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CYCLOPENTADIENYL- AND PENTAMETHYLCYCLOPENTADIENYL-RHODIUM(III) COMPLEXES CONTAINING ISOCYANIDE LIGANDS

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Summary

The complexes $[(\eta^5\text{-}C_5H_5)RhCl_2]_2$ and $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ react with stoichiometric amounts of isocyanide ligands L to give $(\eta^5\text{-}C_5H_5)RhLCl_2$ and $(\eta^5\text{-}C_5Me_5)RhLCl_2$ (L = CNC_6H_{11}, $CNC_6H_4CH_3\text{-}p$); an excess of ligand L reacts further with $(\eta^5\text{-}C_5Me_5)RhLCl_2$ to give the cationic complex $[(\eta^5\text{-}C_5Me_5)RhL_2Cl]^+$ which was isolated as tetraphenylborate salt. The cationic complexes $[(\eta^5\text{-}C_5Me_5)RhL(PPh_3)Cl]^+$ and $[(\eta^5\text{-}C_5Me_5)Rh(Ph_2PC_2H_4PPh_2)Cl]^+$ were obtained in the reaction of $(\eta^5\text{-}C_5Me_5)RhLCl_2$ with PPh_3 and $Ph_2PC_2H_4PPh_2$ respectively. Unidentified solids which do not contain the cyclopentadienyl moiety were obtained in the analogous reactions of $(\eta^5\text{-}C_5H_5)RhLCl_2$ with an excess of isocyanide or of tertiary phosphine.

The complexes $(\eta^5\text{-}C_5H_5)Rh(CNC_6H_{11})Cl_2$ and $(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})Cl_2$ react with SCN^- or $SeCN^-$ giving the corresponding dithiocyanate or diselenocyanate derivatives in which the pseudohalogen groups are S- or Se-bonded to the metal atom. The analogous reactions with C_6Cl_5MgCl gave the chiral complexes $(\eta^5\text{-}C_5H_5)Rh(CNC_6H_{11})(C_6Cl_5)Cl$ and $(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})(C_6Cl_5)Cl$.

The potentially chelating anion Ph_2PSS^- reacts with $(\eta^5\text{-}C_5H_5)Rh(CNC_6H_{11})Cl_2$ and $(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})Cl_2$ to give $(\eta^5\text{-}C_5H_5)Rh(CNC_6H_{11})(SSPPh_3)Cl$ and $(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})(SSPPh_2)Cl$ in which the dithio ligand acts as monodentate; these compounds react with MeI or EtI to give the dihalide derivatives and the esters Ph_2PSSMe and Ph_2PSSEt. The complex $[(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})(SSPPh_2)]Cl$ was obtained by refluxing a benzene solution of the corresponding neutral complex; the cyclopentadienyl derivative failed to give the analogous chelate complex.

The complexes $(\eta^5\text{-}C_5H_5)RhLCl_2$, $(\eta^5\text{-}C_5Me_5)RhLCl_2$ and $[(\eta^5\text{-}C_5Me_5)RhL_2Cl]^+$ (L = CNC_6H_{11}) were found to be unreactive towards amines.

Introduction

Substrates of rhodium(I) and rhodium(III) usually react with organic isocyanides to give cationic complexes [1]. The few examples of neutral rhodium(I) isocyanide complexes include $RhCl(CO)(CNR)_2$ (R = *p*-anysyl) [2], $Rh(PPh_3)_2(CNR)X$ (R = Me, t-Bu, *p*-tolyl; X = Cl, Br, I) [3—4] and $(\eta^5\text{-}C_5H_5)Rh(CO)(CNC_6H_{11})$ [5]; some neutral rhodium(III) isocyanide complexes have been obtained by oxidative addition to the $Rh(PPh_3)_2(CNR)X$ complexes [3—4].

