

Syntheses and NMR Studies of Five-co-ordinate Rhodium(I) Complexes with α -Diimines ($R-N=C(H)C(H)=N-R$): $[RhCl(CO)(\eta^2-C_2H_4)(\alpha\text{-diimine})]$ and $[RhCl(L)_2(\alpha\text{-diimine})]$ ($R = t\text{-Bu, EtMe}_2C-$; $L = CO, PF_3$)

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Interaction of α -diimines ($RN=CHCH=NR$ abbreviated as *R-dim*) with $[LL'Rh(\mu\text{-Cl})_2RhLL']$ ($L=L'=CO$ or PF_3 and $L=L'=CO$, $L'= \eta^2-C_2H_4$) gives rise to various equilibrium mixtures whose nature depends on *L*.

$[RhCl(CO)(\eta^2-C_2H_4)(R\text{-dim})]$, which can be isolated, has according to 1H and ^{13}C NMR spectra a five-co-ordinate structure. The $\sigma, \sigma-N, N'$ chelate *R-dim* and η^2 -olefin ligands are in the trigonal plane of a trigonal bipyramidal array with the *Cl* and *CO* groupings residing in the axial positions, a geometry similar to that of recently reported $[PtCl_2(\eta^2\text{-styrene})(t\text{-Bu-dim})]$.

The dynamic behaviour of $[RhCl(CO)(\eta^2-C_2H_4)(R\text{-dim})]$ which involves rotation of the ethylene around the $Rh-\eta^2-C_2H_4$ axis, has been studied. These complexes readily lose ethylene providing four-co-ordinate $[RhCl(CO)(R\text{-dim})]$.

Five-co-ordinate $[RhCl(CO)_2(R\text{-dim})]$ obtained in solution are in equilibrium (slow on the NMR time scale) with free *R-dim*, the ionic $[Rh(CO)_2(R\text{-dim})][RhCl_2(CO)_2]$ and the dinuclear species $\{[RhCl(CO)_2]_2(R\text{-dim})\}$ of which the latter two are four-co-ordinate Rh^I species. 1H and ^{13}C NMR spectra point to a trigonal bipyramidal structure of the five-co-ordinate species in which the intramolecular exchange between the axial and equatorial *CO* groups is fast on the NMR time scale.

According to 1H , ^{13}C , ^{19}F and ^{31}P NMR spectra analogous $[RhCl(PF_3)_2(R\text{-dim})]$ complexes have a trigonal bipyramidal structure with *cis*- PF_3 groups of which one PF_3 group occupies the axial position trans to *Cl*.

The stability of the five-vs. the four-co-ordinate geometry of these $Rh-R\text{-dim}$ complexes is discussed in terms of the branching at C^α of *R*. A comparison is made with iso-electronic and iso-structural platinum(II)- η^2 -olefin-*R-dim* complexes.

The $[RhCl(CO)(\eta^2-C_2H_4)(R\text{-dim})]$ complexes readily undergo reversible *R-dim* exchange with 2,4,6-*Me*₃pyridine but afforded $[RhCl(CO)(PPh_3)_2]$ irreversibly with *PPh*₃.

Introduction

In recent papers we have shown that the α -diimines, $RN=C(H)C(H)=NR$ (*R-dim*), have an intriguing and versatile co-ordination chemistry [1–3]. In addition to the $\sigma, \sigma-N, N'$ chelate bonding mode, which is the only interaction found for related 2,2'-bipy and phen ligands [4] the *R-dim* ligand has a variety of other possibilities for its interaction with mono or polynuclear metal centres. Thus the *R-dim* ligand can be bonded either monodentate ($\sigma-N$), or bridging ($\sigma-N, \sigma-N'$; $\sigma-N, \mu^2-N'$, η^2-CN' ; $\sigma-N, \sigma-N'$, η^2-CN, η^2-CN'). The interesting point is that the *R-dim* ligand may contribute, via its $\sigma(N)$ and additionally via its $\pi(C=N)$ electron system, a different number of electrons (2e up to 8e) to the metal entity depending on its bonding mode.

Important factors which determine the stability of the *R-dim* metal interaction as well as the co-ordination mode (which will be found for complexes in the ground state) are: the type of metal, the co-ligands and the substituents on the $N=C-C=N$ skeleton. A clear demonstration of the influence of the imine *R* substituent, which seems mainly to arise from the type of branching at the C^α and C^β atoms, is given by various types of metal complexes found in Fe^0 , Ru^0 and Os^0 carbonyl- α -diimine chemistry, e.g. singly branched at C^α : $[Ru_3(CO)_8(i\text{-dim})]$ ($\sigma-N, \sigma-N', \eta^2-CN, \eta^2-CN'$); doubly branched at C^α and singly at C^β : $[Ru_2(CO)_6(i\text{-Pr-dim})]$ ($\sigma-N, \sigma-N', \eta^2-CN'$); doubly branched at C^α and C^β : $[Ru(CO)_3(i\text{-Pr}_2C(H)\text{-dim})](\sigma, \sigma-N, N')$ [2, 3].

In the case of *Rh*, *Pd* and *Pt* *R-dim* complexes the *R-dim* ligand is bonded only via the lone pairs on the nitrogen atoms. The first examples of $\sigma-N$

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monodentate and σ -N, σ -N' bridge bonded R-dim ligands were established by extensive multinuclear NMR studies, isotope labelling (^{15}N) and X-ray structure analyses [1, 5]. Furthermore, by using the R-dim ligand stable five-co-ordinate platinum(II)-olefin complexes $[\text{PtCl}_2(\eta^2\text{-olefin})(\text{R-dim})]$ [6–8] could be synthesized and studied by multinuclear NMR spectrometry [5]. The use of a phosphine or arsine instead of the olefin as a co-ligand destabilized the five-co-ordinate geometry and $[\text{PtCl}_2(\text{PBU}_3)(\text{t-Bu-dim-}^{15}\text{N}_2)]$, for example in the ground, state is four-co-ordinate with a σ -N monodentate bonded R-dim ligand [1, 5]. This paper reports the results of a comparative study directed to the isolation and characterization of the Rh^{I} analogues of the already studied five-co-ordinate platinum–R-dim complexes. It will be shown that the rhodium(I) complexes of the type $[\text{RhClL}^1\text{L}^2(\text{R-dim})]$ ($\text{L}^1=\text{L}^2=\text{CO}$ or PF_3 ; $\text{L}^1=\text{CO}$, $\text{L}^2=\text{C}_2\text{H}_4$) are less stable and, in solution, are in equilibrium with $[\text{Rh}_2\text{Cl}_2(\text{CO})_4(\text{R-dim})]$ (either the neutral dinuclear or the ionic species) and the free R-dim ligand. Moreover, examples will be discussed which demonstrate that the type of imine substituent (R) in combination with the imine-carbon substituent have a large influence on the stability of the five-co-ordinate Rh–R-dim complexes. This was already apparent from the observation that whereas $[\text{Rh}_2\text{Cl}_2(\text{CO})_4(\text{t-Bu-dim})]$ contains in solution a σ -N, σ -N' bridging t-Bu-dim ligand [9, 10] the ionic complex $[\text{Rh}(\text{CO})_2(\text{i-Pr}_2\text{C}(\text{H})\text{-dim})]$ $[\text{RhCl}_2(\text{CO})_2]$ has a σ , σ -N, N' chelate bonded i-Pr₂C(H)-dim ligand [11]. In a subsequent paper these results will be reported [10].

