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THE INTERACTION OF ORGANIC ISOTHIOCYANATES WITH COMPLEXES OF RUTHENIUM AND RHODIUM. FORMATION OF π-BOUND ISOTHIOCYANATE, ISONITRILE-DITHIOCARBONIMIDATO COMPLEXES AND A NEW ROUTE TO ISONITRILE-DIOXYGEN COMPLEXES OF RHODIUM.

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Summary

Simple π-bound isothiocyanate complexes result from the interaction of $Ru(CO)_2(PPh_3)_3$ with RNCS (R = Ph, Et, Me). Both $Ru(CO)_2(PPh_3)_2(\pi$-RNCS) (I) and $Ru(CO)_2(PPh_3)_3$ react with excess RNCS to yield the isonitrile-dithiocarbonimidato derivatives, $Ru(CO)(CNR)(S_2CNR)(PPh_3)_2$(II). When $RhCl(PPh_3)_3$ reacts with RNCS (R = Bz, c-hex, Ph, ^{t}Bu, ^{n}Bu, Et), a simple π-RNCS adduct may not be isolated but is a presumed intermediate in the formation of the isonitrile-dithiocarbonimidato derivatives $RhCl(CNR)(S_2CNR)(PPh_3)_2$(III). Methyl iodide effects alkylation at the nitrogen of the dithiocarbonimidato ligand of III to give the series of cationic complexes, $[RhCl(CNR)\{S_2CN(Me)R\}(PPh_3)_2]I$ (R = Bz, Ph, Et) (IV). Complex III also reacts with triphenylphosphine to give in solution trans-$RhCl(CNR)(PPh_3)_2$, which rapidly coordinates dioxygen to give complexes of the type, $RhCl(CNR)(PPh_3)_2(O_2)$ (R = Ph, c-hex, ^{t}Bu, ^{n}Bu) (V).

Introduction

Many transition-metal complexes in low oxidation states, which are known to be capable of coordinating dioxygen have also been found to coordinate carbon disulphide in a similar oxidative addition reaction [1,2]. Alkyl and aryl isothiocyanates are considered to have bonding properties similar with that of carbon disulphide and in general have been shown to bond to metal complexes in an analogous manner [3-5], although exceptions do occur [6-9].

In an early report, Wilkinson et al. [10] have reported the formation of the isothiocyanate complexes $Pt(PPh_3)_2(\pi\text{-}RNCS)$ (R = Ph, Me) and $RhCl(\sigma\text{-}RNCS)(PPh_3)_2(\pi\text{-}RNCS)$ (R = Ph) from the interaction of the appropriate isothiocyanate with $Pt(PPh_3)_4$ and $RhCl(PPh_3)_3$, respectively. More recently, Haszeldine et al. [6] have shown that $Pt(PPh_3)_4$ and $Pt(PPh_3)_2(\pi\text{-}RNCS)$ (R = Ph, Me) react in excess isothiocyanate to give the dithiocarbonimidato complex, $Pt(S_2CNR)(PPh_3)_2$ (R = Ph, Me) as the major product. The isonitrile complex, $Pt(CNR)(S_2CNR)(PPh_3)$ may be obtained as the minor product. Similarly, it has been reported that both $Pd(PPh_3)_2(\pi\text{-}EtCONCS)$ and $Pd(S_2CNOCEt)(PPh_3)_2$ may be obtained from the reaction between $Pd(PPh_3)_4$ and EtCONCS [9].

In this paper, we describe the formation of several π-bound isothiocyanate and isonitrile-dithiocarbonimidato complexes which result from the reaction of alkyl and aryl isothiocyanates with $Ru(CO)_2(PPh_3)_3$ and $RhCl(PPh_3)_3$. In particular, the complex previously proposed to be $RhCl(\sigma\text{-}PhNCS)(PPh_3)_2(\pi\text{-}PhNCS)$ has been reformulated as $RhCl(CNPh)(S_2CNPh)(PPh_3)_2$ - an isonitrile-dithiocarbonimidato complex.

Results and Discussion

Simple π-complexes have been reported in the reaction of $Ru(CO)_2(PPh_3)_3$ with small molecules such as O_2 [11], CS_2[12] and CSe_2 [13]. In a similar manner, trans-$Ru(CO)_2(PPh_3)_3$ reacts with stoichiometric amounts of RNCS (R = Ph, Et, Me) to give yellow crystals of $Ru(CO)_2(PPh_3)_2(\pi\text{-}RNCS)$(I) in 80% yield. These complexes are all air stable, yet lose the coordinated π-ligand when redissolved in organic solvents. They are therefore, very similar to the products obtained with CS_2 [12]. In I the phosphines are assumed to be trans and the π-bound RNCS ligand is expected to bond across the softer CS bond.

