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Four-co-ordinate Rhodium(I) Complexes $[\{Rh(CO)_2Cl\}_n(\alpha\text{-diimine})]$ (n = 1, 2) with σ,σ-N,N′ Chelate or σ-N, σ-N′ Bridge Bonded RN=C(R′)C(R″)=NR Ligands.
Influence of the Branching at C^α of R on the Rh^I–α-diimine Interaction

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RN=C(R′)C(R″)=NR ligands (R-dim{R′,R″}) react quantitatively with $[(CO)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2]$ *via a bridge splitting reaction to form complexes with* $[Rh_2Cl_2(CO)_4(R\text{-dim}\{R',R''\})]$ *stoichiometry. An extensive infrared,* ^1H *and* ^{13}C *NMR study revealed that the nature of* $[Rh_2Cl_2(CO)_4(R\text{-dim}\{R',R''\})]$ *depends on the substituents R,R′ and R″ connnected to the –N=C–C=N– skeleton.*

Complexes with R-dim{R′,R″} ligands having R′=R″=H, R=i-Pr-, $i\text{-}Pr_2C(H)\text{-}2,6\text{-}Me_2Ph$*; R′=H, R″=Me, R=i-Pr; R′=R″=Me, R=4-MePh- have ionic structures* $[Rh(CO)_2(R\text{-dim}\{R',R''\})][RhCl_2(CO)_2]$ *both in polar (acetone) and less polar* ($CHCl_3$, C_6H_6) *solvents. The cation contains a* σ,σ*-N,N′ chelate bonded R-dim{R′,R″} ligand. In contrast, when for R-dim{H,H} the R group is t-Bu or* $EtMe_2C$ *the complex in solution at low temperature exists as an equilibrium mixture of the dinuclear species* $[(CO)_2ClRh(\mu\text{-}(\sigma\text{-}N,\sigma\text{-}N')\text{-}R\text{-dim}\{R',R''\})RhCl(CO)_2]$ *(as the major component) and the ionic species* $[Rh(CO)_2(R\text{-dim}\{R',R''\})][RhCl_2(CO)_2]$ *(in minor amounts). The dinuclear species is most probably present as two stereoisomers. At room temperature the exchange between these species becomes fast on the NMR time scale.*

The different structures are explained in terms of the branching at C^α *in R. For R substituents which are triply branched at* C^α *the interaction with the cis-CO ligands in a* σ,σ*-N,N′ chelate bonded R-dim{R′,R″} ligand is larger than in a complex with a* σ*-N bonded R-dim{R′,R″} ligand.*

Comparison of the ^{13}CO *chemical shifts of the ionic and dinuclear species with those of* $Bu_4N[RhCl_2(CO)_2]$ *as well as the* ^1H *and* ^{13}C *resonance patterns of complexes in which the R substituent contained prochiral groupings (*e.g. $EtMe_2C$-*) were particularly helpful for the structural assignment of the species in solution.*

Introduction

In the previous paper the synthesis and structural characterization of the first examples of five-co-ordinate rhodium-α-diimine complexes have been reported [1]. This study showed that the stability of these complexes strongly depends on the substituents on the N=C–C=N skeleton as well as the co-ligands on the Rh^I centre. Stable complexes were obtained for α-diimines (RNC(R′)C(R″)NR is R-dim {R′,R″}) in which the R substituent is connected to the imine nitrogen atom by a triply branched C^α atom. Furthermore $[RhCl(CO)(\eta^2\text{-}C_2H_4)(R\text{-dim}\{R',R''\})]$ appeared to be far more stable than $[RhCl(CO)_2(R\text{-dim}\{R',R''\})]$. An interesting aspect of the five-coordinate Rh^I-R-dim{R′,R″} complexes is their electronic and structural analogy with the five-co-ordinate Pt^{II} complexes $[PtX_2(\eta^2\text{-olefin})(R\text{-dim}\{R',R''\})]$ that we reported earlier [2]. Furthermore, in solution the $[Rh_2Cl_2(CO)_4(t\text{-Bu-dim}\{H,H\})]$ complex contained a σ-N, σ-N′ bridging t-Bu-dim{H,H} ligand* a structural feature which was found for the platinum(II) complex $[\{PtCl_2(PBu_3)\}_2(t\text{-Bu-dim}\{H,H\})]$ in the solid state [2a, 3]. A multinuclear NMR study of the latter dinuclear platinum complexes, including ^{15}N labelled derivatives revealed that a σ-N, σ-N′ bridging α-diimine ligand is also present in solution [4].

In this paper we report the synthesis and characterization of the $[Rh_2Cl_2(CO)_4(R\text{-dim}$

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{R',R''})] complexes and the study of the complexes present in mixtures of [{Rh(CO)$_2$Cl}$_2$] and R-dim{R',R''} in a molar ratio increasing from 0 to 1.

The R-dim ligands used in this study have been selected on the basis of our recent finding that the branching at C$^\alpha$ in the R group of R–N=C(R')–C(R'')=N–R as well as the presence of R' and R'' substituents, have a large influence on the stability of the species formed.

Experimental

Preparation of the Compounds

α-Diimines, RNC(H)C(H)NR (R-dim {H,H}; R = i-Pr, i-Pr$_2$C(H)-, t-Bu, EtMe$_2$C-, 2,6-Me$_2$C$_6$H$_3$), i-Pr-NC-(Me)C(H)N-i-Pr (i-Pr-dim{H,Me}), 4-MeC$_6$H$_4$NC(Me)-C(Me)NC$_6$H$_4$Me-4 (*p*-Tol-dim{Me,Me}) [5] and the starting complex [{Rh(CO)$_2$Cl}$_2$] [6] were prepared by published methods. Bu$_4$N[RhCl$_2$(CO)$_2$] was synthesized according to Vallarino [7].

The preparations of the new complexes were carried out in a N$_2$ atmosphere and are described below. Solvents were purified and distilled before use.

[Rh$_2$Cl$_2$(CO)$_4$(R-dim{R',R''})]

A solution of R-dim (0.9 mmol) in hexane (5 ml) was added to a stirred solution of [{RhCl(CO)$_2$}$_2$] (1 mmol) in hexane (5–10 ml). After 5 min the microcrystalline precipitate [Rh$_2$Cl$_2$(CO)$_4$(R-dim)] was collected by filtration, washed with hexane (3 X 10 ml), in order to remove the excess of [{RhCl(CO)$_2$}$_2$], and dried *in vacuo* at room temperature. Yield 70–90%. Analytical data are given in Table I.

