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Rhodium(I) complexes with aromatic diamines

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Abstract

The reaction of $[\{Rh(L_2)Cl\}_2]$ ($L_2 \equiv$ *cyclo*-octa-1,5-diene (COD), norbornadiene (NBD)) and 3,4-diaminotoluene (dat), 1,2-diaminobenzene (daphen) or 2,3-diaminopyridine (dapy), irrespective of the stoichiometric ratios employed, gave $[Rh_2(COD)_2Cl_2(LL)]$ or pentacoordinate $[Rh(Cl)(NBD)(LL)]$ when LL ≡ dat or daphen, and tetracoordinate [Rh(Cl)(diolefin)(LL)] when LL ≡ dapy, bonded through the pyridine nitrogen. Mixtures of $[\{Rh(CO)_2Cl\}_2]$ and LL(1/1) gave $[Rh(CO)_2(LL)][Rh(CO)_2Cl_2]$ when LL ≡ dat, daphen or dapy. In solution, $[Rh_2(COD)_2Cl_2(LL)]$ or $[Rh(Cl)(NBD)(LL)]$ is in equilibrium with the corresponding $[Rh(L_2)(LL)]^+$ cations. At low temperature, the cationic species becomes predominant. Dapy is usually monodentate through the pyridine nitrogen if a coordinating anion, such as chlorine, is present. If not, chelate coordination through both amino groups occurs.

1. Introduction

Recently, we reported the reactions of chloro-bridged rhodium dimers $[\{Rh(L_2)Cl\}_2]$ ($L_2 \equiv$ cyclo-octa-1,5-diene(COD), norbornadiene (NBD)) with aliphatic diamines (LL) [1,2] that give ionic $[Rh(L_2)(LL)][Rh(L_2)Cl_2]$, pentacoordinate $[Rh(L_2)(LL)Cl]$ or neutral tetracoordinate $[Rh(L_2)(LL)Cl]$ compounds, depending on the ligand and/or the stoichiometric ratios employed. These complexes undergo various association or dissociation equilibria in solution. We now report the reactions of the chloro-bridged rhodium dimers with aromatic diamines, such as 1,2-diaminobenzene and related compounds.

The high catalytic activity of rhodium carbonyl–aromatic diamine systems for the selective reduction of aromatic nitrocompounds to amines has been reported [3,4]. On complexation, diamines may lose hydrogen and transform into anionic groups that can chelate or bridge [5–7]. Rhodium compounds with such anionic derivatives have been described [6], though the corresponding diolefinic or carbonylated compounds were obtained when using starting materials containing hydrogen-abstracting groups (2,4-pentanedionate or MeO) [8,9]. 1,2-Diaminobenzene has been reported to remain neutral when reacting with $[\{Rh(COD)Cl\}_2]$ [10] or $[Rh(CO)_2Cl_2]^-$ [11].

In the present paper, we describe the reaction of $[\{Rh(L_2)Cl\}_2]$ ($L_2 \equiv$ COD, NBD; L ≡ CO) with aromatic diamines (LL). Different products are obtained depending on the nature of L_2 or LL and irrespective of the stoichiometric ratios employed. When L ≡ CO, complex salts are obtained with Rh/LL ratios of 2/1. The solution behaviour of the different complexes is described.

2. Results and discussion

Reactions of aromatic diamines (LL), such as 1,2-phenylenediamine (daphen), 3,4-diaminotoluene (dat) or 2,3-diaminopyridine (dapy), with $[\{Rh(L_2)Cl\}_2]$ ($L_2 \equiv$ COD, NBD, L ≡ CO) yield different products depending on LL or L_2. These reactions are summarized in Scheme 1. Table 1 contains analytical and physical data of the corresponding compounds and of $[Rh(L_2)LL]ClO_4$ ($L_2 \equiv$ COD, L ≡ CO) prepared for comparison (see Section 3).