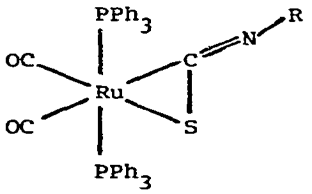
In their IR spectra (Table 1), the shift to higher energy of ν(CO) is quite typical for oxidative addition at Ru(O). In $Ru(CO)_2(PPh_3)_2(\pi\text{-}PhNCS)$, the carbonyl absorptions appear at 2010 and 1950 cm^{-1}, which is shifted from 1905 cm^{-1} in trans-$Ru(CO)_2(PPh_3)_3$. The existance of two ν(CO) absorptions in complexes Ia-c indicates that a stereochemical change to a cis arrangement of carbonyl ligands has occured. In addition, the IR spectra of Ia-c display a strong absorption around 1650 cm^{-1}, which is readily attributable to ν(CN) of a π-bound isothiocyanate molecule.

Table 1: INFRARED SPECTRA OF RUTHENIUM COMPOUNDS

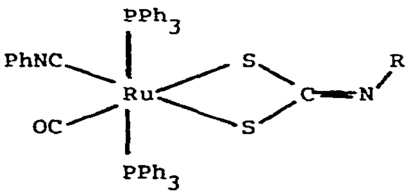
COMPOUND^a		ν(CN)(cm^{-1})	ν(CO)(cm^{-1})	ν(CS)(cm^{-1})^b
	$Ru(CO)_2L_3$		1905	
Ia	$Ru(CO)_2L_2(\pi\text{-PhNCS})$	1640	2010,1905	
Ib	$Ru(CO)_2L_2(\pi\text{-EtNCS})$	1644	2020,1955	
Ic	$Ru(CO)_2L_2(\pi\text{-MeNCS}$	1645	2021 1958	
IIa	$Ru(CO)(CNPh)(S_2CNPh)L_2$	2158,1532	1962	932
IIb	$Ru(CO)(CNEt)(S_2CNEt)L_2$	2218,1545	1980	940
IIc	$Ru(CO)(CNMe)(S_2CNMe)L_2$	2220,1552	1978	968

[a] L = PPh_3, all bands are extremely intense and obtained as Nujol mulls.

[b] weak



Ia (R = Ph)
Ib (R = Et)
Ic (R = Me)



IIa
IIb
IIc

If the reaction is carried out in the presence of excess isothiocyanate, then the products isolated are the isonitrile-dithiocarbonimidato derivative (II). For example, the reaction of trans-$Ru(CO)_2(PPh_3)_3$ with excess phenyl isothiocyanate gives $Ru(CO)_2(CNPh)(S_2CNPh)(PPh_3)_2$(IIa) in 75% yield. This product may also be obtained in lower yield (60%) by reacting $Ru(CO)_2(PPh_3)_2(\pi\text{-PhNCS})$(Ia) with excess phenyl isothiocyanate.

In comparison with the structures of $[Ru(CO)_2(PPh_3)_2(CS_2Me)]I$ [14] and its carbon diselenide analogue $[Ru(CO)_2$

$(PPh_3)_2(CSe_2Me)]I$ [13] which are known to have cis-carbonyls and trans-phosphines, it would appear most probable that the stereochemistry of complexes IIa-c involve trans-phosphines and that the carbonyl and isonitrile ligands are cis to one another. These light yellow products are all air stable and less sensitive to decomposition in solution than the corresponding π-RNCS complexes, Ia-c.

The IR spectra of the isonitrile-dithiocarbonimidato ruthenium complexes (Table 1) contain two strong absorption bands in the regions 2200 cm^{-1} and 1970 cm^{-1}. As suggested previously [15,16], the former may be attributed to ν(CN) of the coordinated isonitrile ligand while the latter is due to ν(CO) of the carbonyl ligand. The dithiocarbonimidato ligand may be observed to exhibit two characteristic absorptions around 1540 cm^{-1} and 930 cm^{-1}. In IIa, the ν(CN) absorption occurs at 1540 cm^{-1} which is approximately 100 cm^{-1} lower than in the corresponding π-RNCS complex Ia (Table 1). Weak ν(CS) absorptions are also observed in the region 970-930 cm^{-1}. The exact origin of this vibration is difficult to assign as dithioformato complexes [17,18], N-alkyl and N-aryl-thioformamido complexes [3] and thiocarboxamido complexes [18] all exhibit this characteristic ν(CS) absorption.