Experimental

Preparation of the Compounds

The α -diimines $\text{R-N}=\text{CHCH}=\text{N-R}$ (abbreviated as R-dim; $\text{R}=\text{t-Bu}$, EtMe_2C) [1] as well as the starting complexes $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]$ [12a], $[\{\text{Rh}(\text{COT})_2\text{Cl}\}_2]$ [12b] and $[\{\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}\}_2]$ [12c] were prepared by standard methods. $[\{\text{Rh}(\text{CO})(\eta^2\text{-C}_2\text{H}_4)\text{Cl}\}_2]$ was prepared via the reaction of an equimolar mixture of $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]$ and $[\{\text{Rh}(\eta^2\text{-C}_2\text{H}_4)_2\text{Cl}\}_2]$ in benzene as described by Powell and Shaw [13]. $[\{\text{Rh}(\text{PF}_3)_2\text{Cl}\}_2]$ was obtained from a direct substitution of COT in $[\{\text{Rh}(\eta^2\text{-COT})_2\text{Cl}\}_2]$ by PF_3 in hexane [14].

The preparation of the metal complexes, carried out in a N_2 atmosphere, are described below. Solvents were dried and distilled before use.

$[\text{RhCl}(\text{CO})_2(2,4,6\text{-trimethylpyridine})_2(5)]$ [15]

From a 1/2 molar reaction mixture of $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]$ and 2,4,6-Me₃py in hexane $[\text{RhCl}(\text{CO})_2(2,4,6\text{-Me}_3\text{py})]$ was obtained as a yellow coloured micro-

crystalline product in a 70–80% yield. *Anal.* Calcd. for $[\text{RhCl}(\text{CO})_2((\text{CH}_3)_3\text{C}_5\text{H}_2\text{N})]$: C, 38.03; H, 3.49; N, 4.39%. Found: C, 38.19; H, 3.64; N, 4.39%. Infrared $\nu(\text{CO})$: 1974, 2000, 2050, 2072 cm^{-1} (Nujol mull) 2005, 2080 cm^{-1} (CHCl_3 solution). ^1H NMR (CDCl_3 , 34 °C): δ 2,6-Me₂, 2.73; δ 4-Me, 2.30; δ 3-H, 6.97 ppm. ^{13}C NMR (CDCl_3 , –50 to 34 °C): δ 2,6-Me₂, 25.85; δ 4-Me, 19.82; δ py 123.43, 150.57, 158.09; δ CO, 178.82 (73.5 Hz), 182.95 ppm ($J(^{103}\text{Rh}-^{13}\text{C}) = 67$ Hz).

Mixture of Cis and Trans Isomer of $[\text{RhCl}(\text{CO})(\eta^2\text{-C}_2\text{H}_4)(2,4,6\text{-trimethylpyridine})]$ (4) [15]

From a 1/2 molar reaction mixture of $[\{\text{Rh}(\text{CO})\eta^2\text{-C}_2\text{H}_4\text{Cl}\}_2]$ and 2,4,6-Me₃py in hexane consisting as a 1/1 mixture of two isomers with *trans* positioned CO-py and C₂H₄-py was obtained as a yellow-orange coloured microcrystalline product in a 70–80% yield. *Anal.* Calcd. for $[\text{RhCl}(\text{CO})(\eta^2\text{-C}_2\text{H}_4)((\text{CH}_3)_3\text{C}_5\text{H}_2\text{N})]$: C, 41.84; H, 4.75; N, 4.44; Cl, 11.25%. Found: C, 41.39; H, 4.72; N, 4.31; Cl, 11.61%. Infrared $\nu(\text{CO})$: 1941, 2004 cm^{-1} (KBr). ^1H NMR (CDCl_3 , 34 °C): δ 2,6-Me₂, 3.07; δ 4-Me, 2.31; δ 3-H, 6.85, 6.98; δ H₂C=, 3.33 (1 Hz), 4.17 ppm ($^2J(^{103}\text{Rh}-^1\text{H}) < 1$ Hz). ^{13}C NMR (–50 to 34 °C): δ , 2,6-Me₂, 25.33, 26.58; δ 4-Me, 20.50; δ C=, 55.93 (12.5 Hz), 63.26 (10.7 Hz); δ py, 123.78, 124.05, 150.16, 157.24, 158.26; δ CO, 179.75 (74.1 Hz), 183.75 ppm ($^1J(^{103}\text{Rh}-^{13}\text{C}) 68.5$ Hz).

$[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$ [16]

From a 1/4 molar reaction mixture of $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]$ and PPh_3 in hexane $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$ was obtained in almost quantitative yield as a yellow microcrystalline product. *Anal.* Calcd. for $[\text{RhCl}(\text{CO})(\text{C}_{18}\text{H}_{15}\text{P})_2]$: C, 64.30; H, 4.34; Cl, 5.15; P, 8.98; O, 2.32%. Found: C, 64.15; H, 4.52; Cl, 5.34; P, 8.51; O, 2.17%. Infrared $\nu(\text{CO})$ 1961 cm^{-1} (Nujol mull). ^{31}P NMR (CDCl_3 , 34 °C) δ PPh_3 , 29.2 ppm ($J(^{103}\text{Rh}-^{31}\text{P}) 127$ Hz).

$[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$ starting from: $[\text{Rh}_2\text{Cl}_2(\text{CO})_4(\text{R-dim})]$, $[\text{RhCl}(\text{CO})_2(\text{R-dim})]$, $[\text{RhCl}(\text{CO})_2(2,4,6\text{-Me}_3\text{py})]$, $[\text{RhCl}(\text{CO})(\eta^2\text{-C}_2\text{H}_4)(\text{R-dim})]$ and $[\text{RhCl}(\text{CO})(\eta^2\text{-C}_2\text{H}_4)(2,4,6\text{-Me}_3\text{py})]$.

A solution of triphenylphosphine (1.5 mmol) in chloroform was added dropwise to a stirred solution of $[\text{RhCl}(\text{CO})\text{L}^1\text{L}^2]_n$ (0.5 mmol) in chloroform (3–5 ml). During the addition of PPh_3 gas (CO or C₂H₄) was liberated, while the solution turned pale yellow and $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$ started to precipitate. The reaction mixture was stirred for an additional 30 min and 10–20 ml hexane was added to complete precipitation. The complex was collected by filtration, washed with hexane (5 × 10 ml) and dried *in vacuo* (yield 80–90%).