Reaction of [Rh$_2$Cl$_2$(CO)$_4$(R-dim{R',R''})] with Excess of Triphenylphosphine

A solution of triphenylphosphine (1.5 mmol) in dichloromethane (3 ml) was added to a stirred solution of [Rh$_2$Cl$_2$(CO)$_4$(R-dim{R',R''})] (0.5 mmol) in dichloromethane (3 ml). During the addition of the PPh$_3$ a gas (CO) was liberated. The solution turned pale yellow and [RhCl(CO)(PPh$_3$)$_2$] started to precipitate. The reaction mixture was stirred for 15 min and the solvent removed at reduced pressure. The residue was washed with hexane (5 X 10 ml) to remove the free R-dim ligand as well as the excess of PPh$_3$ and was dried *in vacuo* at room temperature. Yield 80–90%; ^{1}H NMR spectra of freshly prepared reaction mixtures in CDCl$_3$ confirmed that the exchange reaction had taken place quantitatively.

Physical Measurements

Microanalyses were performed under the supervision of Mr. W. J. Buis of the Institute for Organic Chemistry T.N.O. (Utrecht, the Netherlands).

TABLE I. Analytical Data for [Rh$_2$Cl$_2$(CO)$_4$(R-dim{R',R''})] Complexes.

R-dim{R',R''}	%C		%H		%Cl		%N		Mol. wt[a] Found (calcd.)	Concentration mol/liter × 10^{-2}
	Found	(calcd)	Found	(calcd)	Found	(calcd)	Found	(calcd)		
i-Prdim{H,H} (1a)	27.63	(27.25)	3.58	(3.05)						
i-Pr$_2$C(H)-dim{H,H} (1b)									421 (641)	0.3
									442	0.7
									495	1.6
2,6-Me$_2$Ph-dim{H,H} (1c)	41.37	(40.43)	3.03	(3.06)	10.39	(10.87)	4.43	(4.29)	445 (653)	0.7
									433	2.0
									438	3.4
i-Pr-dim{H,Me} (2)	28.86	(28.73)	3.37	(3.31)	13.25	(13.07)	5.05	(5.16)	391 (543)	0.7
									472	1.2
									519	3.5
4-MePh-dim{Me,Me} (3)	40.18	(40.43)	2.78	(3.06)	11.01	(10.87)	4.28	(4.29)	379 (653)	0.7
									485	1.6
									469	2.3
t-Bu-dim{H,H} (4a)	30.09	(30.16)	3.86	(3.59)	12.22	(12.75)	4.70	(5.03)	512 (556)	1.0
EtMe$_2$C-dim{H,H} (4b)	32.92	(32.85)	4.16	(4.13)	12.05	(12.12)	4.72	(4.79)	557 (585)	0.7

[a] In chloroform at 34 °C (VPO).

TABLE II. Infrared Spectra of the ν(C≡O) Region in $R_4N[RhCl_2(CO)_2]$, $[Rh(CO)_2(N{-}N)]X$, $[RhCl(CO)_2N]$, $[\{RhCl(CO)_2\}_2(N{-}N)]$ and $[Rh(CO)_2(N{-}N)][RhCl_2(CO)_2]$ Complexes.

		ν(CO) in solid[a]				ν(CO) in solution[b]				Lit.
$[Rh(CO)_2$(i-Pr-dim){H,H}] $[RhCl_2(CO)_2]$	(1a)	1988	2026	2060	2086					c
$[Rh(CO)_2$(i-Pr-dim){H,Me}] $[RhCl_2(CO)_2]$	(2)	2000	2020	2055	2073	1995	2025	2070	2085	c
					2080					
$[Rh(CO)_2$(i-Pr_2C(H)-dim{H,H})] $[RhCl_2(CO)_2]$	(1b)	1975	2030	2065	2098	2000	2033	2073	2095	c
		1982	2038							
						2002	2037	2075	2100	[8]
$[Rh(CO)_2$(2,6-Me_2Ph-dim{H,H})] $[RhCl_2(CO)_2]$	(1c)	1988	2020	2050	2083	1993	2035	2068	2090	c
$[Rh(CO)_2$(4-MePh-dim{Me,Me})] $[RhCl_2(CO)_2]$	(3)	1999	2036	2072	2096	2001	2047	2076	2100	c
$[Rh(CO)_2$(bipy)] $[RhCl_2(CO)_2]$		1984	2015	2056	2088					[9]
		1995	2028	2063	2095					
$[Rh(CO)_2$(phen)] $[RhCl_2(CO)_2]$		1963	1995	2041	2088					[10]
		1981	2021	2061	2101					
$[Rh(CO)_2$(bipy)] ClO_4		2050	2108							[11]
$[Rh(CO)_2$(phen)] BF_4		2050	2112							[11]
$[Rh(CO)_2(HNC(CH_3)CH_2C(CH_3)NH)]BF_4$		2040	2090							[12]
$Bu_4N[RhCl_2(CO)_2]$		1974	2058							[7]
		1976	2056							c
$Me_4N[RhCl_2(CO)_2]$		2000	2066							[13]
$[\{RhCl(CO)_2\}_2$(t-Bu-dim{H,H})]	(4a)	1984	2010	2064	2080	2020	2084			c
$[\{RhCl(CO)_2\}_2$ ($EtMe_2$C-dim{H,H})]	(4b)	1988	2026	2060	2086	2004	2072			c
$[RhCl(CO)_2$(pyridine)]		1980	2010	2060	2075	2016	2087			[13] [14]
$[RhCl(CO)_2$(2,4,6-Me_3pyridine)]		1974	2000	2050	2072	2008	2088			c
$[RhCl(CO)_2(4\text{-}MePh{-}NH_2)]$		2027	2089			2011	2086			[14]
$[RhCl(CO)_2(EtNH_2)]$		1979	2022	2057	2083	2005	2084			[14]

[a]Spectra recorded as Nujol mull or in KBr. [b]Spectra recorded as $CHCl_3$ solution. [c]This work.

^{1}H NMR spectra were recorded on a Varian A-60, T-60, HA-100 or on a Bruker WP 250 spectrometer with tetramethylsilane (TMS) as internal standard; ^{13}C NMR spectra were obtained on a Varian CFT-20 using TMS as internal standard.

Infrared spectra were measured on either a Beckman 4250 or Perkin-Elmer M 283 spectrophotometer.

The field desorption mass spectra were obtained with a Varian MAT 711 double focussing mass spectrometer equipped with a combined EI/FI/FD ion source and coupled to a spectrosystem MAT 100 data acquisition unit. The samples were dissolved either in hexane or chloroform and then loaded onto the emitters with the dipping technique.

Results

The complexes with the general formula $[Rh_2Cl_2(CO)_4$(R-dim{R′,R″})], R′=R″=H, R = i-Pr (1a) R = i-Pr_2C(H) (1b), R = 2,6-$Me_2C_6H_3$ (1c); R′ = H, R″ = Me, R = i-Pr (2); R′=R″=Me, R = 4-MeC_6H_4– (3); R′=R″=H, R = t-Bu (4a), R = $EtMe_2$C– (4b) were obtained as crystalline solids from the 1/1 reaction of $[\{Rh(CO)_2Cl\}_2]$ with R-dim{R′,R″} in hexane. Elemental analysis confirmed the 2/1 Rh/R-dim{R′,R″} stoichiometry (see Table I).