The reaction of $RhCl(PPh_3)_3$ with RNCS (R = Bz, Ph, c-hex, ^tBu, ^nBu, Et) differs from that of trans-$Ru(CO)_2(PPh_3)_3$ in that a π-RNCS complex could not be isolated. Instead, isonitrile-dithiocarbonimidato complexes of the type $RhCl(CNR)(S_2CNR)(PPh_3)_2$ (IIIa-f) were obtained in approximately 85% yield (Table 2). Complexes of type III may be formed in at least two ways. The first involves internal migration of sulphur from one isothiocyanate to the other presumably via the unstable species, $RhCl(\sigma\text{-}RNCS)(PPh_3)_2(\pi\text{-}RNCS)$. Intermediates of this type have recently been proposed in the reaction of $RhCl(PPh_3)_3$ with EtCONCS [9]. The second involves sulphur abstraction from an external isothiocyanate yielding dithiocarbonimidato and isonitrile ligands. Sulphur abstraction forming an isonitrile complex has been observed in the reaction of $Fe(CO)_5$ and $Mo(CO)_6$ with phenyl isothiocyanate to give the complexes, $Fe(CO)_4(CNPh)$ and $Mo(CO)_5(CNPh)$, respectively [20,21].

The IR spectra of the orange air-stable complexes (IIIa-f) contain absorptions in the regions 2228-2180 and 1574-1540 cm^{-1} (Table 2). The former band may be attributed to ν(CN) of the coordinated isonitrile ligand while the latter is due to ν(CN)

Table 2: IR DATA FOR RHODIUM ISONITRILE-DITHIOCARBONIMIDATO COMPLEXES AND THEIR DITHIOCARBAMATE DERIVATIVES.

COMPLEX[a]		ν(C≡N) (cm^{-1})[b]	ν(C=N) (cm^{-1})[b]	ν(C-S) (cm^{-1})[d]
IIIa	RhCl(CNPh)(S$_2$CNPh)L$_2$	2180	1540	927
IIIb	RhCl(CNBz)(S$_2$CNBz)L$_2$	2222	1565	913
IIIc	RhCl(CN$\underline{c}$-hex)(S$_2$CN$\underline{c}$-hex)L$_2$	2218, 2200	1555, 1570	930, 918
IIId	RhCl(CN^{t}Bu)(S$_2$CN^{t}Bu)L$_2$	2216	1566	902
IIIe	RhCl(CN^{n}Bu)(S$_2$CN^{n}Bu)L$_2$	2220	1574	900
IIIf	RhCl(CNEt)(S$_2$CNEt)L$_2$	2228	1570	918
IVa	[RhCl(CNPh){S$_2$CN(Me)Ph}L$_2$]I	2190	1532[c]	968
IVb	[RhCl(CNBz{S$_2$CN(Me)Bz}L$_2$]I	2229	1538[c]	962
IVc	[RhCl(CNEt){S$_2$CN(Me)Et}L$_2$]I	2230	1533[c]	970

[a] L = PPh$_3$, measured as Nujol mulls

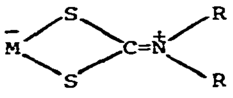
[b] intense

[c] medium

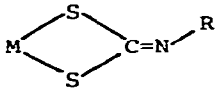
[d] weak

of the bidentate dithiocarbonimidato ligand. The IR spectra also display characteristic band in the region 930-900 cm^{-1}, assigned to ν(CS) of the dithiocarbonimidato ligand. This absorption appears about 30 cm^{-1} lower than that observed in analogous N-cyanocarbimate complexes [22,23]. These rhodium complexes were too insoluble in common deuterated solvents to allow NMR spectra to be obtained.

Structurally, complexes IIIa-f are believed to be similar to that of dithiocarbamate complexes [24,25]; in fact, Chatt and co-workers [26] have suggested that the canonical form A makes the most significant contribution to the structure of dithiocarbamate complexes. In an X-ray study of [Ni(S$_2$CN-CN)$_2$][AsPh$_4$], Cotton and Harris [27] have shown that there are no significant differences between any of the corresponding angles of the ligands in the two types of structures A and B.



