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SYNTHESIS AND STUDY OF NEW CARBONYL COMPLEXES OF RHODIUM(I) WITH (*S*,*S*)-DONOR LIGANDS AND TERTIARY PHOSPHINES

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Summary

The reaction of the dimeric diolefin-rhodium(I) chloride complexes with (*S*,*S*)-donor ligands gives complexes of the type [Rh(NBD)(R_2dtc)]. These react with carbon monoxide with displacement of the diolefin and formation of [Rh(R_2dtc)$(CO)_2$]. The carbon monoxide can be partly or completely replaced (depending upon the reaction conditions) by addition of triarylphosphines to yield complexes of the type [Rh(R_2dtc)(CO)(P(4-$XC_6H_4)_3$)] and [Rh(R_2dtc)(P(4-$XC_6H_4)_3)_2$].

Introduction

Few examples of the preparation of 1,1-dithiocarbamate-rhodium complexes are known. The reactions [1] of [Rh$(CO)_4Cl_2$] with several *N*,*N*-dialkyldithiocarbamate ions were studied by Cotton et al. They obtained dithiocarbamate-carbonyl derivatives in low yield. Wilkinson et al. [2,3] prepared compounds of the type [Rh$(Me_2dtc)_3$], [Rh$(R_2dtc)_3(PPh_3)$] (R = Et, Me), [Rh$(Me_2dtc)(PPh_3)_2$], [Rh$(Me_2dtc)(CO)(PPh_3)$], [Rh$(Et_2dtc)_2(PPh_3)_2$]BF_4 and [Rh$(CO)(PPh_3)(Me_2dtc)_3$]. In the most of the *N*,*N*-dialkyldithiocarbamate-rhodium complexes synthesized the oxidation state of the metal atom is III. The rhodium(I) complexes are less well known and their synthesis can give rise to products mixture.

In this paper we report the synthesis of the new *N*,*N*-dialkyldithiocarbamate-rhodium(I) complexes containing carbon monoxide along with phosphine ligands which can stabilize the compounds because of their π-acceptor capacity.

Results and discussion

[Rh(NBD)(R_2dtc)] complexes (R = Et, Me)

Addition of NaR_2dtc (R = Et, Me) to an acetone solution of the complex

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TABLE 1

ANALYTICAL DATA AND INFRARED ABSORPTION BANDS (cm^{-1})

Complex	Colour	Analysis (Found (calcd) (%))			ν(C≡O) (cm^{-1})	ν(CN) (cm^{-1})
		C	H	N		
Rh(NBD)(Et$_2$dtc)	yellow	41.75 (42.00)	5.10 (5.24)	3.70 (4.07)		1502vs
Rh(NBD)(Me$_2$dtc)	yellow	37.87 (38.10)	4.67 (4.44)	4.91 (4.44)		1505s
Rh(Et$_2$dtc)(CO)$_2$	orange	27.40 (27.70)	3.30 (3.50)	5.50 (5.20)	2062vs, 2000vs	1520s
Rh(Me$_2$dtc)(CO)$_2$	orange	21.50 (21.50)	2.20 (2.20)	4.80 (5.00)	2071vs, 2005vs	1545m
Rh(Et$_2$dtc)(CO)P(4-ClC$_6$H$_4$)$_3$	earth	44.45 (44.71)	3.80 (3.41)	2.10 (2.17)	1970vs	1496s
Rh(Et$_2$dtc)(CO)P(4-FC$_6$H$_4$)$_3$	earth	49.63 (48.42)	3.79 (3.69)	2.71 (2.35)	1965vs	1502sh
Rh(Et$_2$dtc)(CO)P(4-CH$_3$C$_6$H$_4$)$_3$	yellow	55.63 (51.37)	5.69 (4.91)	2.64 (2.21)	1960vs	1505sh
Rh(Et$_2$dtc)(CO)P(4-CH$_3$OC$_6$H$_4$)$_3$	yellow	50.81 (51.37)	5.40 (4.91)	2.82 (2.21)	1958vs	1508sh
Rh(Me$_2$dtc)(CO)P(4-ClC$_6$H$_4$)$_3$	yellow	43.12 (42.85)	3.19 (2.91)	2.27 (1.65)	1965vs	1525s
Rh(Me$_2$dtc)(CO)P(4-FC$_6$H$_4$)$_3$	earth	45.94 (46.58)	3.21 (3.17)	2.42 (2.46)	1962vs	1530s