It follows that reaction of $[\{Rh(COD)Cl\}_2]$ with dat (Rh/LL = 2/1 or 1/1) gives $[Rh_2(COD)_2Cl_2(dat)]$, which may be either dinuclear with LL bridging groups or ionic, *i.e.* $[Rh(COD)(LL)]^+[Rh(COD)Cl_2]^-$. Its IR spectrum (Table 2) indicates coordination through both the amine groups and shows bands in the far IR owing to Rh–Cl stretching vibrations. The displacement of

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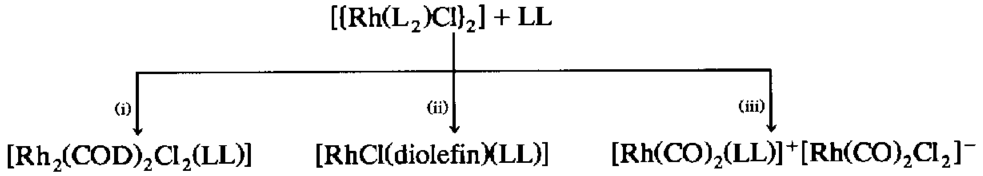


Scheme 1. (i) LL ≡ dat, daphen; L$_2$ ≡ COD, (ii) LL ≡ daphen; L$_2$ ≡ NBD; LL ≡ dapy; L$_2$ ≡ COD, NBD. (iii) LL ≡ dat, daphen, dapy; L$_2$ ≡ CO.

TABLE 1. Analytical and physical data for the complexes

Compound	Analysis found (calc.) (%)			Λ_M (Ω^{-1} cm^{-2} mol^{-1})	Colour	Yield (%)
	C	H	N			
[Rh$_2$(COD)$_2$Cl$_2$(dat)]	44.92	5.66	4.40	< 10 [a], 84 [b]	Yellow	43
	(44.86)	(5.52)	(4.54)			
[Rh(NBD)(daphen)Cl]	45.12	4.48	7.59	< 10 [a], 66 [b]	Yellow	34
	(46.11)	(4.76)	(8.27)			
[Rh(COD)(dapy)Cl]	43.71	5.19	11.48	< 10 [a], 56 [b]	Yellow	58
	(43.86)	(5.34)	(11.81)			
[Rh(NBD)(dapy)Cl]	42.51	4.41	11.19	< 10 [a], 58 [b]	Yellow	56
	(42.44)	(4.45)	(12.37)			
[Rh(CO)$_2$(daphen)][Rh(CO)$_2$Cl$_2$]	24.51	1.67	5.52	70 [a]	Dark green	70
	(24.15)	(1.61)	(5.64)			
[Rh(CO)$_2$(dapy)][Rh(CO)$_2$Cl$_2$]	21.87	1.45	7.73	54 [a]	Red	56
	(21.69)	(1.41)	(8.43)			
[Rh(CO)$_2$(dat)][Rh(CO$_2$)$_2$Cl$_2$]	26.42	2.05	5.57	78 [a]	Dark green	65
	(25.84)	(1.96)	(5.48)			
[Rh(COD)(daphen)]ClO$_4$	39.84	4.81	6.54	136 [a]	Yellow	83
	(40.14)	(4.78)	(6.69)			
[Rh(COD)(dapy)]ClO$_4$	36.22	4.29	10.05	143 [a]	Yellow	66
	(37.19)	(4.53)	(10.01)			
[Rh(COD)(dat)]ClO$_4$	40.94	4.85	6.54	108 [a]	Yellow	50
	(41.61)	(5.08)	(6.47)			
[Rh(CO)$_2$(daphen)]ClO$_4$	26.17	2.14	7.65	152 [a]	Yellow	80
	(26.19)	(2.18)	(7.64)			
[Rh(CO)$_2$(dat)]ClO$_4$	27.75	2.55	7.02	57 [b]	Green	72
	(28.40)	(2.63)	(7.36)			

Conductivity measurements were carried out in [a] acetone or [b] methanol solutions of about 2.5 × 10^{-4} M.