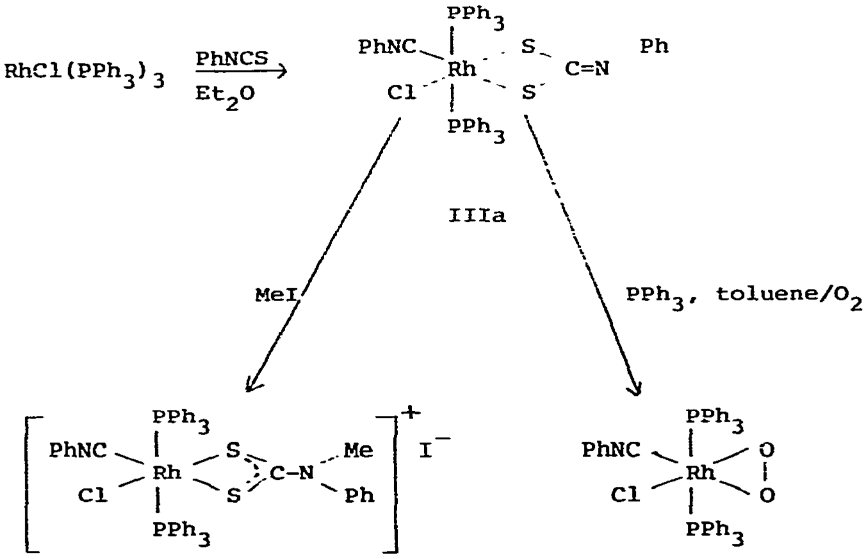
A (R = Et)



B (R = CN)

Complexes of type III were found to be readily alklated at the dithiocarbonimidato nitrogen when reacted with methyl iodide to give cationic dithiocarbamate complexes of type IV, $[RhCl(CNR)\{S_2CN(Me)R\}(PPh_3)_2]I$ (R = Bz, Ph, Et) (Scheme 1).

Scheme 1: Formation and Reactions of $RhCl(CNPh)(S_2CNPh)(PPh_3)_2$(III)



IVa

Va

The IR spectra exhibit the expected changes upon methylation; for example ν(C=N) in $[RhCl(CNPh)\{S_2CN(Me)Ph\}(PPh_3)_2]I$ drops from 1540 to 1532 cm^{-1} while ν(C≡N) and ν(CS) increase slightly to 2190 and 968 cm^{-1}, respectively (Table 2). These complexes also exhibit weak IR absorptions in the 290 cm^{-1} region which is in agreement with those reported for ν(Rh-Cl) in other isonitrile [28,29] and thiocarboxamido complexes of rhodium [19].

The NMR spectra for complexes of type IV exhibit a sharp methyl singlet ca. δ3.40 ppm which confirms that methylation is occurring at nitrogen rather than at sulphur. It has been shown previously that the PMR signal of the methyl group in $[Os(CO)_2(PPh_3)_2(CS_2Me)]I$ {derived from $Os(CO)_2(PPh_3)_2(\pi\text{-}CS_2)$ and methyl iodide} occurs at δ2.10 ppm [12]. During the course of this work, Grundy and Roper [4] have reported that MeI methylation of nitrogen in $Os(CO)_2(PPh_3)_2$(π-p-tolyl NCS) yields $[Os(CO)_2(PPh_3)_2\{\eta^2\text{-}SCN(Me)\text{p-tolyl}\}]I$, the PMR of which contains a sharp signal at δ3.4 ppm assignable to the bidentate thiocarboxamido methyl group. The above data are in accord with the PMR data of $RhCl(S_2CNMe_2)(SCNMe_2)(PPh_3)$ [19]. The complexes (IVa-c) are considered to be structurally similar to $RhCl(S_2CNMe_2)(SCNMe_2)(PPh_3)$ whose structure has been determined by X-ray crystallography [19].