The results of molecular weight determinations of the complexes in $CHCl_3$ did not allow us to draw reliable conclusions concerning their aggregation state. The data obtained for t-Bu-dim{H,H} and $EtMe_2$C-dim{H,H} complexes (4a,b), suggested that these complexes exist mainly as non ionic $[Rh_2Cl_2(CO)_4$(R-dim{H,H})] molecules in $CHCl_3$. In contrast the other complexes appeared to have concentration dependent molecular weights pointing to dissociation of the dinuclear rhodium species into smaller units (see discussion).

On the basis of the combined IR, ^{1}H and ^{13}C NMR data the complexes can be divided according to their main structural features in solution into two types: *i*, the complexes *1–3* having an ionic structure $[Rh(CO)_2$(R-dim){R′,R″})] $[RhCl_2(CO)_2]$ with a σ,σ-N,N′ chelate bonded R-dim{R′,R″} ligand in the cation and *ii*, complexes *4a,b* which are mainly

TABLE III. ^{1}H NMR of [RhCl$_2$(CO)$_4$(R-dim{R′, R″})] and [RhCl(CO)$_2$(R-dim{R′, R″})] Complexes.[a]

		CH$_3$	CH$_2$	CH	HC=N
[Rh$_2$Cl$_2$(CO)$_4$(t-Bu-dim{H,H})]	+34°, CDCl$_3$, 60 MHz	1.65 s			9.22 br
[b]assigned to: [{RhCl(CO)$_2$}$_2$(t-Bu-dim)]	−50°, CDCl$_3$, 60 MHz	1.68 s			9.30 t
[{RhCl(CO)$_2$}$_2$ (t-Bu-dim)]		–			9.23 t
[Rh(CO)$_2$(t-Bu-dim)] [A][e]		1.54 s			8.55 d [2.5]
[RhCl(CO)$_2$(t-Bu-dim{H,H})][c]	+34°, CDCl$_3$, 60 MHz	1.45 s			8.40 s
	−50°, CDCl$_3$, 60 MHz	1.46 s			8.41 d [1]
[Rh$_2$Cl$_2$(CO)$_4$(t-Bu-dim{H,H})]	+34°, aceton-d$_6$, 60 MHz	1.56 s			9.61 b
[b]assigned to: [{RhCl(CO)$_2$}$_2$(t-Bu-dim)]	−50°, aceton-d$_6$, 60 MHz	1.55 s			9.53 t
[{RhCl(CO)$_2$}$_2$ (t-Bu-dim)]		–			9.70 t
[Rh(CO)$_2$(t-Bu-dim)] [A][e]		1.45 s			8.77 d [2.5]
[RhCl(CO)$_2$(t-Bu-dim{H,H})][c]	+34°, aceton-d$_6$, 60 MHz				
	−50°, aceton-d$_6$, 60 MHz	1.41 s			8.83 d [1]
[Rh$_2$Cl$_2$(CO)$_4$(EtMe$_2$C-dim{H,H})]	+34°, CDCl$_3$, 60 MHz	1.57 s	1.90 q	0.93 t^d	9.23 br
[b]assigned to: [{RhCl(CO)$_2$}$_2$(EtMe$_2$C-dim)]	+25°, CDCl$_3$, 250 MHz	1.57 s, 1.62 s	1.95 q	0.93 m^d	9.31 s^1
[{RhCl(CO)$_2$}$_2$ (EtMe$_2$C-dim)]		–	1.77 m	0.93 m^d	9.23 s^1
[Rh(CO)$_2$(EtMe$_2$C-dim)] [A][e]		1.43 s	1.77 m	0.93 m^d	8.61 s^1
[Rh$_2$Cl$_2$(CO)$_4$(EtMe$_2$C-dim{H,H})]					
[b]assigned to: [{RhCl(CO)$_2$}$_2$(EtMe$_2$C-dim)]	+25°, C$_6$D$_6$, 250 MHz	1.22 s, 1.15 s	1.58 m	0.64 m^d	9.28 s^1
[{RhCl(CO)$_2$}$_2$(EtMe$_2$C-dim)]					9.23 s^1
[Rh(CO)$_2$(EtMe$_2$C-dim)] [A][e]		1.08 s	1.47 m		8.58 s^1
[Rh(CO)$_2$((i-Pr)$_2$C(H)-dim{H,H})] [A][e]	+34°, CDCl$_3$, 60 MHz	1.04 d		2.13 sp, 3.18 t	8.70 s^1
	+25°, CDCl$_3$, 250 MHz	1.02 d		2.13 sp, 3.13 br	8.71 s^1
	+25°, aceton-d$_6$, 250 MHz	1.03 d		2.22 sp, 33.32 br	8.57 s^1
[Rh(CO)$_2$(i-Pr-dim{H,H})] [A][e]	+34°, aceton-d$_6$, 60 MHz	1.49 d		4.37 sp	8.67 s^1
[Rh(CO)$_2$(i-Pr-dim{H,Me})] [A][e]	+34°, CDCl$_3$, 60 MHz	1.40 d, 1.50 d		4.2 m	8.67 s^1, 2.60^f
	+25°, CDCl$_3$, 250 MHz	1.37 d, 1.48 d		4.12 br, 4.21 br	8.71 s^1, 2.57^f
	+25°, C$_6$D$_6$, 250 MHz	1.12 d, 1.43 d		3.61 br, 4.04 br	8.87 s^1, 2.39^f
[Rh(CO)$_2$(2,6-Me$_2$Ph-dim{H,H})] [A][e]	+34°, CDCl$_3$, 60 MHz	2.43 s			8.80 s^1
[Rh(CO)$_2$(4-MePh-dim{Me,Me})[A][e]	+34°, CDCl$_3$, 60 MHz	2.33 s			2.37 s^f

[a] Chemical shifts (δ ppm) relative to TMS. s: singlet, s^1: broadened singlet due to small $^nJ(^{103}Rh-^1H)$, d: doublet, t: triplet, q: quartet, sp: septet, m: multiplet, br: broad. [b] Species observed in a solution of one sample. [c] [RhCl(CO)$_2$(R-dim{R′,R″})] in the presence of [Rh$_2$Cl$_2$(CO)$_4$(R-dim{R′,R″})]. [d] CH$_3$ of the ethyl-group. [e] [A] is [RhCl$_2$-(CO)$_2$] anion. [f] CH$_3$ of N=C–CH$_3$.

dinuclear in solution with a σ-N, σ-N′ R-dim{R′, R″} ligand bridging two $RhCl(CO)_2$ units.

[$Rh_2Cl_2(CO)_4$(R-dim{R′,R″})] Complexes (1–3) Having an Ionic Structure

The infrared spectra of the complexes *1–3*, recorded as solids in Nujol or dissolved in $CHCl_3$ are given in Table II.