We previously described [6—7] the preparation of some neutral chiral cyclopentadienyl-rhodium(III) and -iridium(III) complexes and we now report the preparation of neutral and cationic cyclopentadienyl- and pentamethylcyclopentadienyl-rhodium(III) complexes containing isocyanide ligand and the reactions of some of the neutral complexes with a variety of nucleophiles. This study included an investigation of the attack of nucleophiles on the coordinated isocyanide ligand in a rhodium(III) complex.

Experimental

The complexes $[(\eta^5\text{-}C_5H_5)RhCl_2]_2$ and $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ were prepared by published methods [8]. The organic cyanides were prepared from $COCl_2$ [9]. The salt $[Ph_2PSS][NH_4]$ was obtained as described by Higgins et al. [10]. Other chemicals were reagent grade and were used without purification. Infrared spectra were recorded with a Perkin—Elmer model 457 spectrometer using a polystyrene film for calibration. A Perkin—Elmer R24B at 60 MHz spectrometer was used to obtain ^1H NMR spectra. A conductivity meter WTW LBR was used for conductivity measurements. Elemental analyses were by Bernhardt Mikroanalytisches Laboratorium, Elbach über Engelskirchen, Germany.

All reactions were carried out under oxygen-free nitrogen, although this is probably unnecessary in most cases.

Analytical data for the prepared complexes are listed in Table 1; Table 2 shows the characteristic stretching frequencies and the ^1H NMR resonances.

Dichlorocyclohexylisocyanide(cyclopentadienyl)rhodium(III)

A solution of cyclohexyl isocyanide (0.186 g, 1.7 mmol) in dichloromethane was added dropwise to a well-stirred suspension of $[(\eta^5\text{-}C_5H_5)RhCl_2]_2$ (0.40 g, 0.84 mmol) in the same solvent. The mixture was stirred for 15 min. The solution was filtered and the solvent partially evaporated under reduced pressure. Addition of hexane gave a red-orange solid, which was filtered off, washed with hexane, and dried. Dichlorocyclopentadienyl(*p*-tolylisocyanide)rhodium(III) was similarly obtained.

Dichlorocyclohexylisocyanide(pentamethylcyclopentadienyl)rhodium(III)

To a solution of $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ (0.50 g, 0.82 mmol) in dichloromethane, cyclohexyl isocyanide (0.18 g, 1.64 mmol) in the same solvent was added dropwise. The progress of the reaction was followed by IR spectroscopy. The mixture was stirred for ca. 15 min, then filtered. The solvent was evaporated to a small volume and hexane added to give a red-orange solid. This was recrystallized from diethyl ether.