TABLE 2. Selected IR [a] data for isolated compounds (cm^{-1})

Compound	ν(N–H)	py	ν(C≡O)	ν(Rh–Cl)
[Rh$_2$(COD)$_2$Cl$_2$(dat)]	3180m, 3150m, 3080m			270m
[Rh(COD((dat)]ClO$_4$	3265m, 3220m, 3190sh			
[Rh(CO)$_2$(dat)][Rh(CO)$_2$Cl$_2$]	3160broad		2100s, 2075m, 2030s, 1995w	320m, 280m
[Rh(CO)$_2$(dat)]ClO$_4$	3250s, 3200w, 3120m		2100s, 2040s	
[Rh(COD)(daphen)]ClO$_4$	3280s, 3220s, 3180m			
[Rh(NBD)(daphen)Cl]	3195sh, 3125m			310m
[Rh(CO)$_2$(daphen)][Rh(CO)$_2$Cl$_2$]	3200m, 3130m		2210s, 2100s, 2020s, 1990s	305w, 270w
[Rh(CO)$_2$(daphen)]ClO$_4$	3270s, 3210s, 3120m		2100s, 2040s	
[Rh(COD)(dapy)Cl]	3400s, 3330m, 3305m, 3260m	1615m		250w
[Rh(NBD)(dapy)Cl]	3400s, 3330m, 3310sh, 3245m	1615m		265w
[Rh(COD)(dapy)]ClO$_4$	3330m, 3220m, 3140m	1600m		
[Rh(CO)$_2$(dapy)][Rh(CO)$_2$Cl$_2$]	3290s, 3260sh, 3140m	1605m	2100s, 2070m, 2049m, 2020s	310m, 280m

[a] Nujol mulls.

the corresponding ν(N–H) vibrations towards lower frequencies is larger than that observed for cationic [Rh(COD)(dat)]ClO$_4$ and may be due to intramolecular N–H ··· /Cl bonding. Furthermore, the conductivity in acetone is very low. All these data suggest dimer formation, similar to that suggested for [Rh$_2$(COD)$_2$-Cl$_2$(daphen)] on spectroscopic grounds [10], but its insolubility or easy decomposition in most solvents has prevented molecular weight determinations. In more ionizing solvents, such as methanol, [Rh$_2$(COD)$_2$Cl$_2$-(LL)] (LL ≡ dat, daphen) behaves as 1 : 1 electrolyte, suggesting an ionic nature [Rh(COD)-(LL)]$^+$[Rh-(COD)Cl$_2$]$^-$.

Solutions of similar complexes containing other bidentate N-donors have been reported to contain the dinuclear compound and the ionic form in equilibrium [2,12,13]. Therefore, we undertook a ^{1}H NMR study at variable temperature of [Rh$_2$(COD)$_2$Cl$_2$(LL)] (LL ≡ daphen, dat). Owing to the insolubility of these compounds in most deuterated solvents, spectra were obtained from methanol-d_4 solutions, where the NH$_2$ signal is masked by solvent resonances. The spectra indicate an equilibrium (Table 3). At room temperature, the dat compound shows two signals of equal intensity for the olefinic protons and three signals for the methylenic protons, which indicates the presence of two different COD groups. These signals are broad probably because of the exchange of the Rh(COD) unit between the cationic and anionic species. On lowering the temperature, the signals at 4.35 and 1.97 ppm, that correspond to the cationic [Rh(COD)(dat)]$^+$ species increase in intensity (Fig. 1). Because the signals of lower intensity must correspond to the starting dimer [{Rh(COD)Cl}$_2$] which has low solubility in methanol, these results can be rationalized in terms of equilibrium, as shown in Scheme 2, probably through intermediate dinuclear species. The relative intensities show that the equilibrium lies largely on the right-hand side at low temperatures.