All complexes give four ν(CO) absorptions, *e.g.* 1988, 2020, 2050 and 2083 cm^{-1} for *1c*. Some of the I.R. spectra of the solid compounds gave more than four ν(CO) bands (*e.g. 1b, 2*) most probably due to site symmetry splitting. A comparison of these data with other ionic rhodium complexes containing the *cis*-$Rh(CO)_2$ fragment present either in the anion, the cation or both revealed that the complexes *1–3* must have an ionic structure.

The ^1H (60–250 MHz) and ^{13}C (20 MHz) NMR data of *1–3* are presented in Tables III and IV.

A common feature of the spectra is that only one resonance pattern is observed for hydrogen and carbon atoms of the R-dim{R′,R″} ligand which points to the presence of a single rhodium(I)–R-dim species in solution. This has been observed both in polar (acetone-d_6) and less polar solvents ($CDCl_3$ and C_6D_6).

The ^{13}C NMR spectra have been recorded at low temperature in order to depress decomposition of the solutions during data accumulation (12–24 h) and to improve the S/N ratio. This allowed us to observe the carbon resonances of the CO groups. For each of the complexes *1–3* four ^{13}C carbonyl resonances were observed which, when taking into account expected $^{103}Rh–^{13}C$ couplings, points to the presence of two unique CO groups in the complex.

The combined data then indicates that *1–3* have an ionic structure in $CHCl_3$ consisting of a *cis*-[$RhCl_2(CO)_2$] anion and a [$Rh(CO)_2$(R-dim{R′,R″})] cation in which the CO groups are likewise *cis* positioned as a result of a σ,σ-N,N′ chelate bonding of the R-dim{R′,R″} ligand. This conclusion is strongly supported by comparison of the carbon CO resonances of *1–3* with the doublet centred at 180.9 ppm ($J(^{103}Rh–^{13}C)$ 72 Hz) in the ^{13}C NMR spectrum of $Bu_4N[RhCl_2(CO)_2]$. On this basis the four ^{13}CO resonances in the spectra of *1–3* could be split into two doublets, one of which was assigned to a [$RhCl_2(CO)_2$] anion ($J(^{103}Rh–^{13}C)$ 72 Hz) and the other ($J(^{103}Rh–^{13}C)$ 69 Hz) to a [$Rh(CO)_2$(R-dim{R′,R″})] cation.

It is interesting to note that addition of $Bu_4N[RhCl_2(CO)_2]$ to [$Rh_2Cl_2(CO)_4$(i-Pr_2C(H)-dim{R′, R″})] (for example 1b) resulted in an intensity increase of the doublet at 180.2 ppm while the resonances at 181.5 ppm doublet remained unaffected (see Fig. 2) thus supporting our assignment. Furthermore, the observation of isochronous R–N=C(R′)-

TABLE IV. ^{13}C NMR Spectra[a] of [{$RhCl(CO)_2$}$_2$(R-dim{R′,R″})], [$RhCl(CO)_2$(R-dim{R′,R″})], [$Rh(CO)_2$(R-dim{R′,R″})] [$RhCl_2(CO)_2$] and $Bu_4N[RhCl_2(CO)_2]$ Complexes.

	CH_3	CH/CH_2	C–N	C=N	^{13}CO resonances observed	^{13}CO assigned	$[^1J(^{103}Rh–^{13}C]$
[{$RhCl(CO)_2$}$_2$(t-Bu-dim{H,H})]	30.49		66.44	162.89	176.89, 180.19, 180.56, 183.59	179.08 [73.3]	182.22 [68.4]
[$RhCl_2(CO)_2$] [$Rh(CO)_2$(t-Bu-dim{H,H})][b]	28.61		64.97	167.72	178.16, 181.78	179.97 [72.4]	
[$RhCl(CO)_2$(t-Bu-dim{H,H})][c]	29.90		62.31	160.80	179.49, 182.98	181.23 [69.7]	
[{$RhCl(CO)_2$}$_2$($EtMe_2$C-dim{H,H})]	7.99, 26.44, 29.47	35.37	69.40	163.63	176.79, 179.97, 180.44, 183.36	178.62 [73.0]	181.66 [67.7]
[$RhCl_2(CO)_2$] [$Rh(CO)_2$($EtMe_2$C-dim{H,H})][b]	8.31, 28.28		67.32	168.78	177.98, 181.64	179.81 [73.2]	
[$RhCl(CO)_2$($EtMe_2$C-dim{H,H})][c]	8.05, 26.92	34.93	64.92	161.06	179.23, 182.75	180.59 [70.3]	
[$RhCl_2(CO)_2$] [$Rh(CO)_2$((i-pr)$_2$C(H)-dim{H,H})]	20.62, 30.73	19.29	84.33	171.61	178.39, 179.75, 182.05, 183.26	180.22 [73.2]	181.51 [70.1]
[$RhCl(CO)_2$((i-Pr)$_2$C(H)-dim{H,H})][c]	19.52, 28.95	18.17	85.60	164.75	179.25, 182.75	181.00 [70.0]	
[$RhCl_2(CO)_2$] [$Rh(CO)_2$(i-Pr-dim{H,H_3})]	19.32[d], 21.99		55.39, 63.74	172.73, 178.32	178.61, 180.99, 182.20, 184.38	180.40 [72.3]	182.69 [68.4]
[$RhCl(CO)_2$] [$Rh(CO)_2$(2,6-Me_2-Ph-dim{H,H})]	18.83			173.90	177.88, 178.65, 181.57, 182.15	179.72 [72.4]	180.40 [70.3]
[$RhCl_2(CO)_2$] [$Rh(CO)_2$(4-Me-Ph-dim{CH_3CH_3})]	21.12			180.60	178.75, 180.55, 182.35, 184.00	180.55 [72.3]	182.34 [69.3]
$Bu_4N[RhCl_2(CO)_2]$	13.70	19.48 23.68	58.26		179.07, 182.69	180.88 [72.4]	
[$RhCl(CO)_2$(2,4,6-Me_3py)]					176.99, 180.66, 181.28, 184.61	178.82 [73.5]	182.94 [67.0]

[a] ^{13}C NMR (20 MHz) (δ ppm); $^nJ(^{103}Rh–^{13}C)$ in brackets, Hz; TMS internal standard; in $CDCl_3$; temperature between −45 °C and −55 °C. [b] Small amount of [$Rh(CO)_2$(R-dim{R′,R″})] [$RhCl_2(CO)_2$] present in spectrum of [{$RhCl(CO)_2$(R-dim{R′,R″})]; only δ $^{13}C{\equiv}O$ of the [{$RhCl(CO)_2$(R-dim{R′,R″})]; only δ $^{13}C{\equiv}O$ of the [$RhCl_2(CO)_2$] anion is observed. [c] The value of the five-co-ordinate [$RhCl(CO)_2$(R-dim{R′,R″})] complex is given for comparison, *cf.* ref. 1. [d] CH_3–C=N.

halves of the R-dim-{R′,R′} ligand is in agreement with the symmetry expected for a [Rh(CO)$_2$(R-dim-{R′,R″})] cation. In the ^{1}H NMR of *1b* the singlet at 8.70 ppm arising from the imine hydrogen atom appears to be broadened which might be due to a small (<1 Hz) $^3J(^{103}Rh-^1H)$. In general this coupling in rhodium complexes with σ,σ-N,N′ bonded R-dim{R′,R″} ligands is in the range of 0–4 Hz as we have found in five co-ordinate [RhCl(CO)(η^2-C$_2$H$_4$)(R-dim{H,H})] [1].

