenium nitrosyl analog VII-PF_6 forms much better crystals and it is hoped that the structure of this compound can be determined.

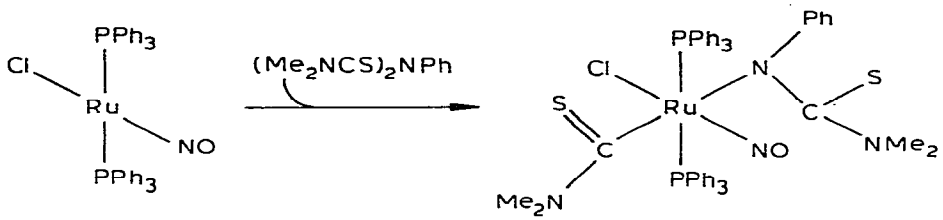
Reactions of $(Me_2NCS)_2NPh$

It was hoped that additional information on the stereochemistry of these reactions could be obtained by studying the reaction of $(Me_2NCS)_2NPh$ with Vaska-type complexes to give thiocarboxamido-thioureido species, analogous to the known reaction of $(Me_2NCS)_2NPh$ with $(Ph_3P)_3RhCl$ to give $Ph_3Rh(\eta^2$-$CSNMe_2)[(NPh)CSNMe_2]Cl$ (XI) [10]. In such complexes it is possible to distinguish which "end" of the thioureido ligand was originally attached to the thiocarboxamido carbon (i.e., the nitrogen atom), whereas in the case of dithiocarbamate complexes derived from $(Me_2NCS)_2S$, this information is lost.

Unfortunately, $(Me_2NCS)_2NPh$ is not sufficiently reactive to add to either $(Ph_3P)_2RhCOCl$ or $(Ph_3P)_2IrCOCl$, even in refluxing toluene. A reaction did take place with the much more reactive $(Ph_3P)_2RuNOCl$, but it took a surprising course; the only product obtained was [*trans*-$(Ph_3P)_2Ru(\eta^2$-$CSNMe_2)NOCl]PF_6$ (VII-PF_6), formed in nearly the same yield as from Me_2NCSCl.

This behavior can perhaps be ascribed (based on inspection of molecular models) to steric repulsion between the phenyl groups on *cis* triphenylphos-

phine and *N*-phenylthioureido ligands in an octahedral complex:



The effect of this repulsion could be either to cause dissociation of the *N*-thiouredio ligand, or to render it easily displaced by chloride ion (which is fomed during closure of the Ru—C—S ring).

NMR spectra

One of the objects of this study was to attempt to detect η^1-thiocarboxamido intermediate species by monitoring the NMR spectra of reactions in which η^2 complexes were formed. Because of the extreme air-sensitivity of $(Ph_3P)_2RuNOCl$ and because of the low yields of products obtained from this complex, its reactions were not studied in this way. However, the reactions of $(Ph_3P)_2RuCOCl$ and $(Ph_3P)_2IrCOCl$ with $(Me_2NCS)_2S$ and Me_2NCSCl were all monitored by NMR. In only one instance ($(Ph_3P)_2RhCOCl$ with $(Me_2NCS)_2S$, discussed above) was any intermediate species observed; in no case could any peaks attributable to complexes containing η^1-thiocarboxamido or monodentate dithiocarbamato ligands be detected.

In the reaction of $(Me_2NCS)_2S$ with $(Ph_3P)RhCOCl$, the oxidative addition and the formation of both the η^2-thiocarboxamido and dithiocarbamato ligand rings were complete within 1—2 minutes at room temperature (i.e. the time required to insert the sample into the spectrophotometer). Presumably a similar rapid closing of the thiocarboxamido ring occurs in the reaction of Me_2NCSCl with $(Ph_3P)_2RhCOCl$. In the reactions of $(Ph_3P)_2IrCOCl$, the ring closures may or may not be comparably rapid, but they are in any case much faster than the oxidative additions.

Acknowledgements

This work was supported by a grant from the Research Corporation. The author also thanks Mr. G.J. Snipes for assistance in obtaining the NMR spectra.

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