TABLE 1

ANALYTICAL DATA

Compound	Colour	Analysis (found (calcd.) (%))				
		C	H	N	Cl	S
$(\eta^5\text{-}C_5H_5)Rh(CNC_6H_{11})Cl_2$	Red-brown	41.51	4.68	3.96	20.29	
		(41.40)	(4.63)	(4.02)	(20.37)	
$(\eta^5\text{-}C_5H_5)Rh(CNC_6H_4CH_3\text{-}p)Cl_2$	Orange	43.66	3.38	3.87	20.02	
		(43.62)	(3.40)	(3.91)	(19.80)	
$(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})Cl_2$	Red-orange	48.75	6.21	3.22	16.67	
		(48.82)	(6.27)	(3.34)	(16.95)	
$(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_4CH_3\text{-}p)Cl_2$	Orange	51.24	5.06	3.32	16.47	
		(51.07)	(5.17)	(3.26)	(16.52)	
$[(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})_2Cl]BPh_4$	Yellow	71.24	6.73	3.17	4.48	
		(71.07)	(7.08)	(3.45)	(4.37)	
$[(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})(PPh_3)Cl]BPh_4$	Yellow	73.54	6.42	1.33	3.58	
		(73.49)	(6.37)	(1.45)	(3.67)	
$(\eta^5\text{-}C_5H_5)Rh(CNC_6H_{11})(SCN)_2$	Orange	42.71	4.13	10.71		16.16
		(42.76)	(4.10)	(10.68)		(16.28)
$(\eta^5\text{-}C_5H_5)Rh(CNC_6H_{11})(SeCN)_2$	Orange	34.37	3.29	8.71		
		(34.52)	(3.31)	(8.63)		
$(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})(SCN)_2$	Orange	49.06	5.72	9.11		13.66
		(49.23)	(5.65)	(9.06)		(13.85)
$(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})(SeCN)_2$	Orange	40.85	4.68	7.48		
		(40.95)	(4.70)	(7.54)		
$(\eta^5\text{-}C_5H_5)Rh(CNC_6H_{11})(C_6Cl_5)Cl$	Red-orange	38.21	2.92	2.56	37.58	
		(38.47)	(2.87)	(2.49)	(37.85)	
$(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})(C_6Cl_5)Cl$	Orange	43.62	4.20	2.14	33.54	
		(43.70)	(4.15)	(2.21)	(33.65)	
$(\eta^5\text{-}C_5H_5)Rh(CNC_6H_{11})(SSPPh_2)Cl$	Yellow-orange	55.64	5.16	2.49	6.56	12.36
		(55.76)	(5.07)	(2.71)	(6.86)	(12.40)
$(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})(SSPPh_2)Cl$	Red-orange	54.96	5.82	2.20	5.58	10.21
		(55.10)	(5.74)	(2.21)	(5.61)	(10.14)
$[(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})(SSPPh_2)]Cl$	Orange	55.22	5.86	2.19	5.49	10.18
		(55.10)	(5.74)	(2.21)	(5.61)	(10.14)
$[(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})(SSPPh_2)]BPh_4$	Orange	69.60	6.21	1.58		7.21
		(69.51)	(6.16)	(1.53)		(7.00)

TABLE 2

CHARACTERISTIC STRETCHING FREQUENCIES AND ^{1}H NMR RESONANCES

Compound	ν(CN) [a,b]	$\tau(\eta^5\text{-}C_5H_5)$ or $\tau(\eta^5\text{-}C_5Me_5)$ [c,d] (ppm)	Other IR bands
$(\eta^5\text{-}C_5H_5)Rh(CNC_6H_{11})Cl_2$	2220vs	4.20	295s, 275s ν(Rh—Cl)
$(\eta^5\text{-}C_5H_5)Rh(CNC_6H_4CH_3\text{-}p)Cl_2$	2185vs	4.14	285s, 270s ν(Rh—Cl)
$(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})Cl_2$	2200vs	8.32	290s, 275s ν(Rh—Cl)
$(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_4CH_3\text{-}p)Cl_2$	2180vs	8.28	295s, 270s ν(Rh—Cl)
$[(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})_2Cl]BPh_4$	2212vs	8.35	
$[(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})(PPh_3)Cl]BPh_4$	2210vs	8.07 [e]	285s ν(Rh—Cl)
$(\eta^5\text{-}C_5H_5)Rh(CNC_6H_{11})(SCN)_2$	2210vs	4.32	2115vs ν(CN)
$(\eta^5\text{-}C_5H_5)Rh(CNC_6H_{11})(SeCN)_2$	2205vs	4.24	2108vs ν(CN)
$(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})(SCN)_2$	2204vs	8.13	2115vs ν(CN)
$(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})(SeCN)_2$	2195vs	8.06	2108vs ν(CN)
$(\eta^5\text{-}C_5H_5)Rh(CNC_6H_{11})(C_6Cl_5)Cl$	2215vs	4.41	
$(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})(C_6Cl_5)Cl$	2195vs	8.30	
$(\eta^5\text{-}C_5H_5)Rh(CNC_6H_{11})(SSPPh_2)Cl$	2220vs	4.29	
$(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})(SSPPh_2)Cl$	2212vs	8.14	
$[(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})(SSPPh_2)]Cl$	2200vs	8.35	

[a] In nujol mull. [b] Of the isocyanide ligand. [c] In $CDCl_3$ solution relative to $SiMe_4$ as internal standard.
[d] As singlet. [e] Doublet, J(HP) 3 Hz.