When the complexes $RhCl(CNR)(S_2CNR)(PPh_3)_2$ (R = Ph, c-hex, ^{t}Bu, ^{n}Bu) are reacted with an excess of triphenylphosphine in toluene under reflux, a bright yellow solution is formed after 30 min from which green or greenish-yellow powders of stoichiometry corresponding to $RhCl(CNR)(PPh_3)_2$-(O_2) (R = Ph, c-hex, ^{t}Bu, ^{n}Bu) (V) may be obtained by the addition of hexane. The filtrate from the reactions was found to contain excess triphenylphosphine and triphenylphosphine sulphide. If the reaction conditions and work up are handled under an atmosphere of purified nitrogen, then trans-$RhCl(CNR)(PPh_3)_2$ may be obtained. For example, the presence of trans-$RhCl(CNPh)(PPh_3)_2$(Va) may be readily detected in the IR by an intense ν(CN) absorption at 2085 cm^{-1} typical of rhodium(I) isonitrile complexes [28,29]. Upon exposure to the atmosphere, this absorption at 2085 cm^{-1} decreases and is replaced by a new band at 2148 cm^{-1} attributable to ν(CN) of the rhodium(III) isonitrile complex. Also new absorptions appear in the IR at 893 and 581 cm^{-1} which are assignable to coordinated dioxygen. The stereochemistry and IR assignment for these complexes has been made on the basis of Nakamura et al. [28] who have previously synthesized $RhCl(CNR)(PPh_3)_2(O_2)$ (R = ^{t}Bu, c-hex, p-tolyl) from $RhCl(PPh_3)_3$, CNR and molecular oxygen.

The IR spectra of the series of dioxygen adducts (Table 3) prepared in this study exhibit patterns identical to the previously reported $RhCl(CNR)(PPh_3)_2(O_2)$ complexes [28,29].

Table 3: IR DATA FOR ISONITRILE-DIOXGYEN COMPLEXES

COMPLEX[a]	ν(CN) (cm^{-1}) s[b]	ν(O-O) (cm^{-1}) w[b]	ν(Rh-O) (cm^{-1}) w[b]
$RhCl(CNPh)(PPh_3)_2(O_2)$	2148	893	581
$RhCl(CN^tBu)(PPh_3)_2(O_2)$	2149	892	576
$RhCl(CN^nBU)(PPh_3)_2(O_2)$	2142	892	577
$RhCl(CN\underline{c}\text{-hex})(PPh_3)_2(O_2)$	2170	893	579

[a] Measured as Nujol mulls

[b] s = strong, w = weak

The spectra include ν(CN) in the region 2170-2148 cm^{-1}, ν(O-O) in the region 893-892 cm^{-1} and ν(Rh-O) in the region 581-576 cm^{-1}. An ^{18}O isotopic IR study of various dioxygen complexes [30] has shown that neither ν(O-O) nor ν(Rh-O) are pure stretching modes which may account for the relatively small variation in these frequencies.

The mechanism of formation of complexes V from the reaction of $RhCl(CNR)(S_2CNR)(PPh_3)_2$ with triphenylphosphine is probably quite similar to the reaction of triphenylphosphine with coordinated CS_2 [1] and CS_3 [31]. Namely, sulphur abstraction by triphenylphosphine to give triphenylphosphine sulphide, which may be readily observed in the IR spectrum of the crude product before reaction workup.

Synthetically, the reaction of RNCS with $RhCl(PPh_3)_3$ in the presence of excess triphenylphosphine provides a useful alternative route to isonitrile-dioxygen complexes of rhodium.

Experimental Section

The ^1H NMR spectra were obtained on a Varian T60 spectrometer and IR measurements were made with a Beckman IR 12 spectrophotometer. All reactions were carried out under a nitrogen atmosphere using oxygen free solvents except reaction (p) which was carried out under an atmosphere of air. Elemental analyses were performed by Alfred Bernhardt, Mikroanalytisches Laboratorium, West Germany or by Microanalyses Laboratory, Toronto, Canada.

Chlorotris(triphenylphosphine) rhodium was prepared by the method of Osborn and Wilkinson [32]. Biscarbonyltris (triphenylphosphine)ruthenium was prepared using the method of Cavit, Grundy and Roper [11]. All of the isothiocyanates were purchased from the Eastman Kodak Co., Rochester, New York.

(a) Preparation of $Ru(CO)_2(PPh_3)_2(\pi\text{-}PhNCS)$ (Ia)

Phenyl isothiocyanate (84.7 mg, 0.67 m mol) was added to 40 ml of petroleum ether and heated to reflux at which point $Ru(CO)_2(PPh_3)_3$ (600 mg, 0.638 m mol) was added. The mixture was refluxed for 20 min, cooled and the pale yellow product was suction filtered, washed with petroleum ether (60-80^{o}) and air dried, Yield 480 mg (91%). Anal. Calcd. for $C_{45}H_{35}O_2NP_2SRu$: C, 66.1; H, 4.37%, Found: C, 65.9; H, 4.81%.