[Rh$_2$Cl$_2$(CO)$_4$(R-dim{H,H})] Complexes Having Predominantly a Dinuclear Structure in Solution

The infrared spectra of [Rh$_2$Cl$_2$(CO)$_4$(R-dim-{H,H})] (4a, R = t-Bu; 4b, R = EtMe$_2$C–) in CHCl$_3$ and C$_6$H$_6$ revealed only two ν(CO) absorptions, both at room temperature and at –50 °C (CHCl$_3$ solution), see Table II. This pointing to a structure for these two compounds which differ from the ionic structures found for *1–3* in solutions and in the solid.

The ^{1}H NMR (60–100–250 MHz) and ^{13}C NMR (20 MHz) spectra were recorded on solutions of *4* in polar (acetone-d$_6$) and less polar solvents (CDCl$_3$, C$_6$D$_6$) see Tables III and IV. In contrast to the ionic complexes *1–3* these spectra were temperature dependent. In the ^{1}H NMR spectra at –55 °C (CDCl$_3$ or acetone-d$_6$) three multiplets, *i.e.* two triplets and one doublet, were observed for the imine hydrogen atoms. The intensity ratio of the multiplets indicate one major and two minor species in solution. Homonuclear spin-spin decoupling experiments revealed that the multiplicity was not a result of $^nJ(^1H-^1H)$ (see discussion for the conclusions concerning intermolecular R-dim{H,H} exchange). However, these patterns slowly broadened going from –50 °C to room temperature resulting finally at 60 °C in one broadened singlet at 9.22 ppm (*4a*, CDCl$_3$).

The ^{13}C NMR data (at –50 °C, CDCl$_3$) showed likewise that in addition to one major species, having a distinctive CO resonance pattern pointing to two unique CO groupings, at least one other species was present having a doublet centred at 181 ppm see Table IV.

Comparison of these ^{1}H and ^{13}C NMR data with those of the ionic complexes *1–3* that obtained earlier for the five-co-ordinate [RhCl(CO)$_2$(R-dim{R′, R″})] [1] and the dinuclear [{PtCl$_2$(PR$_3$)}$_2$(R-dim-{H,H})] [3] allowed an assignment of each of the species present. The doublet for the imine protons in the ^{1}H NMR spectra are at chemical shifts positions characteristic for the ionic species [Rh(CO)$_2$-(R-dim{R′,R″})] [RhCl$_2$(CO)$_2$]. In both cases a $^3J(^{103}Rh-^1H)$ of 2.5 Hz is observed in the low temperature spectra. Moreover, in the ^{13}C NMR spectra the ^{13}CO doublet at 181 ppm ($^3J(^{103}Rh-^{13}C)$ 72 Hz) may be assigned to the [RhCl$_2$(CO)$_2$] anion. The doublet belonging to the ^{13}CO resonances of the cation coincide with those of the other (dinuclear) species (see below). The imine proton chemical shift of the major species, characterised by pseudo-triplet at 9.30 ppm (*4a*, CDCl$_3$) is 1.47 ppm downfield from that of the free ligand and 0.75 ppm (*4a*) downfield from that of the ionic species. This large downfield shift is characteristic for a σ-N, σ-N′ bridging R-dim-{R′,R″} ligand with a s-*trans* conformation of the –N=C–C=N– skeleton (*cf.* [{PtCl$_2$(PR$_3'$)}$_2$(R-dim-{H,H})] δ CH=N 9.10–10.21 ppm [3]). The observation of a triplet for the imine hydrogen atom is also in accord with a R-dim{H,H} ligand bridging two RhCl(CO)$_2$ units. The (pseudo) triplet pattern arises from ^{1}H–^{1}H coupling of magnetically non-equivalent imine hydrogen atoms, and ^{103}Rh–^{1}H couplings with the two rhodium nuclei (*cf.* the multiplet-pattern for the imine hydrogen atoms in [{PdCl$_2$-(PEt$_3$)}$_2$(R-dim{H,H})], Figs. 2, 4 ref. [3]). Computer iterations of the AA′ part of the AA′XX′ spectrum for the imine hydrogen atoms resulted in a good fit of the observed and calculated pattern*.

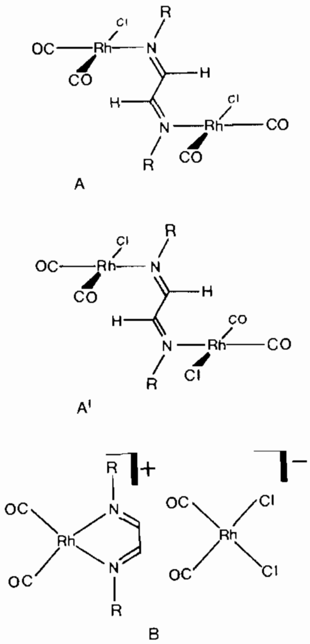

Fig. 1. Proposed structures for [Rh$_2$Cl$_2$(CO)$_4$(R-dim-{R′,R″})] (R = t-Bu, EtMe$_2$C–; R′=R″=H). The two stereoisomers of the neutral species (A and A′); ionic species (B).

Additional evidence for the dinuclear structure comes from the ^{13}C NMR spectra of the complex in

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*Calculated coupling constants of the imine proton pattern (9.30 ppm) of: [(CO$_2$ClRh–(t-Bu–N=CH–CH′=N–t-Bu–Rh′Cl(CO)$_2$] $^5J(^{103}Rh-^{103}Rh')$ = 0, $^3J(^{103}Rh-^1H)$ = $^3J(^{103}Rh'-^1H')$ = 1.92, $^4J(^{103}Rh-^1H')$ = $^4J(^{103}Rh'-^1H)$ = 0.05, $^3J(^1H-^1H')$ = 9.91 Hz, line width 0.5 Hz.

which the EtMe$_2$C– substituents are present. At low temperature (–50 °C) the Me carbon resonances appear as two singlets indicating that these methyl groups are diastereotopic resulting from the dissymmetry in the dinuclear complex at the two Rh centres. In the bridged dinuclear structure (see Fig. 1) the two CO ligands at each Rh centre are nonequivalent thus explaining the presence of the two doublets δ 178.6, 181.7 ppm, $^3J(^{103}Rh–^{13}C)$ 73, 68 Hz (4b) in the ^{13}CO region (see also Table IV).

The low field position and the triplet structure of the second low intensity multiplet in the ^1H NMR spectra of *4* (CDCl$_3$) belongs most probably to a second stereoisomer of the species shown in Fig. 1A,A′ of which the corresponding ^{13}C NMR resonances coincide with those of the major isomer.