A similar procedure gave dichloro(pentamethylcyclopentadienyl)(*p*-tolylisocyanide)rhodium(III).

Chlorobis(cyclohexylisocyanide)(pentamethylcyclopentadienyl)rhodium(III) tetraphenylborate

Method a. To a solution of (η^5-C_5Me_5)Rh(CNC_6H_{11})Cl_2 (0.22 g, 0.52 mmol) in dichloromethane (50 ml), a slight excess of CNC_6H_{11} (0.066 g, 0.6 mmol) was added, and the mixture was stirred for ca. 3 h. The solvent was evaporated, the residual oil treated with diethyl ether, and the crude product dissolved in methanol. Addition of a solution of $NaBPh_4$ in methanol to the complex in the same solvent gave a yellow solid. This was filtered off, washed with methanol and diethyl ether, and dried in air.

Method b. A solution of CNC_6H_{11} (0.30 g, 2.7 mmol) in dichloromethane (10 ml) was quickly added to one of [(η^5-C_5Me_5)$RhCl_2$]$_2$ (0.42 g, 0.68 mmol) in 70 ml of dichloromethane. After stirring at room temperature for 2 h, the solution was filtered, and the solvent partially removed under reduced pressure. Addition of heptane gave a solid, which was separated and dissolved in methanol. Addition of a solution of $NaBPh_4$ in the same solvent gave the pure product as a yellow solid.

Chlorocyclohexylisocyanide(pentamethylcyclopentadienyl)triphenylphosphinerhodium(III) tetraphenylborate

Triphenylphosphine (0.19 g, 0.72 mmol) was added to a solution of (η^5-C_5Me_5)Rh(CNC_6H_{11})Cl_2 (0.25 g, 0.60 mmol) in 50 ml of dichloromethane. The solution was gently warmed, set aside for 3 h and then filtered. The solvent was removed in vacuo and the solid washed several times with diethyl ether. The crude product was dissolved in methanol, and $NaBPh_4$ in methanol was added to give a yellow-orange solid. This was filtered off, washed with methanol and diethyl ether, and dried.

Reaction of (η^5-C_5Me_5)Rh(CNC_6H_{11})Cl_2 with 1,2-bis(diphenylphosphino)ethane

To a solution of (η^5-C_5Me_5)Rh(CNC_6H_{11})Cl_2 (0.32 g, 0.76 mmol) in dichloromethane (80 ml) 1,2-bis(diphenylphosphino)ethane (0.36 g, 0.90 mmol) was added with vigorous stirring. The progress of the reaction was followed by IR spectroscopy; coordinated and free isocyanide were characterized by ν(CN) at 2200 and 2140 cm^{-1}, respectively. When the IR spectrum showed no further variation, some more ligand (0.12 g, 0.3 mmol) was added, but no change was observed. The solvent was evaporated under reduced pressure and the residue washed several times with diethyl ether (to remove the excess of ligand) to give a yellow solid, which analysis showed to be a mixture (see text).

Preparation of (η^5-C_5H_5)Rh(CNC_6H_{11})(XCN)$_2$ and (η^5-C_5Me_5)Rh(CNC_6H_{11})(XCN)$_2$ ($X = S, Se$)

These complexes were all obtained in the same way and as an example we describe the preparation of (η^5-C_5Me_5)Rh(CNC_6H_{11})(SCN)$_2$.

KSCN (0.068 g, 0.70 mmol) was added to a solution of (η^5-C_5Me_5)Rh(CNC_6H_{11})Cl_2 (0.14 g, 0.33 mmol) in dichloromethane and the mixture was stirred for 1 h. The solution was filtered and the solvent removed in vacuo. The solid was recrystallised from diethyl ether to give the pure product as a red-orange solid.