(b) Preparation of $Ru(CO)_2(PPh_3)_2(\pi\text{-}EtNCS)$ (Ib)

The procedure was analogous to that in (a) except ethyl isothiocyanate (59.3 mg, 0.68 m mol) was used. The pale yellow powder was obtained in 85% yield. Anal. Calcd. for $C_{41}H_{35}O_2NP_2SRu$: C, 64.0; H, 4.59%. Found: C, 64.0; H, 4.67%.

(c) Preparation of $Ru(CO)_2(PPh_3)_2(\pi\text{-}MeNCS)$ (Ic)

The procedure was analogous to that in (a) except methyl isothiocyanate (49.7 mg, 0.68 m mol) was used. The pale yellow product was obtained in 84% yield. Anal. Calcd. for $C_{40}H_{33}O_2NP_2SRu$: C, 63.61; H, 4.43; N, 1.82%. Found: C, 63.64; H, 4.50; N, 1.86%.

(d) Preparation of $Ru(CO)(CNPh)(S_2CNPh)(PPh_3)_2$ (IIa)

Phenyl isothiocyanate (847 mg, 6.70 m mol) was added to a degassed solution of petroleum ether (60-80^{o}) and heated to reflux. $Ru(CO)_2(PPh_3)_3$ (600 mg, 0.638 m mol) was added and the solution was refluxed 45 min, cooled, suction filtered and the pale yellow product was washed with petroleum ether and air-dried. Yield 440 mg (76.9%). Anal. Calcd. for $C_{51}H_{40}ON_2P_2S_2Ru$ C, 66.34; H, 4.36; N, 3.03%. Found: C, 65.85; H, 4.35; N, 3.74%.

(e) Preparation of Ru(CO)(CNEt)(S_2CNEt)(PPh_3)$_2$(IIb)

The procedure used was analogous to that in (d) except that ethyl isothiocyanate (593 mg, 6.8 m mol) was used. The pale yellow product was obtained in 80% yield. Anal. Calcd. for $C_{43}H_{40}ON_2P_2S_2Ru$: C, 62.38; H, 4.87%. Found C, 62.79; H, 5.06%.

(f) Preparation of Ru(CO)(CNMe)(S_2CNMe)(PPh_3)$_2$(IIc)

The procedure used was analogous to that in (d) except that methyl isothiocyanate (497 mg, 6.8 m mol) was used. The pale yellow product was obtained in 78% yield. Anal. Calcd. for $C_{41}H_{36}ON_2P_2S_2Ru$: C, 61.56; H, 4.54%. Found: C, 61.89; H, 4.82%.

(g) Preparation of RhCl(CNPh)(S_2CNPh)(PPh_3)$_2$(IIIa)

Phenyl isothiocyanate (565 mg, 4.18 m mol) was added to 30 ml of diethyl ether. RhCl(PPh_3)$_3$ (500 mg, 0.54 m mol) was added and the mixture refluxed for 30 min, suction filtered and the orange product was washed with diethyl ether. Yield 0.55 g (90.1%). Anal. Calcd. for $C_{50}H_{40}N_2ClP_2S_2Rh$: C, 64.3; H, 4.36; N, 3.0; S, 6.81%. Found: C, 64.1; H, 4.50; N, 2.90; S, 6.62%.

(h) Preparation of RhCl(CNBz)(S_2CNBz)(PPh_3)$_2$(IIIb)

This complex was prepared using the method in (g) with benzyl isothiocyanate (498 mg, 3.34 m mol). The bright orange product was obtained in 85% yield. Anal. Calcd. for $C_{52}H_{44}N_2ClP_2S_2Rh$: C, 64.90; H, 4.63%. Found: C, 64.72; H, 4.90%

(i) Preparation of RhCl(CN$\underline{c}$-hex)(S_2CN$\underline{c}$-hex)(PPh_3)$_2$(IIIc)

This complex was prepared using the method in (g) with cyclohexyl isothiocyanate (498 mg, 3.53 m mol). The light orange product was obtained in 81% yield. Anal. Calcd. for $C_{50}H_{52}N_2ClP_2S_2Rh$: C, 63.53; H, 5.67; N, 2.91; S, 6.75%. Found: C, 62.28; H, 5.74; N, 2.73; S, 6.22%.