It is interesting that in acetone-d$_6$ the chemical shift and intensity ratio of the imine proton signals of these two stereoisomers is changed (see Table III). It is not known whether this is a result of solvent–solute interactions or an inversion of the stability of the two isomers. It is important to note that the conclusions drawn in this section concerning the species present in solutions of *4a,b* relate to the situation at low temperature. The NMR spectra clearly show that at room temperature intermolecular exchange occurs between the various species (see discussion).

For *4a,b* the observation in Nujol mull IR spectra of four ν(CO) absorptions suggests an ionic structure in the solid state *cf. 1–3* in Table II. However, care must be taken with such conclusions based on the number of ν(CO) absorptions observed because square planar, mononuclear [RhCl(CO)$_2$(2,4,6-Me$_3$-py)] (see FD. mass, *vide infra*) likewise shows more than two ν(CO) absorptions (see Table II).

*Comparison of the δ^{13}CO in the Ionic [Rh(CO)$_2$-(i-Pr$_2$C(H)-dim{H,H})][RhCl$_2$(CO)$_2$] (*1b*) and Dinuclear [{RhCl(CO)$_2$}$_2$(t-Bu-dim{H,H})] (*4a*) Complexes*

During our investigations of the ^{13}C chemical shift values of the CO ligands present in the dinuclear and ionic rhodium carbonyl complexes *1–4* (in order to obtain further proof for the structures of [Rh$_2$Cl$_2$(CO)$_4$(R-dim{R′,R″})] complexes in solution) it appeared that comparison of these data with those of Bu$_4$N[RhCl$_2$(CO)$_2$], a reference compound containing the [RhCl$_2$(CO)$_2$] anion, can be very helpful and conclusive.

In Fig. 2, the ^{13}C NMR spectra at –50 °C in CDCl$_3$ of *4a* (Fig. 2A) and *1b* (Fig. 2D), as representatives of the two possible structures, are shown.

The spectrum of Bu$_4$N[RhCl$_2$(CO)$_2$] is shown in Fig. 2C. The ^{13}CO region of *4a* shows the two doublets assigned to the bridged dinuclear species and the two smaller resonances at 178.16 and 181.78 ppm which belong to the ionic species [Rh(CO)$_2$-

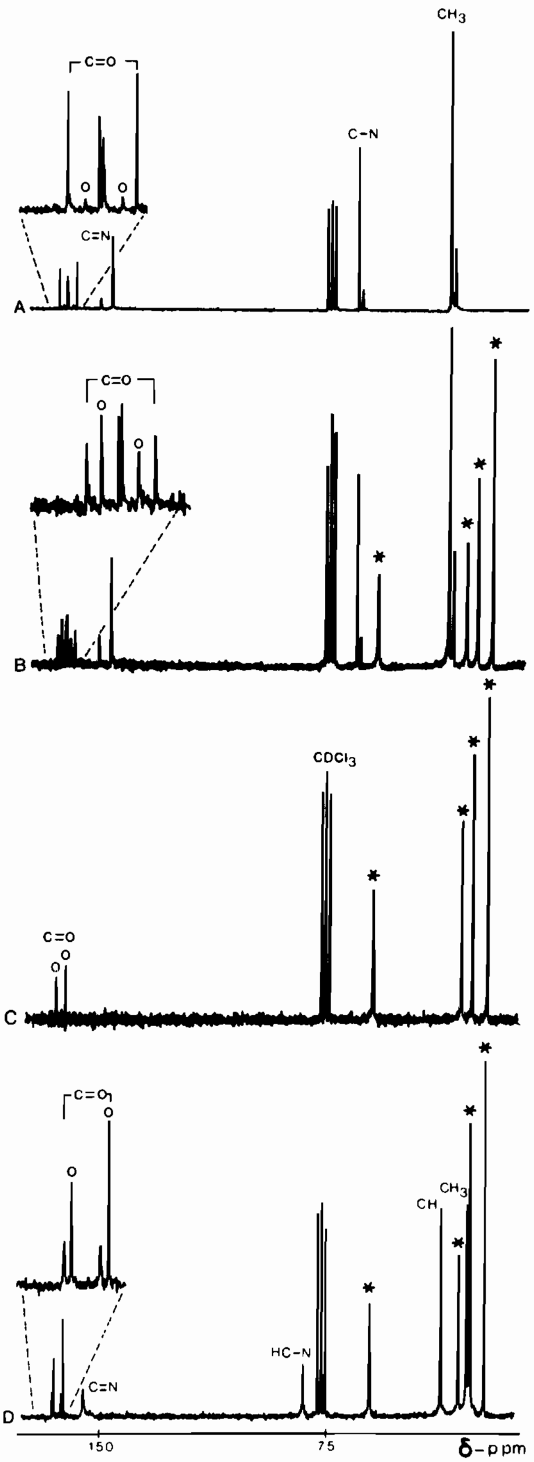


Fig. 2. ^{13}C NMR spectra of [Rh$_2$Cl$_2$(CO)$_4$(R-dim{H,H})] in the presence of Bu$_4$N[RhCl$_2$(CO)$_2$]; Bu$_4$N is indicated by an asterisk, [RhCl$_2$(CO)$_2$] is indicated by an open circle: A, R = t-Bu (*4a*), major component is the dinuclear species, while the ionic species is the minor one; B, R = t-Bu (*4a*), 1 equivalent Bu$_4$N[RhCl$_2$(CO)$_2$] has been added; C, spectrum of Bu$_4$N[RhCl$_2$(CO)$_2$], and D, R = i-Pr$_2$C(H)– (*1b*); ionic species with 1 equivalent of Bu$_4$N[RhCl$_2$(CO)$_2$] added.

(t-Bu-dim{H,H})] [RhCl$_2$(CO)$_2$] (Fig. 2A). Indeed upon addition of Bu$_4$N[RhCl$_2$(CO)$_2$] to *4a* the two small resonances increase in intensity without affecting the other resonances present in the spectrum (Fig. 2B). The ^{13}C NMR spectrum of *1b*, of which the X-ray structure determination was recently reported [8], contains two doublets in the ^{13}CO region of which one doublet increased in intensity upon addition of Bu$_4$N[RhCl$_2$(CO)$_2$] (Fig. 2D).

These experiments confirm the conclusions drawn on the basis of the resonance patterns of the imine-carbon and hydrogen atoms.