$Rh(Me_2dtc)(CO)P(4\text{-}CH_3C_6H_4)_3$	yellow	55.16 (54.07)	5.14 (4.86)	2.26 (2.52)	1958vs	1525s
$Rh(Me_2dtc)(CO)P(4\text{-}CH_3OC_6H_4)_3$	yellow	48.60 (49.77)	4.49 (4.47)	2.71 (2.32)	1957vs	1530m
$Rh(Et_2)dtc)[P(4\text{-}ClC_6H_4)_3]_2$	yellow	49.12 (50.10)	3.45 (3.46)	1.41 (1.42)		1502w
$Rh(Et_2dtc)[P(4\text{-}FC_6H_4)_3]_2$	yellow	54.26 (55.71)	3.90 (3.84)	1.54 (1.58)		1498sh
$Rh(Et_2dtc)[P(4\text{-}CH_3C_6H_4)_3]_2$	yellow	65.10 (65.67)	5.90 (6.05)	1.50 (1.62)		1505sh
$Rh(Et_2dtc)[P(4\text{-}CH_3OC_6H_4)_3]_2$	yellow	58.32 (59.08)	5.49 (5.44)	1.40 (1.46)		1512sh
$Rh(Me_2dtc)[P(4\text{-}Cl\text{-}C_6H_4)_3]_2$	yellow	48.09 (47.23)	3.33 (3.14)	1.31 (1.46)		1520m
$Rh(Me_2dtc)[P(4\text{-}FC_6H_4)_3]_2$	yellow	54.53 (54.76)	3.71 (3.50)	1.76 (1.63)		1520s
$Rh(Me_2dtc)[P(4\text{-}CH_3C_6H_4)_3]_2$	yellow	64.30 (65.00)	5.60 (5.77)	1.50 (1.68)		1540m
$Rh(Me_2dtc)[P(4\text{-}CH_3OC_6H_4)_3]_2$	yellow	57.60 (58.27)	5.02 (5.17)	1.40 (1.50)		1530w

TABLE 2

^{1}H NMR SPECTRAL DATA FOR THE NEW COMPLEXES

	NBD protons	δ (ppm)	Dithiocarbamate protons			Phosphine protons	δ (ppm)
				δ (ppm)	J (Hz)		
Ph(NBD)(Et$_2$dtc)	CH$^+$, –CH	4.12 m	(CH$_3$)	1.22 t	7.2		
	CH$_2$	1.29 m	(CH$_2$)	3.80 q	7.2		
Rh(NBD)(Me$_2$dtc)	CH$^+$, CH	4.22 m	(CH$_3$)	3.20 s			
	CH$_2$	1.24 m					
Rh(Et$_2$dtc)(CO)P(4-ClC$_6$H$_4$)$_3$			(CH$_3$)	1.27 t	7.83	^{1}H aromatic	7.50–7.80 m
			(CH$_2$)	3.77 q	7.83		
Rh(Et$_2$dtc)(CO)P(4-FC$_6$H$_4$)$_3$			(CH$_3$)	1.07 t	6.75	^{1}H aromatic	6.27–6.60 m
			(CH$_2$)	3.32 q	6.75		6.62–7.12 m
Rh(Et$_2$dtc)(CO)P(4-CH$_3$C$_6$H$_4$)$_3$			(CH$_3$)	1.07 t	7.83	^{1}H aromatic	7.12–7.70 m
			(CH$_2$)	3.60 q		(4-CH$_3$)	2.65 s
Rh(Et$_2$dtc)(CO)P(4-CH$_3$OC$_6$H$_4$)$_3$			(CH$_3$)	1.27 t	6.75	^{1}H aromatic	6.88–7.13 m
			(CH$_2$)	3.75 q		(4-CH$_3$O)	3.75 s
Rh(Me$_2$dtc)(CO)P(4-ClC$_6$H$_4$)$_3$			(CH$_3$)	3.27 s		^{1}H aromatic	7.47–7.85 m
Rh(Me$_2$dtc)(CO)P(4-PF$_6$H$_4$)$_3$			(CH$_3$)	3.27 s		^{1}H aromatic	7.15–7.45 m
							7.52–7.90 m
Rh(Me$_2$dtc)(CO)P(4-CH$_3$C$_6$H$_4$)$_3$			(CH$_3$)	3.27 s		^{1}H aromatic	7.20–7.70 m
						(4-CH$_3$)	2.75 s
Rh(Me$_2$dtc)(CO)P(4-CH$_3$OC$_6$H$_4$)$_3$			(CH$_3$)	3.18 s		^{1}H aromatic	6.9–7.1 m
							7.4–7.7 m
						(4-CH$_3$O)	3.83 s
Rh(Et$_2$dtc)[P(4-ClC$_6$H$_4$)$_3$]$_2$			(CH$_3$)	0.93 t	7.83	^{1}H aromatic	7.17–7.55 m
			(CH$_2$)	3.37 q	7.83		7.57–7.92 m
Rh(Et$_2$dtc)[P(4-FC$_6$H$_4$)$_3$]$_2$			(CH$_3$)	1.02 t	9.0	^{1}H aromatic	6.90–7.97 m
			(CH$_2$)	3.37 q	9.0		
Rh(Me$_2$dtc)[P(4-ClC$_6$H$_4$)$_3$]$_2$			(CH$_3$)	2.78 s		^{1}H aromatic	7.1–7.75 m
Rh(Me$_2$dtc)[P(4-FC$_6$H$_4$)$_3$]$_2$			(CH$_3$)	2.75 s		^{1}H aromatic	6.7–7.7 m