$[Rh_2Cl_2(CO)_4(R-dim)]$ ($R = t-Bu$ (7a), $EtMe_2C$ (7b)) [9, 10]

From a 1/1 molar reaction mixture of $[\{Rh(CO)_2Cl\}_2]$ and R-dim in hexane $[Rh_2Cl_2(CO)_4(R-dim)]$ was obtained as a micro-crystalline product in almost quantitative yield. (7a) *Anal.* Calcd. for $[Rh_2Cl_2(CO)_4(C_{10}H_{20}N_2)]$: C, 30.16; H, 3.59; Cl, 12.75; N, 5.03%. Found: C, 30.09; H, 3.86; Cl, 12.22; N, 4.70%. Infrared: $\nu(CO)$: 2080, 2064, 2010, 1984 cm^{-1} (Nujol mull), 2020, 2084 cm^{-1} ($CHCl_3$ solution). 1H NMR ($CDCl_3$, 34 °C): δ Me₃, 1.67; δ CH=N, 9.28 ppm (7b) *Anal.* Calcd. for $[Rh_2Cl_2(CO)_4(C_{12}H_{26}N_2)]$: C, 32.85; H, 4.13; Cl, 12.12; N, 4.79%. Found: C, 32.92; H, 4.16; Cl, 12.05; N, 4.72%. Infrared $\nu(CO)$: 2086, 2060, 2026, 1988 cm^{-1} (Nujol mull) 2004, 2072 cm^{-1} ($CHCl_3$ solution). 1H NMR ($CDCl_3$, 34 °C), δ CH₃, 0.93 (t) 1.57 (s); δ CH₂, 1.90 (q); δ CH=N, 9.23 ppm.

$[RhCl(CO)(\eta^2-C_2H_4)(R-dim)]$ ($R = t-Bu$ (1a), $EtMe_2C$ (1b))

A solution of R-dim (2.2 mmol) in hexane (5 ml) was added to a vigorously stirred solution of $[\{Rh(CO)(\eta^2-C_2H_4)Cl\}_2]$ (1 mmol) in hexane (20 ml). $[RhCl(CO)(\eta^2-C_2H_4)(R-dim)]$ immediately precipitated as a violet microcrystalline product which was collected by filtration after 5 min of additional stirring. The air sensitive product was washed with hexane (3 × 10 ml, removal of the excess of R-dim) and dried *in vacuo* at room temperature. Yield 70–80%. *Anal.* Calcd. for $[RhCl(CO)(C_2H_4)(C_{10}H_{20}N_2)]$ (1a): C, 43.03; H, 6.62; N, 7.72; Cl, 9.79%. Found: C, 42.59; H, 6.77; N, 7.68; Cl, 9.88%.

In situ Preparation of $[RhCl(CO)_2(R-dim)]$ ($R = t-Bu$ (3a), $EtMe_2C$ (3b) and $[RhCl(PF_3)_2(R-dim)]$ ($R = t-Bu$ (6a), $EtMe_2C$ (6b))

$[\{Rh(CO)_2Cl\}_2]$ (1 eq) and R-dim (2.2 eq) were brought into a NMR tube and dissolved in $CDCl_3$ or C_6D_6 . The resulting solution of $[RhCl(CO)_2(R-dim)]$ containing excess of R-dim was used for the NMR spectroscopic studies.

In a similar way solutions of $[RhCl(PF_3)_2(R-dim)]$ were prepared by mixing $[\{Rh(PF_3)_2Cl\}_2]$ and R-dim in a 1/2.2 molar ratio. *Caution: the complexes fume in presence of air and moisture with decomposition.*

$[RhCl(CO)_2(t-Bu-dim)]$ (3a)

A solution of t-Bu-dim (2.2 mmol) in hexane (5 ml) was added to a vigorously stirred solution of $[\{Rh(CO)_2Cl\}_2]$ (1 mmol) in hexane (20 ml). The solution was additionally stirred for 15 min and concentrated to 10 ml. After standing for 7 days at -80 °C a yellow microcrystalline product was formed which was collected by filtration and dried *in vacuo* at 0 °C. *Anal.* Calcd. for $[RhCl(CO)_2(C_{10}H_{20}N_2)]$: C, 39.72; H, 5.52; N, 7.72; Cl, 9.79%. Found: C, 36.74; H, 5.77; N, 7.46; Cl, 10.16%. The lower C value is

probably caused by evolution of CO during the combustion procedure. Recalculation of the carbon present gives C, 36.41%. 1H NMR spectra of solutions of the isolated product in $CDCl_3$ showed the presence of an equilibrium mixture consisting of t-Bu-dim, $[Rh_2Cl_2(CO)_4(t-Bu-dim)]$ (7a) and at least 90% $[RhCl(CO)_2(t-Bu-dim)]$ (3a).

$[RhCl(CO)_2(R-dim)]$ (3a,b) Starting from $[RhCl(CO)(\eta^2-C_2H_4)(R-dim)]$ (1a,b)

Carbon monoxide was bubbled through a solution of $[RhCl(CO)(\eta^2-C_2H_4)(R-dim)]$ in $CDCl_3$ for 10 min. The initially deep-violet coloured solution turned to pale-orange with formation of $[RhCl(CO)_2(R-dim)]$. To remove excess CO, for NMR experiments of *in situ* prepared samples, N_2 was then bubbled through the solution for 5 min*.

$[RhCl(CO)_2(2,4,6-Me_3py)]$ (5) Starting from $[RhCl(CO)_2(R-dim)]$ (3a,b)

2,4,6-Me₃py (3 mmol) was added to a stirred solution of $[RhCl(CO)_2(R-dim)]$ (1 mmol) in chloroform (10 ml). The solution was concentrated to 1 ml and hexane (15 ml) was added followed by stirring for 1 h. During this time the complex slowly crystallized. (Complete crystallization could be accomplished by standing of the solution at -30 °C for several days). The crystals were collected by filtration and washed with hexane (3 × 10 ml) and dried *in vacuo*. Yield ~50%*.

By a similar procedure $[RhCl(CO)(\eta^2-C_2H_4)(2,4,6-Me_3py)]$ (4) was prepared from $[RhCl(CO)(\eta^2-C_2H_4)(R-dim)]$ (1a,b). Yield 50%*.