(j) Preparation of RhCl(CN^{t}Bu)(S_2CN^{t}Bu)(PPh_3)$_2$(IIId)

This complex was prepared using the method in (g) with tert-butyl isothiocyanate (500 mg, 4.34 m mol). The dark orange product was obtained in 87% yield. Anal. Calcd. for $C_{46}H_{48}N_2ClP_2S_2Rh$: C, 61.82; H, 5.40%. Found: C, 61.78; H, 5.47%.

(k) Preparation of $\mathrm{RhCl(CN^nBu)S_2CN^nBu)(PPh_3)_2}$(IIIe)

The procedure used was analogous to that in (g) except that n-butyl isothiocyanate (500 mg, 4.34 m mol) was used. The orange product was obtained in 84% yield. Anal. Calcd. for $\mathrm{C_{46}H_{48}N_2ClP_2S_2Rh}$: C, 61.82; H, 5.40; N, 3.12; S, 7.18% Found: C, 61.53; H, 5.44; N, 3.08; S, 7.00%.

(l) Preparation of $\mathrm{RhCl(CNEt)(S_2CNEt)(PPh_3)_2}$(IIIf)

The procedure used was analogous to that in (g) except that ethyl isothiocyanate (497 mg, 5.71 m mol) was used. The light orange product was obtained in 85% yield. Anal. Calcd. for $\mathrm{C_{42}H_{40}N_2ClP_2S_2Rh}$: C, 60.22; H, 4.83; N, 3.35; S, 7.61%. Found: C, 60.24; H, 4.91; N, 3.16; S, 7.12%.

(m) Formation of $\mathrm{[RhCl(CNPh)\{S_2CN(Me)Ph\}(PPh_3)_2]I}$ (IVa)

An excess of methyl iodide (10 ml) was added to $\mathrm{RhCl(CNPh)(S_2CNPh)(PPh_3)_2}$ (800 mg, 0.85 m mol) and the slurry stirred for 2 min. After 1 hr the addition of petroleum ether (40 ml) completely precipitated the salt. The dark red product was suction filtered, washed with petroleum ether and air dried. The product was recrystalized from dichloromethane/petroleum ether. Yield 640 mg (69.4%) Anal. Calcd. for $\mathrm{C_{51}H_{43}N_2ClIP_2S_2Rh}$: C, 56.93; H, 4.03; N, 2.60%. Found: C, 57.23; H, 4.25; N, 2.74%

(n) Formation of $\mathrm{[RhCl(CNBz)\{S_2CN(Me)Bz\}(PPh_3)_2]I}$ (IVb)

The procedure used was analogous to that in (m) except that $\mathrm{RhCl(CNBz)(S_2CNBz)(PPh_3)_2}$ (800 mg, 0.83 m mol) was used. The dark red product was obtained in 70% yield. Anal. Calcd. for $\mathrm{C_{53}H_{47}N_2ClIP_2S_2Rh}$: C, 57.73; H, 4.29; N, 2.54%. Found: C, 57.37; H, 4.32; N, 2.59%.

(o) Formation of $\mathrm{[RhCl(CNEt)\{S_2CN(Me)Et\}(PPh_3)_2]I}$ (IVc)

The procedure used was analogous to that in (m) except that $\mathrm{RhCl(CNEt)(S_2CNEt)(PPh_3)_2}$ (800 mg, 0.95 m mol) was used. The dark red product was obtained in 71.5% yield. Anal. Calcd. for $\mathrm{C_{43}H_{43}N_2ClIP_2S_2Rh}$: C, 51.71; H, 4.43; N, 2.85%. Found: C, 51.16; H, 4.74; N, 2.67%.

(p) Formation of $\mathrm{RhCl(CNPh)(PPh_3)_2(O_2)}$ (Va)

$\mathrm{RhCl(CNPh)(S_2CNPh)(PPh_3)_2}$ (500 mg, 0.53 m mol) was refluxed in toluene (40 ml) with triphenylphosphine (840 mg, 3.21 m mol) for 1 hr. The resultant yellow solution was concentrated to 10 ml and the light brown product was precipitated with petroleum ether, suction filtered, washed with petroleum ether and air dried Yield 310 mg (72.4%). Anal. Calcd. for $C_{43}H_{35}O_2NClP_2Rh$: C, 64.72; H, 4.42%. Found: C, 63.46; H, 4.85%.

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