The complexes $(\eta^5\text{-}C_5H_5)Rh(CNC_6H_{11})(XCN)_2$ (X = S, Se) were crystallised from benzene/hexane.

Preparation of $(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})(C_6Cl_5)Cl$ *and* $(\eta^5\text{-}C_5H_5)Rh(CNC_6H_{11})(C_6Cl_5)Cl$

These complexes were both prepared by the same method and as an example we describe the preparation of $(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})(C_6Cl_5)Cl$.

$(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})Cl_2$ (0.30 g, 0.7 mmol) was added to a tetrahydrofuran solution (30 ml) of pentachlorophenylmagnesium chloride, made as previously described [11] from hexachlorobenzene (0.43 g, 1.5 mmol) and dry magnesium turnings (0.037 g, 1.5 g-atoms). The mixture was stirred for 10 h, the solvent was removed in vacuo, and the residue dissolved in dichloromethane. The solution was transferred to a dichloromethane/hexane (1/1) packed column of alumina. Dichloromethane/hexane (1/1) elution removed a mixture of hexachlorobenzene and pentachlorobenzene. An orange band was eluted with acetone. Heptane (20 ml) was added and slow evaporation of the acetone/heptane solution gave the product as an orange solid.

Chloro(cyclohexylisocyanide)cyclopentadienyl(diphenyldithiophosphinato)-rhodium(III)

Ammonium diphenyldithiophosphinate (0.112 g, 0.42 mmol) was added to a solution of $(\eta^5\text{-}C_5H_5)Rh(CNC_6H_{11})Cl_2$ (0.14 g, 0.4 mmol) in benzene and the mixture stirred vigorously for ca. 4 h. The solution was filtered and the solvent evaporated off. The crude product was washed with small amounts of methanol, dried, and recrystallised from dichloromethane/pentane, to give a yellow-orange solid.

Chlorocyclohexylisocyanide(diphenyldithiophosphinato)pentamethylcyclopentadienylrhodium(III)

Ammonium diphenyldithiophosphinate (0.107 g, 0.40 mmol) was added to a dichloromethane solution of $(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})Cl_2$ (0.16 g, 0.38 mmol) and the mixture was stirred for ca. 30 min. The solution was filtered, the solvent evaporated off, and the residue extracted with diethyl ether. The solution was allowed to stand at room temperature and the orange crystals deposited were filtered off and dried.

Cyclohexylisocyanide(diphenyldithiophosphinato)pentamethylcyclopentadienylrhodium(III) chloride

A solution of $(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})(SSPPh_2)Cl$ in benzene was refluxed for ca. 12 h. The solvent was evaporated off and the crude product crystallised from dichloromethane/hexane.

The compound was also obtained as the tetraphenylborate salt by adding $NaBPh_4$ in methanol to a solution of $[(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})(SSPPh_2)]Cl$ in the same solvent.

Reactions of $(\eta^5\text{-}C_5H_5)Rh(CNC_6H_{11})(SSPPh_2)Cl$ and $(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})$-$(SSPPh_2)Cl$ with MeI and EtI

A suspension of $(\eta^5\text{-}C_5H_5)Rh(CNC_6H_{11})(SSPPh_2)Cl$ or $(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})$-$(SSPPh_2)Cl$ in MeI or EtI (4 ml) was stirred for ca. 4 h. The solvent was evaporated off and the crude product washed several times with hexane to give the corresponding dihalide derivatives. Evaporation of the hexane solution gave a white solid in each case the ^{1}H NMR and the elemental analyses of these products were consistent with the esters Ph_2PSSR (R = Me, Et).