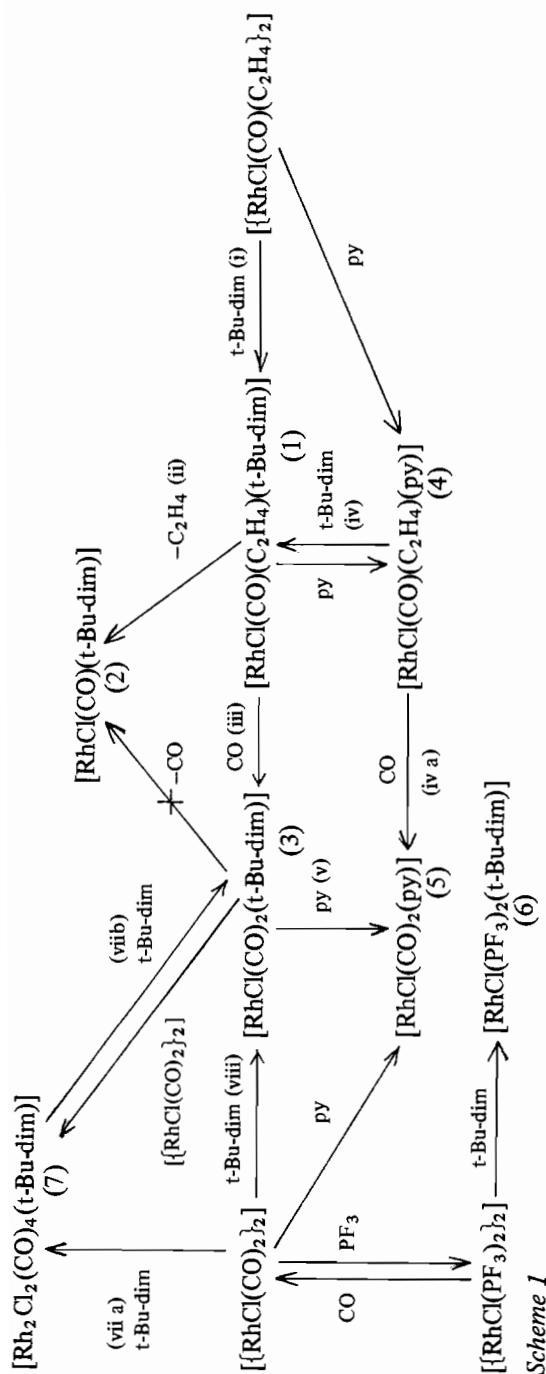
$[RhCl(CO)(\eta^2-C_2H_4)(t-Bu-dim)]$ (1a) Starting from $[RhCl(CO)(\eta^2-C_2H_4)(2,4,6-Me_3py)]$ (4)

A solution of t-Bu-dim (2 mmol) in hexane (2 ml) was added to a stirred suspension of $[RhCl(CO)(\eta^2-C_2H_4)(2,4,6-Me_3py)]$ (0.5 mmol) in hexane (10 ml). The colour of the suspension turned slowly from pale-yellow to deep violet. After 30 min the violet precipitate ($[RhCl(CO)(\eta^2-C_2H_4)(t-Bu-dim)]$) was isolated by filtration, washed with hexane (5 × 10 ml) and dried *in vacuo*. Yield 50–60%*. The final product was contaminated with a small amount of starting complex.

Field Desorption Mass Spectra

The FD 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 spectro-system MAT 100 data acquisition unit. The samples were dissolved either in hexane or chloroform and then loaded onto the emitters with

* ^{13}C NMR spectra of the *in situ* prepared solutions indicated that the reactions proceed quantitatively.



The compounds with *t*-Bu-dim (*1a*–*3a*, *6a*, *7a*) are shown. Similar compounds containing EtMe₂C-dim (*1b*–*3b*, *6b*, *7b*) have also been prepared.

the dipping technique. The source temperature was generally 60 °C. The *m/z* value of the Cl containing fragments relate to the molecular weight calculated on ³⁵Cl.

[RhCl(CO)₂(2,4,6-Me₃py)] calcd. parent ion 315; found: *m/z* 315 and 388 (assigned to [[RhCl(CO)₂]₂]).

[RhCl(CO)(η²-C₂H₄)(*t*-Bu-dim)] calcd. 362; found: *m/z* 334 (assigned to [RhCl(CO)(*t*-Bu-dim)]).

[RhCl(CO)(η²-C₂H₄)(*t*-Bu-dim)] with small excess of [[RhCl(CO)(η²-C₂H₄)]₂] calcd. 388; found: *m/z* 327 (no ^{35,37}Cl isotope pattern; assigned to [Rh(CO)(η²-C₂H₄)(*t*-Bu-dim)]), 334 ([RhCl(CO)(*t*-Bu-dim)]), 362 ([RhCl(CO)(η²-C₂H₄)(*t*-Bu-dim)]), 388 ([[Rh(CO)₂Cl]₂]).

A solution of [RhCl(CO)₂(*t*-Bu-dim)] in chloroform obtained by ethylene to CO exchange from [RhCl(CO)(η²-C₂H₄)(*t*-Bu-dim)] (see scheme 1 eq iii): calcd. 362. Found: *m/z* 327 (no ^{35,37}Cl isotope pattern, assigned to [Rh(CO)₂(*t*-Bu-dim)]⁺) 334 ([RhCl(CO)(*t*-Bu-dim)]), 362 ([RhCl(CO)₂(*t*-Bu-dim)] and 388 ([[RhCl(CO)₂]₂]).

In situ mixture of [[RhCl(CO)(η²-C₂H₄)]₂] (1.5 eq) with *t*-Bu-dim (2 eq) in chloroform (see eqn. i of scheme 1): found: *m/z* 327 (no ^{35,37}Cl isotope pattern, [Rh(CO)₂(*t*-Bu-dim)]), 334 ([RhCl(CO)(*t*-Bu-dim)]), 350 (complex pattern probably [RhCl(CO)(η²-C₂H₄)Rh(CO)(η²-C₂H₄)]), 362 ([RhCl(CO)(η²-C₂H₄)(*t*-Bu-dim)] and 388 ([[RhCl(CO)(η²-C₂H₄)]₂]).

In situ mixture of [[RhCl(CO)₂]₂] (1 eq) with *t*-Bu-dim (2.5 eq) in hexane (see eq. vii and viii of scheme 1); found: *m/z* 327 ([Rh(CO)₂(*t*-Bu-dim)]), 334 ([RhCl(CO)(*t*-Bu-dim)]), 362 ([RhCl(CO)₂(*t*-Bu-dim)] and 388 [[RhCl(CO)₂]₂]).

In all spectra ions with *m/z* values corresponding to the dimer were found of [RhCl(CO)(*t*-Bu-dim)]₂ *m/z* 688 the relative intensity which increased upon raising the temperature.

For the FD-mass spectra of the corresponding EtMe₂C-dim complexes similar results were obtained. The observed *m/z* values and the assignment to respective ions are: *m/z* 335 [Rh(CO)₂(EtMe₂C-dim)]⁺, 362 [RhCl(CO)(EtMe₂C-dim)], 390 [RhCl(CO)₂(EtMe₂C-dim)].