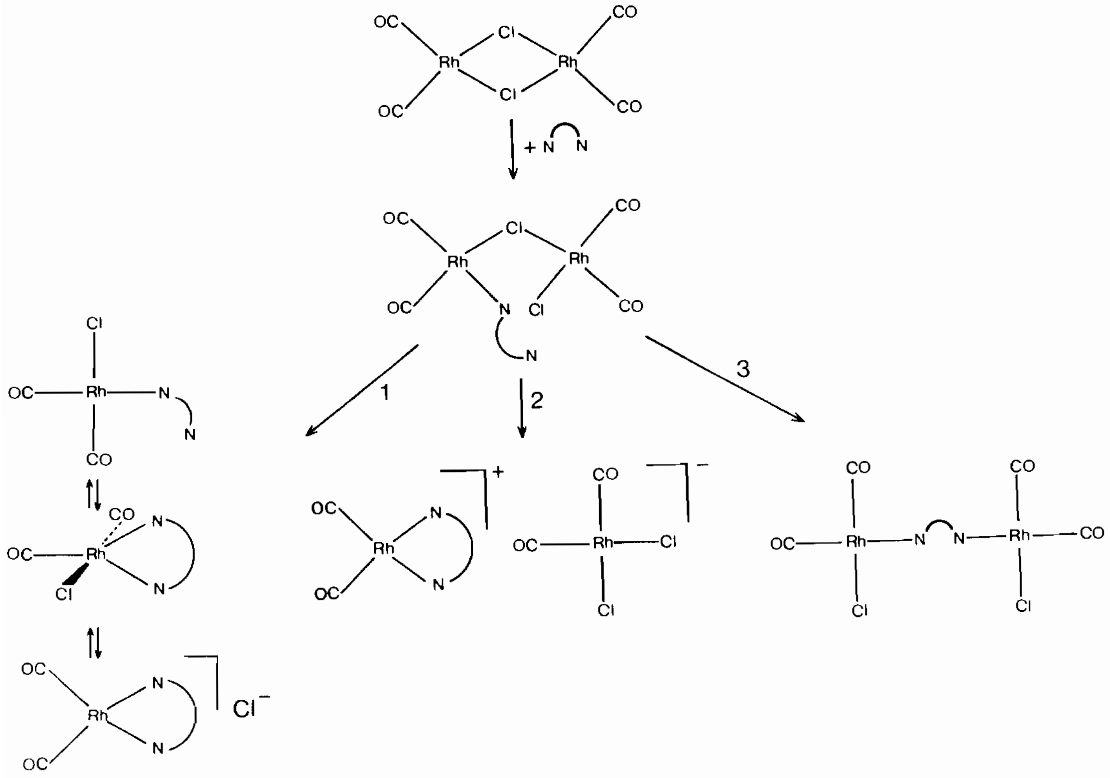
Field Desorption (FD) Mass Spectra

In order to obtain more evidence concerning the stoichiometry of [Rh$_2$Cl$_2$(CO)$_4$(R-dim{R′,R″})] complexes the FD mass spectra of *1*, *2* and *4a* were recorded. By this technique it is possible to obtain mass spectra of non-volatile, neutral or ionic compounds. An important advantage being that the technique is particularly suited for the investigation of labile species [15].

The ionic structure of complex [Rh(CO)$_2$(i-Pr$_2$-C(H)dim{H,H})] [RhCl$_2$(CO)$_2$] (*1b*) in the solid has recently been established by X-ray structural analysis [8]. It is interesting that both *1b* and *2* show only one fragment ion with m/z of 422 and 320, respectively. The isotope pattern of these fragments are characteristic for a species containing one Cl atom. Accordingly the ions have been assigned to [RhCl(CO)(R-dim{R′,R″})]$^+$, *i.e.* a four-co-ordinate Rh^{I} species. Neither the respective [Rh$_2$Cl$_2$(CO)$_4$(R-dim-{R′,R″})] molecular ions (m/z 644 and 542) nor the [Rh(CO)$_2$(R-dim{R′,R″})] cations (m/z 415 and 313) were present in these spectra. At higher (50–100 °C) temperatures in addition to the ions at m/z of 422 and 320, were found patterns at m/z 844 and 640, respectively. These values and the fact that the isotope pattern indicated the presence of two Cl atoms are in accord with a dimeric structure for [RhCl(CO)(R-dim{H,H})].

Although the fragmentation pattern of *4a* was distinctly different from that of *1b* and *2* it showed no molecular ion (m/z 556) but the following ions were observed and assigned m/z 327 [Rh(CO)$_2$(t-Bu-dim{H,H})], 334 [RhCl(CO)(t-Bu-dim{H,H})], 388 [{RhCl(CO)$_2$}$_2$] and 362 [RhCl(CO)$_2$(t-Bu-dim{H,H})]. The latter species can be thought of as emerging directly from the dinuclear [{RhCl(CO)$_2$}$_2$(t-Bu-dim{H,H})] species (with the σ-N, σ-N′ bridging t-Bu-dim{H,H}), whereas the m/z ion 327 would be indicative for an ionic structrure [Rh(CO)$_2$(t-Bu-dim{H,H})][RhCl$_2$(CO)$_2$] (*vide infra*).

For comparative purposes the FD mass spectrum of *cis*-[RhCl(CO)$_2$(2,4,6-Me$_3$py)], which has a monomeric structure, was recorded. The molecular ion (m/z 315) was found as well as a low intensity frag-



Scheme 1.

ment ion pattern corresponding to [$\{RhCl(CO)_2\}_2$] (m/z 388).

These data show that in these cases the FD spectra of both [$Rh(CO)_2$(R-dim{R′,R″})] [$RhCl_2(CO)_2$] (*1,2*) and [$\{RhCl(CO)_2\}_2$R(-dim{H,H})] (*4*) does not provide a reliable basis for the assignment of structures to [$Rh_2Cl_2(CO)_4$(R-dim{R′,R″})] complexes (*cf.* however, ref. 1). By comparison the X-ray analysis of [$Rh_2Cl_2(CO)_4$(i-Pr_2C(H)-dim-{H,H})] (1) clearly showed an ionic structure [8] while the FD mass spectrum of this complex reveals [RhCl(CO)(i-Pr_2C(H)-dim{H,H})] as the most abundant ion.

Discussion

In general reactions of [$(CO)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2$] with N-donor ligands (primary amines or pyridines) involve the consecutive cleavage of two Rh–Cl–Rh bridge bonds. When bidentate N-donor ligands phen [10], bipy [10], quinoline-2-carboxaldehyde-N-methylimine (abbreviated as Rqa) [16] or R-dim{R′, R″} are used the bridge splitting reaction may follow one of the routes shown in Scheme 1.