Results and discussion

The complexes $[(\eta^5\text{-}C_5H_5)RhCl_2]_2$ and $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ react readily with stoichiometric amounts of isocyanide ligands at room temperature to give the derivatives $(\eta^5\text{-}C_5H_5)Rh(CNR)Cl_2$ and $(\eta^5\text{-}C_5Me_5)Rh(CNR)Cl_2$ (R = C_6H_{11}, p-$CH_3C_6H_4$), which can be isolated in high yield. They are red or red-orange, air-stable crystalline compounds, soluble in benzene and chlorinated solvents. In the infrared spectrum the ν(CN) band (Table 2) is higher in frequency by about 50—80 cm^{-1} than the free ligand value; the increase in the CN bond order of the coordinated isocyanide indicates that, in these complexes, the isocyanide ligand effectively reduces the positive charge on the rhodium atom, and so back-donation from the *d*-orbitals of the metal to the isocyanide ligand is relatively unimportant.

In the ^{1}H NMR spectra the cyclopentadienyl and pentamethylcyclopentadienyl resonances appear at ca. τ 4.2 and 8.2 ppm, respectively. These resonances are observed as singlets; the coupling with ^{103}Rh is apparently beyond the resolution of the spectrophotometer.

Compared to the carbonyl ligand in $(\eta^5\text{-}C_5H_5)Rh(CO)Cl_2$ and $(\eta^5\text{-}C_5Me_5)Rh$-$(CO)Cl_2$, the isocyanide ligand in $(\eta^5\text{-}C_5H_5)Rh(CNR)Cl_2$ or $(\eta^5\text{-}C_5Me_5)Rh(CNR)$-$Cl_2$ is more tightly bound to the metal and is far less easily displaced by other neutral ligands. When reaction with such a ligand takes place, displacement of chloride and formation of a cationic complex is in some cases observed. In contrast, the complex $(\eta^5\text{-}C_5H_5)Rh(CO)Cl_2$ could be detected only in solution under an atmosphere of CO; in the solid state, it changes to the starting $[(\eta^5\text{-}C_5H_5)$-$RhCl_2]_2$. The complex $(\eta^5\text{-}C_5Me_5)Rh(CO)Cl_2$ was isolated as a solid, but CO is easily displaced by neutral ligands such as tertiary phosphines. The existence of $(\eta^5\text{-}C_5H_5)Rh(CNR)Cl_2$ and $(\eta^5\text{-}C_5Me_5)Rh(CNR)Cl_2$ as relatively stable complexes reflects the greater ability of isocyanide ligand compared with carbon monoxide to stabilize high oxidation states of transition metals.

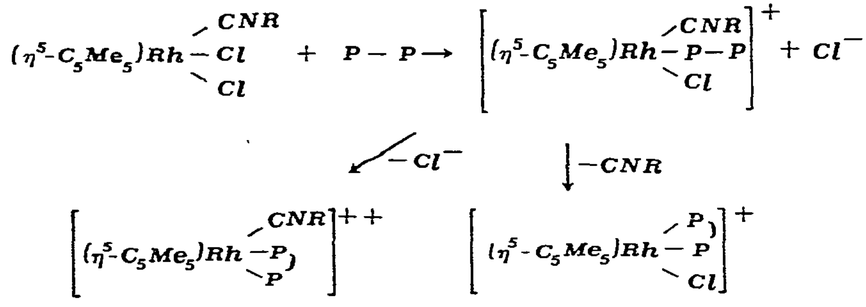
We have investigated in detail some reactions of the cyclohexyl isocyanide derivatives $(\eta^5\text{-}C_5H_5)Rh(CNC_6H_{11})Cl_2$ and $(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})Cl_2$ only, but very similar reactions were observed for the other isocyanide derivatives.