It is worth noting that the *m/z* values of CO and C₂H₄ are similar (28); so assignments are made in combination with NMR results (*vide infra*).

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).

¹H NMR spectra were recorded on a Varian T-60 or on a Bruker WP 250 spectrometer with tetramethylsilane (TMS) as internal standard; ¹³C NMR spectra were obtained on a Varian CFT-20 (TMS internal standard), ¹⁹F and ³¹P NMR spectra on a

TABLE I. ^1H , ^{13}C NMR^a and Infrared^b Spectra of $[\text{RhCl}(\text{CO})(\eta^2\text{-C}_2\text{H}_4)(\text{R-dim})]$, $[\text{RhCl}(\text{CO})_2(\text{R-dim})]$ and $[\text{RhCl}(\text{PF}_3)_2(\text{R-dim})]$ Complexes.

| | ^1H -dim | $[\text{RhCl}(\text{CO})(\text{C}_2\text{H}_4)\text{-}(\text{t-Bu-dim})\text{-}]$ | $[\text{RhCl}(\text{CO})_2\text{-}(\text{t-Bu-dim})]$ | $[\text{RhCl}(\text{PF}_3)_2\text{-}(\text{t-Bu-dim})]$ | $\text{EtMe}_2\text{C-dim}$ +34 °C | $[\text{RhCl}(\text{CO})(\text{C}_2\text{H}_4)(\text{EtMe}_2\text{C-dim})]$ +34 °C | $[\text{RhCl}(\text{CO})_2\text{-}(\text{EtMe}_2\text{C-dim})]$ -55 °C, 250 MHz | $[\text{RhCl}(\text{PF}_3)_2\text{-}(\text{EtMe}_2\text{C-dim})]$ |
|----------------------------------|-------------------|---|---|---|---------------------------------------|---|--|---|
| ¹ H NMR | | | | | | | | |
| CH ₃ | 1.30s | 1.57s | 1.45s | 1.45s | 0.85t, 1.23s | 0.83t, 1.49s 1.57s | 0.74t, 1.47s 1.60s | 0.86t, 1.33s |
| CH ₂ | | | | | 1.63q | 2.0m | 1.93m, 2.14m | 1.73q |
| CH=N | 7.93s | 8.27(1)s | 8.40(1)s | 8.45(9) ^c | 7.88s | 8.20(1)s | 8.21s | 8.62(9) ^c |
| CH ₂ =CH ₂ | | 2.75(2)s, [2.65] ^d | | | | 2.75(2)s | 2.73m ^e | |
| ¹³ C NMR | | | | | | | | |
| CH ₃ | 22.84 | 30.39 | 29.77 | 31.09 | 8.02, 25.97 | 8.18, 25.16 28.66 | 8.18, 27.35 | 8.32, 27.19 27.57 |
| CH ₂ | | | | | 35.08 | 35.03 | 35.39 | 35.42 |
| C-N | 56.94 | 62.65 | 62.31 | 66.86 | 60.16 | 65.03 | 65.06 | 65.23 |
| C=N | 156.59 | 155.69 | 160.58 | 164.19(4) ^f | 157.85 | 156.02 | 161.58 | 161.07(2) ^f |
| C=C | | 34.39(14.5), [33.20(13.6)] ^g | | | | 33.09(14.5) | | |
| C=O | | 183.76(69) | 181.08(71) | | | 183.27(70) | | 181.50(70) |
| Ir | | | | | | | | |
| $\nu(\text{CO})$ | | 1995 | 2010(2020) ^h 2091(2084) ^h | | | 1997 | | 2017 2092 |

^a ^1H (60 MHz) and ^{13}C (20 MHz) NMR, 34 °C, recorded in CDCl_3 δ ppm relative to TMS, $^n\text{J}({}^{103}\text{Rh}-{}^1\text{H})$ and $n\gamma({}^{103}\text{Rh}-{}^{13}\text{C})$ values in brackets (.. Hz). ^b Infrared spectra recorded as CHCl_3 solutions. ^c $^4\text{J}({}^{31}\text{P}-{}^1\text{H})$ coupling. ^d Recorded at -55 °C, 250 MHz, AA'BB' pattern $\Delta\delta$ AB 68 Hz. ^e AA'BB' pattern $\Delta\delta$ AB 72 Hz. ^f $^1\text{J}({}^{31}\text{P}-{}^{13}\text{C})$ coupling. ^g Recorded at -50 °C. ^h Raman data.

Varian XL-100 with CHF_3 and H_3PO_4 as external standard, respectively.

Infrared and Raman spectra were measured on either a Beckman 4250 or Perkin-Elmer M283 (IR) and a Ramanor HG 25 Raman spectrophotometer.

Results

Scheme 1 shows the various routes via which the novel Rh^1 -R-dim complexes (R = t-Bu or EtMe_2C) 1–3 and 6 have been prepared.

The complexes have low stability, $[\text{RhCl}(\text{CO})(\eta^2\text{-C}_2\text{H}_4)(\text{R-dim})]$ (1) readily loses C_2H_4 affording complex $[\text{RhCl}(\text{CO})(\text{R-dim})]$ (2) while $[\text{RhCl}(\text{CO})_2(\text{R-dim})]$ (3) and $[\text{RhCl}(\text{PF}_3)_2(\text{R-dim})]$ (6) slowly decompose into intractable products. This made identification of the complexes by elemental analysis difficult because often invariable and inconsistent data were obtained. However, the complexes could be directly made quantitatively *in situ* from well characterized Rh^1 precursors. Furthermore, their structure in solution could be studied by extensive ^1H and ^{13}C as well as ^{19}F and ^{31}P NMR spectrometry (*vide infra*). In several cases samples of freshly prepared solutions were concentrated and the residues directly analysed by F.D. mass spectrometry. Finally, selected reactions of the complexes 1 and 3 with phosphines or pyridines resulted in formation of known products (*vide infra*) which were identified by elemental analyses and ^1H and ^{13}C NMR data.

$[\text{RhCl}(\text{CO})(\eta^2\text{-C}_2\text{H}_4)(\text{R-dim})]$ (R = t-Bu (1a), EtMe_2C (1b))

The reaction of $[\{\text{Rh}(\text{CO})(\eta^2\text{-C}_2\text{H}_4)\text{Cl}\}_2]$ with R-dim (R = t-Bu, EtMe_2C) resulted in the direct precipitation of violet coloured $[\text{RhCl}(\text{CO})(\eta^2\text{-C}_2\text{H}_4)(\text{R-dim})]$ (1a,b) whose elemental analyses confirmed this stoichiometry.

The combined infrared, ^1H (60, 90, 250 MHz) and ^{13}C (20 MHz) NMR data of 1a,b are presented in Table I.

Infrared spectra in both Nujol and CHCl_3 show one absorption in the CO region.