The daphen complex shows a similar behaviour, but the exchange is much faster at room temperature. Only one signal is observed for the olefinic protons at 4.29 ppm, while two signals (2.47 and 1.91 ppm) are observed for the methylene protons. At −40°C, the 4.29 and 1.91 ppm resonances split into two signals of different intensities at 4.34 and 4.16 ppm, and 1.98 and 1.78 ppm respectively (Fig. 2). The more intense signals correspond to [Rh(COD)(daphen)]$^+$ species, and the signals of lower intensity correspond to the starting dimer. If more ligand was added to these solutions and Rh/LL = 1/1 ratios were attained, only the signals due to the cations were observed.

[{Rh(NBD)Cl}$_2$] gives different products on its reaction with these ligands. Its reaction with daphen gives

TABLE 3. Selected ^{1}H-NMR data

Compound	Temperature (°C) (solvent)	NH$_2$	Ph	CH$_3$	HC=	$HC\leqslant$	H$_2$C <
[Rh$_2$(COD)$_2$Cl$_2$(dat)]	16 (Methanol-d_4)	–	7.1	2.31	435; 4.18		2.44; 1.96, 1.80
	−40 (Methanol-d_4)	–	7.05	2.31	435; 4.16		2.44; 1.97, 1.78
[Rh(COD)(dat)]ClO$_4$	16 (Methanol-d_4)	–	7.10	2.36	4.35		2.44; 1.99
	16 (Acetone-d_6)	5.87	7.10	2.30	4.50		2.41; 1.97
	−40 (Acetone-d_6)	6.05	7.20	2.28	4.46		2.37; 1.94
[Rh(CO)$_2$(dat)]ClO$_4$	16 (Acetone-d_6)	6.98	7.30	2.38			
	−40 (Acetone-d_6)	7.15	7.30	2.39			
[Rh$_2$(COD)$_2$Cl$_2$(daphen)]	16 (Methanol-d_4)	–	7.22		4.29		2.47; 1.91
	−40 (Methanol-d_4)	–	7.2		4.34; 4.16		2.44; 1.98, 1.70
[Rh(COD)(daphen)]ClO$_4$	16 (Methanol-d_4)	–	7.23s		4.38		2.44; 1.98
	16 (Acetone-d_6)	5.93	7.30		4.50		2.46; 1.98
	−40 (Acetone-d_6)	6.16	7.30		4.49		2.41; 1.95
[Rh(Cl)(NBD)(daphen)]	16 (Acetone-d_6)	–	7.05		3.93	3.68	1.19
	−40 (Acetone-d_6)	5.06	6.75		3.67		1.13
	16 (Methanol-d_4)	–	7.15		4.24	3.95	1.32
	−40 (Methanol-d_4)	–	7.19		4.26	3.97	1.35
[Rh(CO)$_2$(daphen)]ClO$_4$	16 (Acetone-d_6)	7.06	7.50				
	−40 (Acetone-d_6)	7.24	7.40				
[Rh(COD)(dapy)Cl]	16 (Acetone-d_6)	6.15	7.47; 6.93; 6.58		4.64		2.52; 1.88
	−40 (Acetone-d_6)	6.35	7.62; 6.90; 6.57		4.48		2.48; 1.85
	16 (Methanol-d_4)	–	7.23; 6.22		4.30; 4.13		2.44; 1.90
	−40 (Methanol-d_4)	–	7.23; 6.22		4.28; 4.07		2.37; 1.90
[Rh(COD)(dapy)]ClO$_4$	16 (Acetone-d_6)	6.40; 5.78	7.44; 6.32		4.32; 4.24		2.37; 1.89
	−40 (Acetone-d_6)	6.64; 6.01	7.49; 6.35		4.30; 4.20		2.32; 1.88