Addition of an excess of CNC_6H_{11} to a dichloromethane solution of $(\eta^5\text{-}C_5Me_5)$-$Rh(CNC_6H_{11})Cl_2$ leads to the formation of the cationic complex $[(\eta^5\text{-}C_5Me_5)Rh$-$(CNC_6H_{11})_2Cl]^+$, which can be isolated as its tetraphenylborate salt; this complex may also be prepared directly from $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ and an excess of the isocyanide ligand. The same reaction with $(\eta^5\text{-}C_5H_5)Rh(CNC_6H_{11})Cl_2$ or $[(\eta^5\text{-}C_5H_5)RhCl_2]_2$ leads to the formation of a brown solid, which does not contain the cyclopentadienyl ion. The complex $[(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})_2Cl]BPh_4$ is a yellow solid, soluble in acetone or chlorinated solvents, slightly soluble in benzene, and insoluble in ether or hydrocarbon; the ionic nature of the complex was confirmed by conductivity measurements in acetone. The IR spectrum in the ν(CN) stretching region shows a band at a frequency very close to those observed for corresponding neutral complex; in the ^{1}H NMR spectrum the methylcyclopentadienyl proton resonance occurs at τ 8.35 ppm i.e. at fields slightly higher than for the neutral derivatives.

The cationic mixed phosphine—isocyanide complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CNC}_6\text{H}_{11})(\text{PPh}_3)\text{Cl}]^+$ is formed by treating the neutral isocyanide complex with an excess of the tertiary phosphine in dichloromethane; the product can be obtained analytically pure as the tetraphenylborate. The IR spectrum shows the ν(CN) band at 2210 cm^{-1} and the NMR resonance for the pentamethylcyclopentadienyl group appears as a doublet at 8.07 (J(H—P) 3 Hz).

When a dichloromethane solution containing $(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CNC}_6\text{H}_{11})\text{Cl}_2$ and an excess of 1,2-bis(diphenylphosphino)ethane is allowed to stand at room temperature, a ν(CN) band at 2140 cm^{-1} appears in the IR spectrum while the intensity of the ν(CN) band of the starting complex decreases strongly. On addition of more ligand the IR spectrum does not change further. The ^{1}H NMR of the solid product isolated is essentially identical to that reported for $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)\text{Cl}]\text{PF}_2$ [8], and a weak ν(CN) band at 2210 cm^{-1} is present in the IR spectrum; this indicates that the ν(CN) band at 2140 cm^{-1} observed in the course of the reaction is due to released cyclohexyl isocyanide. The analytical data for the solid product differ slightly from those expected for $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)\text{Cl}]\text{Cl}$ and repeated analyses on different samples show the presence of a little nitrogen and we conclude that the solid is $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)\text{Cl}]\text{Cl}$ containing a small amount of an isocyanide complex. We were unable to separate the products, and precipitation by NaBPh$_4$ gave $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)\text{Cl}]\text{BPh}_4$ still containing the isocyanide complex, namely $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CNC}_6\text{H}_{11})(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)][\text{BPh}_4]_2$ *. Scheme 1 may account for the reaction. Initially the 1,2-bis(diphenylphosphino)ethane,

SCHEME I



P—P, acts as monodentate ligand to give a cationic complex similar to that observed in the reaction with triphenylphosphine; the subsequent chelation by the bidentate ligand leads preferentially to $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{P—P})\text{Cl}]\text{Cl}$ by

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* The formation of a binuclear complex in which the $\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2$ ligand bridges between rhodium atoms is unlikely in view of excess of ligand present [8].

displacement of the coordinated isocyanide. The by-product $[(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})(P\text{—}P)]^{2+}$ is formed in a chelation involving chloride displacement; this process is not preferred over the other because it leads to a dicationic complex.

Attempts to obtain dicationic tris-isocyanide complexes $[(\eta^5\text{-}C_5Me_5)Rh(CNR)_3[PF_6]$ by treating the solvate complex $[(\eta^5\text{-}C_5Me_5)Rh(acetone)_3][PF_6]_2$ [12] were unsuccessful, and mixtures of unidentifiable products were repeatedly obtained.

The complexes $(\eta^5\text{-}C_5H_5)Rh(CNC_6H_{11})Cl_2$ and $(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})Cl_2$ react with SCN^- or $SeCN^-$ to give the corresponding dithiocyanate or diselenocyanate derivatives, in which, as shown by IR spectra, the pseudohalogen groups are S- or Se-bonded to the metal. Other rhodium(III) complexes containing pseudohalogen groups S- or Se-bonded have recently been reported [13—14]. All attempts to obtain chiral complexes containing as coordinated anionic ligands the chloride and the thiocyanate or selenocyanate group failed.