In the ^{13}C NMR spectra at both +34 °C and at –50 °C one carbon resonance is observed for the carbonyl carbon atom which as a result of a $J(^{103}\text{Rh}-^{13}\text{C})$ of 70 Hz is split into a doublet.

For the t-Bu-dim ligand in 1a only one ^{13}C and ^1H NMR resonance pattern is observed in the temperature range studied (–50 °C to +34 °C; see Table I) which indicates that both t-Bu–N=C(H) halves of the ligand are in equivalent chemical environments. Moreover, a $^4J(^{103}\text{Rh}-^1\text{H})$ of 1 Hz is observed on both imine protons. These observations point to a $\sigma,\sigma\text{-N,N}'$ co-ordination mode of the t-Bu-dim ligand in 1a on the NMR time scale.

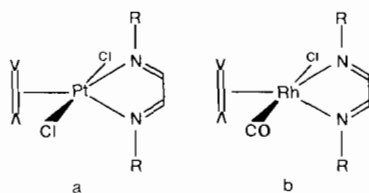


Fig. 1. A, Trigonal bipyramidal structure of five-coordinate $[\text{PtCl}_2(\eta^2\text{-olefin})(\text{R-dim})]$ complexes. B, Proposed structure for five-coordinate $[\text{RhCl}(\text{CO})(\eta^2\text{-C}_2\text{H}_4)(\text{R-dim})]$ complexes.

The ethylene carbon resonances in 1 are isochronous and are observed as a doublet due to $^{103}\text{Rh}-^{13}\text{C}$ coupling of 14.5 Hz which is present from –50 °C to +34 °C. Moreover, these ethylene carbon resonances have undergone a distinct upfield shift of about 30 ppm with respect to olefinic carbon resonances in four-coordinate $[\text{RhCl}(\eta^2\text{-C}_2\text{H}_4)(\text{C-L})]$ complexes (see Tables I, II).

These NMR data are consistent with a trigonal bipyramidal structure shown in Fig. 1 which is analogous to the five-coordinate structure reported for *trans*- $[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)(\text{t-Bu-dim})]$ [7, 8].

The olefin and the chelate bonded R-dim ligand reside in the equatorial plane with the CO ligand and Cl atom occupying the axial positions.

That the bidentate and the three monodentate ligands are indeed bonded to the Rh centre is supported by the NMR resonance patterns observed for the EtMe_2C -substituents in 1b. The EtMe_2C -group contains two prochiral centres, *i.e.* the $\text{C}(\text{Me})_2$ and the $\text{C}(\text{H})_2$ group by which dissymmetry in such a trigonal bipyramidal array can be detected.

The two EtMe_2C -groupings as well as the imine $\text{CH}=\text{N}$ groups in $[\text{RhCl}(\text{CO})(\eta^2\text{-C}_2\text{H}_4)(\text{EtMe}_2\text{C-dim})]$ give rise to single resonance patterns. This is in accord with the presence of an apparent molecular symmetry plane which is perpendicular to the trigonal equatorial plane and contains the Cl–Rh–CO entity as well as the Rh–olefin bond axis. Accordingly the EtMe_2C -groups reside in enantiotopic surroundings and are isochronous. However, the fact that the CH_2 protons appear in the ^1H NMR spectrum as two multiplets (from an ABX_3 spin system) indicates that they are diastereotopic. This is in line with the fact that the proposed trigonal bipyramidal array is dissymmetric with respect to the $\text{C}(\text{H})_2$ centre. The observation of two singlets for the $\text{C}(\text{Me})_2$ carbon atoms, which indicates that these groups are also diastereotopic provides a further confirmation for the proposed structure (see Fig. 2a for the ^1H NMR spectrum).

The olefinic resonance pattern is the only part of the ^1H NMR spectrum which is temperature dependent. At –50 °C a four line $\text{AA}'\text{BB}'$ pattern with $\Delta\delta$ AB of about 70 Hz is present in the 90 and 250 MHz spectra. In the 60 MHz NMR spectrum this pattern coalesces near room temperature (34 °C)

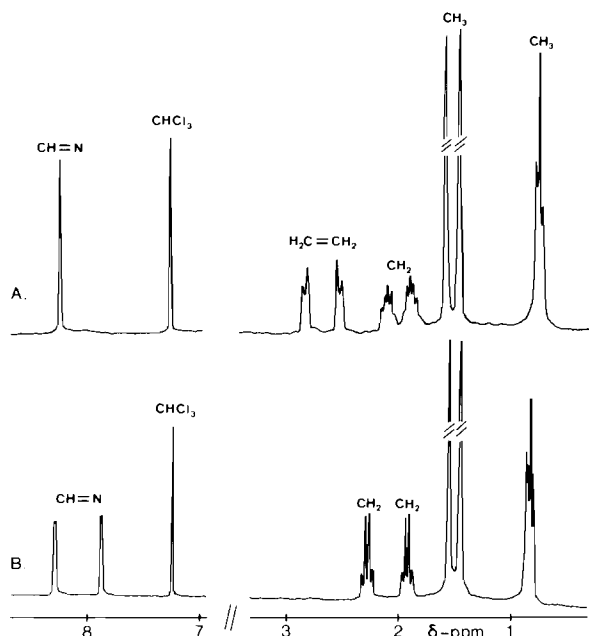


Fig. 2. ^1H NMR spectra (250 MHz, 34°C , CDCl_3) of $[\text{RhCl}(\text{CO})(\eta^2\text{-C}_2\text{H}_4)(\text{EtMe}_2\text{C-dim})]$ (A) and $[\text{RhCl}(\text{CO})(\text{EtMe}_2\text{C-dim})]$ (B): the latter complex was obtained by decomposition of (A) according to equation $[\text{RhCl}(\text{CO})(\eta^2\text{-C}_2\text{H}_4)(\text{EtMe}_2\text{C-dim})] \rightarrow [\text{RhCl}(\text{CO})(\text{EtMe}_2\text{C-dim})] + \text{C}_2\text{H}_4$.

resulting in one resonance split into a doublet by $^2\text{J}(^{103}\text{Rh}-^1\text{H})$ of 2 Hz.

This behaviour of the olefin resonances is connected with rotation of the olefin around the rhodium-olefin bond axis. In the slow exchange limit (-50°C) the olefin has a conformation in which the $\text{C}=\text{C}$ bond is co-planar with the equatorial plane of the trigonal bipyramid (see Discussion). Accordingly the olefinic carbon atoms reside in enantiotopic surroundings and are isochronous as indeed is observed in the ^{13}C NMR spectrum (-50°C to $+34^\circ\text{C}$). By contrast the geminal olefinic hydrogen atoms reside in diastereotopic environments, owing to the axial Cl and CO ligands, and this results in $\text{AA}'\text{BB}'$ ^1H NMR pattern (-50°C). The multiplet is, however, slightly broadened because of rhodium coupling.