$(RhCl(NBD))_2$ gives compounds of the type $[Rh(NBD)(R_2dtc)]$. The compounds are micro-crystalline, and soluble in acetone. Their analytical and infrared data are given in Table 1.

The IR spectra show a broad ν(CN) band centered in the range 1500–1505 cm^{-1}. This indicates that the canonical form [4] containing the C=N bond contributes significantly to the structure of the compounds and thus that the dialkyldithiocarbamate group is functioning as a bidentate ligand [2].

Table 2 lists the chemical shifts (δ, ppm) and coupling constants (J, Hz) for these complexes.

$[Rh(R_2dtc)(CO)L]$ complexes

Bubbling of carbon monoxide in atmospheric pressure through acetone solutions of $[Rh(NBD)(R_2dtc)]$ gives the $[Rh(R_2dtc)(CO)_2]$ complexes [1]. Addition of phosphorus donor ligands to a suspension of $[Rh(R_2dtc)(CO)_2]$ in acetone in 1/1 molar ratio gives monocarbonyl compounds of the type $[Rh(R_2dtc)(CO)L]$ ($L = P(4\text{-}XC_6H_4)_3$, X = Cl, F, CH_3, CH_3O). The IR spectra of these complexes show a band in the 1520–1495 cm^{-1} (R = Et) and 1530–1520 cm^{-1} (R = Me) region, which is assigned to the C⩦N stretching frequency [5,6]. The ν(CO) bands appear in the 1970–1950 cm^{-1} range which is indicative of a formal oxidation state of I for the rhodium atom. The ν(CO) frequency increases as the basicity of the phosphine is decreased.

The ^1H NMR spectra (Table 2) show peaks due to the phosphine ligands. The ethyl groups of the *N*,*N*-diethyldithiocarbamate ligand give a single resonance, and so the two groups are equivalent on the ^1H NMR time scale, as a result of free rotation around the C–N bond.

When R = Me the NMR spectra of the $[Rh(R_2dtc)(CO)L]$ ($L = P(4\text{-}XC_6H_4)_3$, X = Cl, F, CH_3, CH_3O) show only one single broad peak at δ 3.25 ppm for both CH_3 groups, and this can be attributed to the equivalence of the two methyl groups, but when the phosphine ligand is $P(4\text{-}FC_6H_4)_3$ or $P(4\text{-}CH_3OC_6H_4)_3$ a second peak is observed. This implies either that there is a partial decomposition of these compounds on dissolution or that the rotation about the C–N bond is restricted because of its multiple bond character.

All the complexes, are relatively stable in air at room temperature, and soluble but unstable in ordinary solvents. Elemental analyses (carbon, hydrogen and nitrogen) and infrared absorption bands are listed in Table 1.