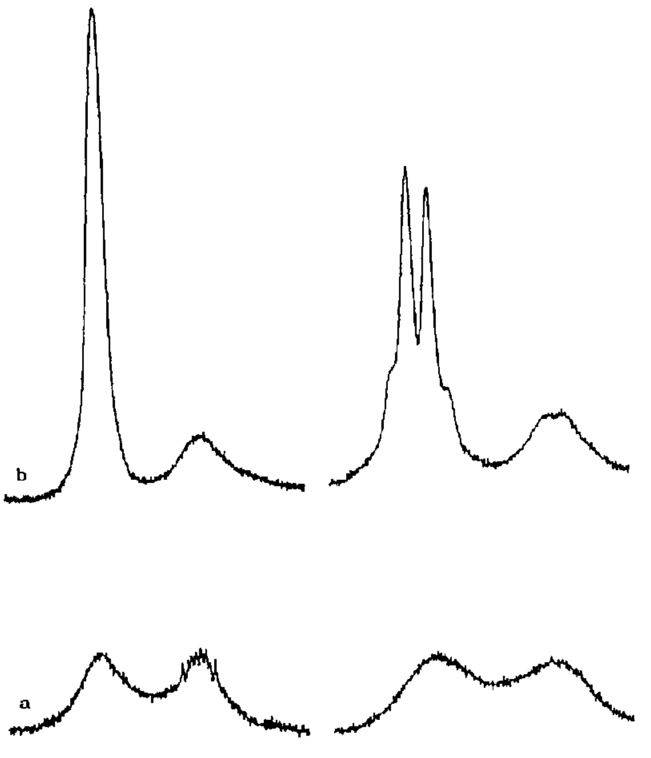


Fig. 1. ^{1}H NMR spectra of [$Rh_2(COD)_2Cl_2$(dat)] in methanol-d_4: (a) temperature +16°C; (b) temperature −40°C.

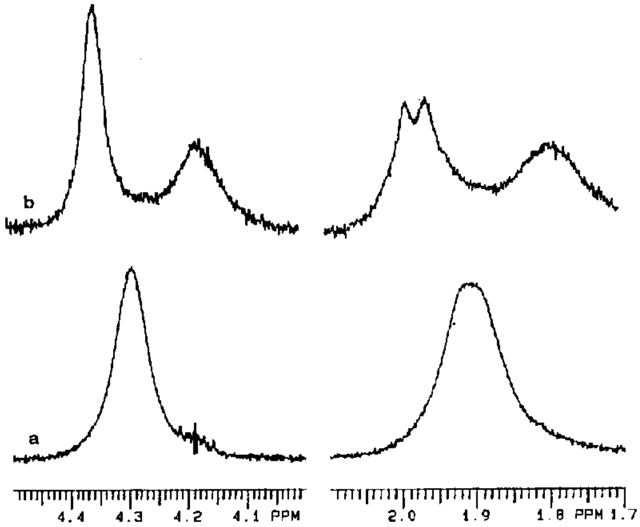
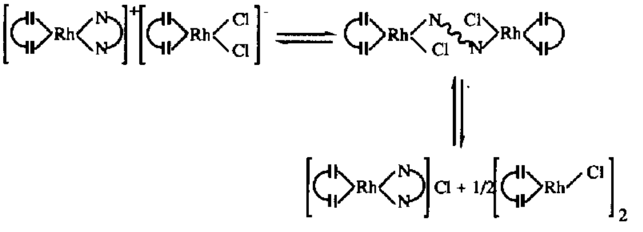


Fig. 2. ^{1}H NMR spectra of [$Rh_2(COD)_2Cl_2$(daphen)] in methanol-d_4: (a) temperature +16°C; (b) temperature −40°C.