At $+34^\circ\text{C}$ fast rotation of the olefin is evidenced by coalescence of the olefin-proton resonance multiplet into one resonance with $^2\text{J}(^{103}\text{Rh}-^1\text{H})$. The observation of ^{103}Rh couplings on both ^1H and ^{13}C olefinic signals at temperatures studied indicates that the processes are intramolecular and that occurrence of reversible olefin-rhodium bond dissociation/association processes do not occur.

Five-co-ordinate $[\text{RhCl}(\text{CO})(\eta^2\text{-C}_2\text{H}_4)(\text{R-dim})]$ (*1a,b*) are rather labile species which slowly decompose in solution and in the solid state. Preliminary experiments on solutions of *1a* and *1b*, followed by ^1H NMR spectroscopy, showed that thermal decomposition resulted in release of C_2H_4 ; the 2 Hz $^{103}\text{Rh}-^1\text{H}$ coupling to the olefinic protons was lost and

their chemical shift moved downfield to the position of free ethylene. The final spectra obtained (see Fig. 2b) are in accord with a four-co-ordinate species* $[\text{RhCl}(\text{CO})(\text{R-dim})]$ ($\text{R} = t\text{-Bu}$ (*2a*), $\text{EtMe}_2\text{C-}$ (*2b*)); see also FD mass results) in which there is dissymmetry in the co-ordination plane and the two N donors of the $\sigma,\sigma\text{-N,N}'$ bonded R-dim ligand are co-ordinated to a $\text{RhCl}(\text{CO})$ entity. The $t\text{-Bu}$ and $\text{EtMe}_2\text{C-}$ groups in *2a* and *b*, respectively, are anisochronous and appears in the ^1H spectrum as two doublets. The second splitting of the $\text{HC}=\text{N}$ resonance is due to $^3\text{J}(^{103}\text{Rh}-^1\text{H})$, and not to $^3\text{J}(^1\text{H}-^1\text{H})$. This was deduced from homonuclear proton decoupling experiments in which the doublet resonance pattern remained unaffected by irradiation at either 7.86 (1965) or 8.27 ppm (2067 Hz).

The absence of an observable $^3\text{J}(^1\text{H}-^1\text{H})$ in $\text{N}=\text{C}(\text{H})\text{C}(\text{H})=\text{N}$ skeletons of R-dim ligands, in which the $\text{N}=\text{C}(\text{H})$ halves are anisochronous, is a common feature. This has been found for example in $[\text{PtCl}_2(\eta^2\text{-styrene})(t\text{-Bu-dim})]$ complex at the olefin non rotation limit [8] and in $[\text{M}_2(\text{CO})_6(\text{R-dim})]$ ($\text{M} = \text{Fe}, \text{Ru}$) complexes which contain $\sigma\text{-N}$, $\mu^2\text{-N}'$, $\eta^2\text{-CN}'$ bonded R-dim [2, 3].

$[\text{RhCl}(\text{CO})_2(\text{R-dim})]$ ($\text{R} = t\text{-Bu}$ (*3a*), $\text{EtMe}_2\text{C-}$ (*3b*))

The addition of an equivalent of R-dim to a suspension of $[\text{Rh}_2\text{Cl}_2(\text{CO})_4(\text{R-dim})]$ (*7a,b*) (see Experimental) or the 2/1 reaction of R-dim with $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]$ in hexane resulted in the direct formation of $[\text{RhCl}(\text{CO})_2(\text{R-dim})]$ ($\text{R} = t\text{-Bu}$ (*3a*), $\text{EtMe}_2\text{C-}$ (*3b*)). However, attempts to isolate *3a,b* either by evaporation of the solvent or by crystallization at -80°C failed (see Experimental).

Assignment of a structure for *3a,b* on the basis of infrared, Raman, ^1H and ^{13}C NMR data is difficult.

The infrared and Raman spectra of *in situ* prepared samples of *3a,b* in chloroform revealed two absorptions in the $\nu(\text{CO})$ stretching region (2010, 2087 cm^{-1} ; *3a*) indicating the presence of two carbonyl ligands terminally bonded to rhodium. In the $200\text{--}400\text{ cm}^{-1}$ region the infrared spectra show two almost equally strong absorptions at 361 and 313 cm^{-1} . In the Raman spectra the latter bond is very weak. On this basis we assign the strong band at 361 cm^{-1} to a terminal $\text{Rh}-\text{Cl}$ stretching vibration.

The ^1H and ^{13}C NMR spectra were recorded on *in situ* prepared solutions of $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]$ with R-dim in a 1/2.2 molar ratio. The excess R-dim appeared in these spectra as a sharp resonance pattern at the position of the free ligand (see Discussion).

One resonance is observed in the ^{13}C NMR spectra of *3a,b* for the carbonyl carbon atoms which as a result of $\text{J}(^{103}\text{Rh}-^{13}\text{C})$ of 71 Hz (*3a*) is split into a

* ^1H NMR data (CDCl_3 , 25°C , 250 MHz) of $[\text{RhCl}(\text{CO})(\text{EtMe}_2\text{C-dim})]$: δ CH_3 0.80 t, 1.43 s, 1.53 s; CH_2 1.91 q, 2.27 q; $\text{CH}=\text{N}$ 7.86 ($^3\text{J}(^{103}\text{Rh}-^1\text{H}) < 1\text{ Hz}$), 8.27 ppm ($^3\text{J}(^{103}\text{Rh}-^1\text{H})$ 4 Hz).