$[Rh(R_2dtc)L_2]$ complexes

Addition of an excess of the phosphine $P(4\text{-}XC_6H_4)_3$ (X = Cl, F) to an acetone solution of $[Rh(R_2dtc)(CO)_2]$ leads to the complete replacement of the carbonyl groups. Use of more basic phosphines $P(4\text{-}XC_6H_4)_3$ (X = CH_3, CH_3O) does not lead to complete substitution of the carbonyl groups, indicating that the reaction occurs via a pentacoordinate intermediate. It is neccessary to expose the reaction mixture to UV light to bring about complete replacement of the second carbonyl group.

The infrared spectrum of all these complexes shows a ν(CN) band or a shoulder in the 1500–1540 cm^{-1} region [2].

The characteristic ^1H NMR resonances of these complexes are summarized in Table 2. They could not be observed in all the cases because some of the complexes quickly decompose in solution. These spectra show the signals of the phosphine ligand.

When R = Et the spectra show one set of signals from the CH_3 protons and one set from the CH_2 protons, indicating the equivalence of the two ethyl groups. As in the case of the [Rh(R_2dtc)(CO)L] complexes, except for L = P(4-FC_6H_4)$_3$, when R = Me the spectrum shows only one singlet due to CH_3 groups, and this can be attributed either to partial decomposition or to restricted rotation around the C–N bond.

The compounds are relatively air-stable, soluble and unstable in common solvents. The analytical and infrared spectral data are listed in Table 1.

Experimental

The IR spectra were recorded on a Perkin–Elmer 325 spectrophotometer (over the 4000–200 cm^{-1} range) using KBr discs. The ^1H nuclear magnetic resonance (NMR) spectra were recorded on a Perkin–Elmer R-12 apparatus at 60–90 MHz. Conductance measurements performed with 3×10^{-4} *M* acetone solution with a Radiometer Copenhagen CDC 104 conductimeter.

All reactions were carried out under dry nitrogen and the solvents were distillated before use.

Preparation of [Rh(NBD)(R_2dtc)] complexes

The complex [RhCl(NBD)]$_2$ reacts at room temperature in acetone under nitrogen with a stoichiometric amount of R_2dtcNa (R = Et, Me). After stirring for 1 h, the solution was filtered to remove NaCl and the filtrate evaporation under vacuum. The yellow solid obtained was washed with degassed water and dried in vacuo.

Preparation of [Rh(R_2dtc)(CO)$_2$] complexes

Carbon monoxide was bubbled through a solution of the complex [Rh(NBD)(R_2dtc)] in acetone at room temperature. The colour of the solution changed from yellow to orange. The bubbling of carbon monoxide was continued in order to concentrate the solution. The residue was recrystallized from n-pentane [4].

Preparation of [Rh(R_2dtc)(CO)(P(4-XC_6H_4)$_3$)] complexes

A stoichiometric amount of P(4-XC_6H_4)$_3$ (X = Cl, F, CH_3, CH_3O) was added to an acetone suspension of the [Rh(R_2dtc)(CO)$_2$] complex. The mixture was stirred for 1 h at room temperature, then evaporated under vacuum until an oil or oily solid separated. The product was recrystallized from acetone by addition of diethyl ether/n-hexane, and dried under vacuum.

Preparation of [Rh(R_2dtc)P(4-XC_6H_4)$_3$)$_2$] complexes

An excess of P(4-XC_6H_4)$_3$ (X = Cl, F) was added to an acetone solution of [Rh(R_2dtc)(CO)$_2$] and the solvent was then partially evaporated off under vacuum. The complexes were precipitated by addition of a mixture of diethyl ether and n-hexane. The yellow solid was filtered of, washed with hexane, and dried under vacuum over P_2O_5.

When the triarylphosphine was P(4-$CH_3C_6H_4$)$_3$ or P(4-$CH_3OC_6H_4$)$_3$ the reaction mixture had to be irradiated with UV light for 4.5 h to give the complexes free from carbon monoxide. The volume was subsequently reduced by evaporation under vacuum and the product was precipitated by addition of benzene/dichloromethane (1/1 v/v) and diethyl ether. The yellow solid so formed was filtered off, washed with n-hexane, and dried under vacuum.

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