only pentacoordinate [Rh(Cl)(NBD)(daphen)] and, therefore, requires a stoichiometric ratio Rh/LL of 1/1 for all the starting dimer to react; NBD is known to give pentacoordinate complexes. The IR spectrum, showing ν(N–H) and ν(Rh–Cl) of the ligands, confirms this pentacoordination in the solid state. The compound is a non-electrolyte in acetone. Nevertheless, the ^{1}H NMR spectrum in acetone solution at room temperature shows one broad signal at 3.93 ppm for the olefinic protons and one broad signal at 3.68 ppm for the $\geqslant$C–H protons of NBD. The equilibrium could involve rapid chlorine dissociation and, at −40°C, the olefinic resonance is only a sharp singlet at 3.67 ppm. The signal due to the $\geqslant$C–H resonance is probably masked by the acetone resonance at 3.35 ppm. As expected, in methanol solution chloride ionization is complete at room temperature, as indicated by conductivity measurements and ^{1}H NMR spectra (Table 3).

We thought it interesting to compare these simple aromatic diamines with 2,3-diaminopyridine that may coordinate via the pyridine and monodentate, the amines and bidentate, or both. Prior studies with 2,6-diaminopyridine [18] have shown a preference for monodentate coordination through the pyridine nitrogen. There is no possibility of chelating diamine coordination. In our case, [{Rh(L_2)Cl}$_2$]/dapy = 1/1 or 1/2 mixtures (L_2 ≡ COD, NBD) yield neutral tetracoordinate compounds in the solid state. Their IR spectra (Table 2) show ν(Rh–Cl) in the far IR and no displacement of amine stretching vibrations towards lower frequencies, showing these groups to be uncoordinated. The characteristic pyridine vibration around 1600 cm^{-1} appears slightly shifted towards higher frequencies, indicating coordination [15]. Furthermore, the cationic [Rh(COD)(dapy)]ClO_4, that must have chelate coordination through the two amino groups, shows displacement of the ν(N–H) vibration, while the pyridine stretching band remains unaltered. We conclude that 2,3-diaminopyridine prefers monodentate pyridine coordination when a coordinating anion, such as a chloride, is available, but when the anion has a low coordinating tendency, chelation is preferred. [Rh(COD)(dapy)]ClO_4 is a 1/1 electrolyte, while [Rh(Cl)(diolefin)(dapy)] are non-electrolytes in acetone solution. In methanol solution, [Rh(Cl)(diolefin)(dapy)] behaves as 1 : 1 electrolyte, and probably coordination changes to the chelate form. ^{1}H NMR spectra confirm these con-



Scheme 2.

clusions. In acetone-d_6, [Rh(COD)(dapy)]ClO_4 shows two signals for the olefinic protons mutually *trans* to the different amino groups, which also show two different resonances. In contrast, Rh(Cl)(COD)(dapy) shows only one signal for all olefinic protons and one signal for the amino groups—this must be due to an equilibrating process, probably through ligand dissociation. In methanol-d_4, two signals for the olefinic protons of the cation $[Rh(COD)(dapy)]^+$ in Rh(COD(dapy)(Cl) are observed, but the NH_2 signals are masked by the solvent. The spectra are invariable in the range −40°C to +16°C.

While the reaction of $[\{Rh(diolefin)Cl\}_2]$ with these aromatic diamines preferably gives neutral compounds that dissociate into ionic species in methanol solution, $[\{Rh(CO)_2Cl\}_2]$ with Rh/LL = 2/1 yields ionic $[Rh(CO)_2(LL)][Rh(CO)_2Cl_2]$ complexes (see Scheme 1). These compounds also can be obtained by displacement of COD by CO from $[\{Rh(COD)Cl\}_2]$/LL (1/1). The complexes obtained show four bands in the ν(C≡O) region, *i.e.* two due to the cation and two due to the anion, along with stretching vibration bands of the bidentate diamines and the expected ν(Rh–Cl). They behave as 1 : 1 electrolytes in acetone solution, though the conductivity values are slightly low owing to cation–anion association. The compounds are dark in the solid state but give yellow solutions, suggesting cation–anion interaction in the solid state, possibly through stacking [1,16,17]. We are trying to grow crystals suitable for X-ray diffraction studies. Thus, dapy along with dat and daphen coordinate as chelates through the diamine groups. Also, this behaviour is similar to that of aliphatic diamines [1,2] and probably is promoted by the high stability of the $[Rh(CO)_2Cl_2]^-$ anion.