The chiral complexes $(\eta^5\text{-}C_5H_5)Rh(CNC_6H_{11})(C_6Cl_5)Cl$ and $(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})(C_6Cl_5)Cl$ were obtained by treating the dihalogen derivatives with the Grignard reagent C_6Cl_5MgCl. The analogous reactions with C_6H_5MgBr gave the phenyl derivatives in an impure form because of a considerable hydrolysis. It is interesting to observe that compounds containing two σ-bonded organic ligands on the rhodium atom were formed in these reactions. This result is in agreement with Gardner and Rausch's preparation of rhodium—carbon σ-bonded complexes stabilized by strongly π-bonding ligands such as η^5-cyclopentadienyl and triphenylphosphine [15], but differs from that reported by Maitlis et al., who were able to obtain the derivative $(\eta^5\text{-}C_5Me_5)Rh(PPh_3)Me_2$ [8].

The potentially chelating anion diphenyldithiophosphinate Ph_2PSS^- reacts readily with $(\eta^5\text{-}C_5H_5)Rh(CNC_6H_{11})Cl_2$ and $(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})Cl_2$ complexes at room temperature to give compounds of formula $(\eta^5\text{-}C_5H_5)Rh(CNC_6H_{11})(SSPPh_2)Cl$ and $(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})(SSPPh_2)Cl$. The complexes are crystalline solids, soluble in benzene, diethyl ether and chlorinated solvents, and slightly soluble in methanol; they are monomers as indicated by molecular-weight measurements in benzene or dichloromethane, and non-conducting in benzene. Thus, in the prepared complexes the dithio ligand acts as a monodentate ligand.

The neutral complexes $(\eta^5\text{-}C_5H_5)Rh(CNC_6H_{11})(SSPPh_2)Cl$ and $(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})(SSPPh_2)Cl$ react with MeI or EtI to give, as final products, the dihalide derivatives, along with the esters Ph_2PSSMe or Ph_2PSSEt, which were isolated and characterized. Analogous reactions had been observed by us [16] for other substrates containing the dithio ligand coordinated to the metal as unidentate. A mechanism involving electrophilic attack of the alkyl group at sulphur, with formation of a labile cationic complex, followed by nucleophilic attack of iodide at the metal with displacement of the coordinated esters has been suggested [16].

The cationic chelate complex $[(\eta^5\text{-}C_5Me_5)Rh(CNC_6H_{11})(SSPPh_2)]Cl$ was obtained by refluxing a benzene solution of the corresponding neutral complex for several hours. Under the same conditions, the cyclopentadienyl derivative did not give the corresponding cationic chelate complex, and the unidentified product mixture did not contain the cyclopentadienyl moiety. The ionic nature of the chelate complex was confirmed by conductivity measurements in acetone, and by precipitation of the product as the tetraphenylborate salt.

The spectra of the corresponding neutral and cationic complexes show significant differences; the IR spectra differ considerably in the region in which absorptions due to the dithio ligand appear. Thus bidentate coordination is characterized by a very strong band at about 575 cm^{-1} and unidentate coordination by two very strong bands at 645 and 545 cm^{-1}. The chemical shift observed for the pentamethylcyclopentadienyl proton resonances was at higher fields for the cationic than for the neutral complex.

Coordinated isocyanide is susceptible to attack by nucleophiles, such as amines [17]. In the complexes $(\eta^5\text{-}C_5Me_5)Rh(CNR)Cl_2$ and $[(\eta^5\text{-}C_5Me_5)Rh(CNR)_2Cl]^+$ the carbon atom of the coordinated isocyanide is insufficiently electrophilic to react with amines, and no reaction was observed.

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