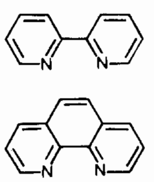
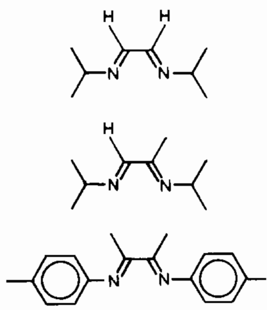
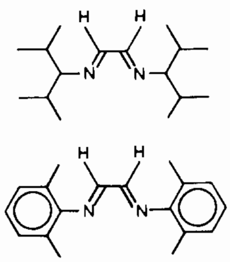
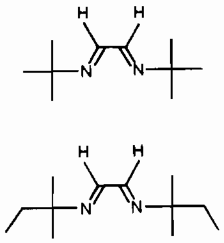
The route favoured by each of the bidentate ligands mentioned depends on the flexibility of their –N=C–C=N– skeletons. In phen this skeleton is locked in the s-*cis* conformation, which excludes the formation of the bridge complexes via route *3*. The increasing flexibility in the bipy, Rqa, R-dim series is reflected by the following observations: *i*, bipy co-ordinates exclusively in the s-*cis* conformation (σ,σ-N,N′); *ii*, Rqa co-ordinates predominantly in the s-*cis* conformation (σ,σ-N,N′) or *via* N (σ-N monodentate) [16]; *iii*, the R-dim{R′,R″} ligand can co-ordinate in either the σ,σ-N,N′, σ-N or σ-N, σ-N′ (bridging) co-ordination modes. The main reason for these differences is the fact that H^β is part of a six membered ring system, when bipy or Rqa co-ordinate in the σ-N mode, but that H^β in σ-N bonded R-dim{H,H} occupies the fifth atom position of the $\overline{\mathrm{M{-}N{=}C{-}C{-}H}}$ ring system. Accordingly for bipy and phen formation of complexes only via routes *1* and *2* can be anticipated whereas for R-dim{H,H} route *3* is also possible.

The ability to form Rh-R-dim{R′,R″} complexes appeared to be dependent on the type of R as well as on the combination of R with R′, R″ see Table V.

Factors which favour the formation of the complexes with an ionic structure are the presence of substituents on the imine-C atoms and imine-N substituents which are doubly or singly branched at C^α. In contrast when R is t-Bu or $EtMe_2C$- dinuclear complexes with a σ-N, σ-N′ bridging R-dim ligand are the predominant species in solution.

Theoretically for triply branched substituents (t-Bu) the steric interaction with *cis*-CO groups is larger for a σ,σ-N,N′ than for a square planar complex having a σ-N bonded R-dim{R′,R″} ligand (see Fig. 3; compare the co-ordination around the Rh centre in 3B and 3A, respectively)*.

TABLE V. *A*: Ionic species: [$Rh(CO)_2L_2$] [$RhCl_2(CO)_2$]. *B*: Mainly di-nuclear: [$(CO)_2ClRh(\mu\text{-}L_2)RhCl(CO)_2$].

singly branched at C_α A	doubly branched at C_α A singly branched at C_β
	
doubly branched at C_α A doubly branched at C_β	triply branched at C_α B
	

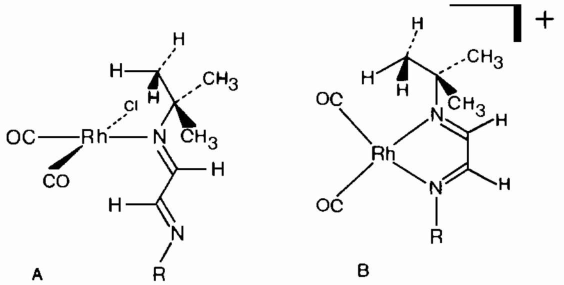


Fig. 3. Comparison of the steric interaction of the t-Bu groupings in the t-Bu-dim{H,H} ligand with the metal and co-ligands: A, σ-N monodentate bonded; B, σ,σ-N,N′ chelate bonded.

Doubly branched C^α substituents can be expected to adjust the steric interaction between the R group and the *cis*-ligands in the chelate bonded

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*Note added in proof: This conclusion is confirmed by the X-ray structure determination of *trans*-[$PdCl_2(PPh_3)$\{σ-*N*-(t-Bu-dim)\}].

species by turning the smaller hydrogen atom towards the *cis*-ligands thus reducing the possible difference between the chelate and σ-N monodentate bonded situation.

The presence of C substituents on one or both of the central carbon atoms N=C(R′)C(R″)=N can be predicted to favour the s-*cis* conformation for the R-dim{R′,R″} ligand and thus the σ,σ-N,N′ chelate co-ordination mode because in this conformation the vicinal interactions will be minimal.

Thus for the [$Rh_2Cl_2(CO)_4$R-dim{R′,R′})] complexes the ionic structure should be favoured for the R-dim{R′,R″} ligands which are not triply branched at C^α, and the neutral dinuclear structure for the t-Bu and $EtMe_2C$-dim{H,H} ligands.

This is indeed the case for the complexes in solution on the NMR time scale. However, the species are observed to be in equilibrium with each other. Dissolution of [$Rh_2Cl_2(CO)_4$(R-dim{H,H})] (R = t-Bu, $EtMe_2C$-) (*4*) in $CHCl_3$ results in a mixture which at the slow exchange limit consists of the dinuclear species in two stereo-isomeric forms as well as the ionic complex. However, intermolecular exchange between the three species and five-co-ordinate [RhCl(CO)$_2$(R-dim{H,H})] could be established by spin saturation experiments (^{1}H NMR 250 MHz of an approximate 1 to 1 mixture in $CDCl_3$). Irradiation in the imine proton resonance of [$Rh_2Cl_2(CO)_4$-(t-Bu-dim{H,H})] (9.30 ppm) results in a strongly decreased intensity of the imine proton resonance of [RhCl(CO)$_2$(t-Bu-dim{H,H})] at 8.40 ppm.

At ambient temperature and above the three species exhibit fast exchange on the NMR time scale and it is interesting to observe that their imine hydrogen resonance patterns coalesce at the chemical shift position of that of the bridged species. Since the downfield shift of the imine proton in this latter species is caused by the paramagnetic anisotropy of the square planar rhodium(I) unit (see Fig. 1A,A′) the above observations indicate that the imine hydrogen spends most of its time close to the rhodium centre *i.e.* above the co-ordination plane.

Additional information on the intramolecular exchange process comes from the Me groups in the prochiral CMe_2 grouping which, in agreement with a bridging $EtMe_2C$-dim structure are diastereotopic for the complex at low temperature (see Results). However, at room temperature the Me groups become homotopic indicating that the dissymmetry is cancelled out by processes which are rapid on the NMR time scale. In view of the downfield shift of the imine-hydrogen resonances this may be explained by processes involving intermolecular Rh–Cl–Rh bridge bond making and breaking which do not affect the conformation of the NCCN skeleton with respect to the Rh^I co-ordination plane.

[$Rh_2Cl_2(CO)_4$(i-Pr_2-C(H)-dim{H,H})] in which the substituent on the imine nitrogen is doubly branched at C^α (and C^β) has an ionic structure in the solid state (see X-ray structure determination [8]). This ionic nature is retained in solution, indicated by (among other observations) the fact, that the Me groups in the prochiral CMe_2 groupings and the C atoms in the C–C^α–C unit are homotopic over the whole temperature range studied (see Fig. 2D), as is expected when the stable symmetrical *cis*-[Rh(CO)$_2$(R-dim{R′,R″})] cation is present.

Acknowledgments

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