These complexes are almost insoluble in organic solvents. To obtain ^1H NMR spectra we prepared $[Rh(CO)_2LL]ClO_4$ compounds by displacement of COD from the corresponding $[Rh(COD)LL]ClO_4$ complexes. These were measured in acetone-d_6 (Table 3) and show the highest displacement towards lower fields of the NH_2 resonance, indicating that the solvent–solute interaction is highest in these compounds containing more π-acceptor CO groups.

3. Experimental details

The preparation of the metal complexes was carried out at room temperature under dinitrogen by standard Schlenk techniques. $[\{Rh(L_2)Cl\}_2]$ [18–20], $[Rh(COD)_2]ClO_4$ [21] and $[Rh_2(COD)_2Cl_2(daphen)]$ [10] were prepared as previously reported.

Microanalyses were carried out with a Perkin–Elmer 240C microanalyser. The conductivities were measured in acetone or methanol solutions with a Metrohm E 518 conductimeter. The IR spectra were recorded with a Perkin–Elmer 598 spectrophotometer in the range 4000–200 cm^{-1} using Nujol mulls between polyethylene sheets. Nuclear magnetic resonance (NMR) spectra were recorded with an XL-300 Varian spectrometer, ^1H (TMS internal standard) spectra were measured from acetone-d_6 or methanol-d_4 solutions at variable temperature in 5 mm tubes.

3.1. Preparation of $[Rh_2(COD)_2Cl_2(dat)]$

To a solution of $[\{Rh(COD)Cl\}_2]$ (0.06 mmol) in CH_2Cl_2 was added an equimolar amount (0.06 mmol) of 3,4-diaminotoluene, upon which a yellow compound was obtained, filtered off, washed with dichloromethane and vacuum dried.

3.2. Preparation of [Rh(diolefin)(LL)Cl]

To a solution of $[Rh(diolefin)Cl]_2$ (0.06 mmol) in benzene or CH_2Cl_2 was added the stoichiometric amount (0.12 mmol) of the corresponding donor LL, upon which the yellow complexes that precipitated were filtered off, washed with the solvent and vacuum dried.

3.3. Preparation of $[Rh(CO)_2(LL)][Rh(CO)_2Cl_2]$

(i) To a solution of $[\{Rh(CO)_2Cl\}_2]$ (0.06 mmol) in CH_2Cl_2 was added the stoichiometric amount (0.06 mmol) of the required ligand donor LL, upon which the corresponding dark complexes which precipitated were filtered off, washed with dichloromethane and vacuum dried.

(ii) Carbon monoxide at room temperature was bubbled for 30 min through dichloromethane or diethyl ether suspensions of equimolar amounts of $[\{Rh(COD)Cl\}_2]$ (0.06 mmol) and LL ≡ dat. The colour darkened and the complexes were filtered off, washed with solvent and vacuum dried.

3.4. Preparation of $[Rh(COD)(LL)]ClO_4$

These complexes were prepared by adding a slight excess of LL (0.15 mmol) to a solution of $[Rh(COD)_2]ClO_4$ (0.12 mmol) in CH_2Cl_2. The yellow products which precipitated immediately were filtered off, washed with diethyl ether and vacuum dried.

3.5. Preparation of $[Rh(CO)_2(LL)]ClO_4$

Carbon monoxide at room temperature was bubbled for 30 min through a dichloromethane suspension of the corresponding $[Rh(COD)(LL)]ClO_4$ compound (0.09 mmol), during which colour intensification (LL ≡ daphen) or darkening (LL ≡ dat) occurred. The complexes were filtered off, washed with diethyl ether and vacuum dried.

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