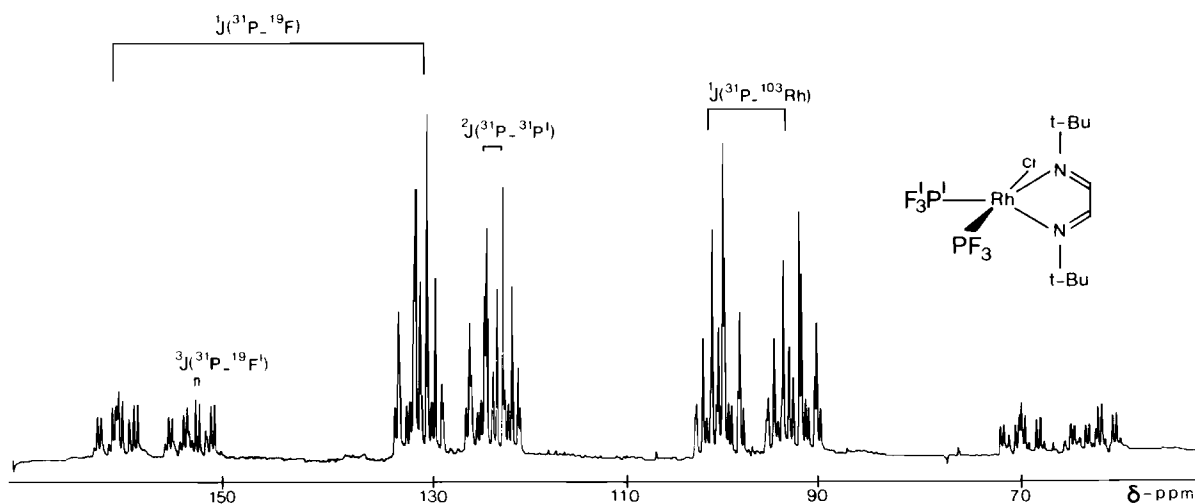


Fig. 3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{RhCl}(\text{PF}_3)(\text{P}'\text{F}_3)(\text{t-Bu-dim})]$ δ $^{31}\text{P} \sim 114$, $^{31}\text{P}' \sim 112$ ppm; $J(^{31}\text{P}-^{19}\text{F}) \cong J(^{31}\text{P}'-^{19}\text{F}') \sim 1300$, $J(^{103}\text{Rh}-^{31}\text{P}) \cong J(^{103}\text{Rh}-^{31}\text{P}') \sim 390$, $^2J(^{31}\text{P}-^{31}\text{P}') \sim 80$ Hz.

doublet over the whole temperature range studied (-110 °C to $+34$ °C).

One, temperature independent, ^1H and ^{13}C NMR resonance pattern is observed for the R-dim ligand. The imine hydrogen atoms appear in the spectrum as one doublet due to $^3J(^{103}\text{Rh}-^1\text{H})$ of 1 Hz. These observations point to a $\sigma,\sigma\text{-N,N}'$ chelate bonded R-dim ligand in which two R-N=CH halves of the ligand are equivalent.

With regards to a possible structure for *3a,b* it is important to note that the above chemical shift and coupling constant values of *3a,b* are distinctly different from the earlier characterized $[\text{Rh}(\text{CO})_2(\text{R-dim})]$ $[\text{RhCl}_2(\text{CO})_2]$ complexes which contain a square planar $[\text{Rh}(\text{CO})_2(\text{R-dim})]$ cation [10].

The observed spectra do not reveal conclusive evidence for the geometry of this complex but the similarity with other systems suggest a trigonal bipyramidal arrangement (see Discussion).

[RhCl(PF₃)₂(R-dim)] (*R* = *t*-Bu (*6a*), *EtMe₂C* (*6b*))

In order to obtain more information about the possible structures of complexes of the type $[\text{RhCl}(\text{L})_2(\text{R-dim})]$, complexes in which L = PF_3 were prepared. It is well accepted [14] that CO and PF_3 are ligands which are electronically closely related. This for example is demonstrated by the reversible, stepwise, PF_3/CO exchange reactions found in Rh^{I} chemistry [14]. An advantage of the PF_3 ligand is that both ^{19}F and ^{31}P can be detected by NMR techniques which can provide important additional structural information concerning these five-coordinate Rh^{I} -R-dim complexes.

The complexes *6a* and *b* could not be isolated as pure products which is mainly due to the extreme sensitivity of the PF_3 ligand towards oxygen and

water and therefore the complexes were carefully prepared *in situ* for NMR experiments. Moreover, a small excess of R-dim was used in order to shift the equilibrium between the complex $[\text{Rh}_2\text{Cl}_2(\text{PF}_3)_4(\text{R-dim})]$ containing a $\sigma\text{-N}, \sigma\text{-N}'$ bridging R-dim ligand to the side of the 1/1 complex (see Discussion).

It is obvious from the ^1H and ^{13}C NMR spectra of *6a,b* that the R-dim is $\sigma,\sigma\text{-N,N}'$ bonded with the R-N=CH halves residing in similar chemical surroundings. Additional information is available from the observation that the imine hydrogen and carbon resonances appear as doublets arising from $^4J(^{31}\text{P}-^1\text{H})$ and $^3J(^{31}\text{P}-^{13}\text{C})$ of 8 and 4 Hz, respectively.

The ^{19}F NMR spectra (94 MHz, CW) clearly show two sets of non-equivalent fluorine atoms and therefore there are two distinct PF_3 ligands bonded to the rhodium centre. The complex resonance pattern consists of the A_3 and B_3 parts of an $\text{A}_3\text{-XMYB}_3$ spin system (δ ^{19}F , 162.5 ppm ($J(^{31}\text{P}-^{19}\text{F})$, 1310; $^2J(^{103}\text{Rh}-^{19}\text{F})$, 330; $^3J(^{31}\text{P}-^{19}\text{F})$, ~ 30 Hz) δ $^{19}\text{F}'$, 185.0 ppm ($J(^{31}\text{P}-^{19}\text{F}')$ 1310; $^2J(^{103}\text{Rh}-^{19}\text{F}')$, 305; $^3J(^{31}\text{P}-^{19}\text{F}')$, ~ 30 Hz)).

Likewise very complex $^{31}\text{P}\{^1\text{H}\}$ spectra were obtained of which the spectrum of *6a* is shown in Fig. 3. Full analysis of the spectrum by simulation was not attempted.

Both the ^{19}F and ^{31}P NMR spectra suggest that the two PF_3 ligands are inequivalent and *cis* positioned to each other. This conclusion and the fact that the R-dim ligands are $\sigma,\sigma\text{-N,N}'$ bonded point to a trigonal bipyramidal structure with one PF_3 group and the Cl atom occupying the axial positions and thus the other PF_3 ligand is in the plane of the Rh-R-dim chelate ring. This arrangement is consistent with the

observation in ^1H NMR spectra of only one four bond ^{31}P -imine proton coupling expected from the equatorial PF_3 group. When the ^{31}P spectrum was run ^1H coupled only the multiplet centred at 114 ppm was broadened and assignment of the two ^{31}P resonances is therefore clear. The resonance at 112 ppm arising from the axial PF_3 would not be expected to give rise to a significant $^4\text{J}(^{31}\text{P}_{\text{cis}}-^1\text{H imine})$.

Conclusive evidence concerning the trigonal bipyramidal geometry comes from the EtMe_2C -pattern in the ^1H and ^{13}C NMR spectra because the dissymmetry in this molecule is similar to that of $[\text{RhCl}(\text{CO})(\eta^2\text{-C}_2\text{H}_4)(\text{EtMe}_2\text{C-dim})]$ (*1b*) (*vide supra*). Anisochronous $\text{C}(\text{Me})_2$ hydrogen and carbon resonances are observed pointing to diastereotopic Me groups in the EtMe_2C -substituents because of the inequivalent axial groupings *i.e.* PF_3 and Cl (see Table I).

Discussion

Bridge splitting reactions of $[(\text{CO})_2\text{Rh}(\mu\text{-Cl})_2\text{Rh}(\text{CO})_2]$ with bidentate N-donor ligands like bipy and phen (N-N) have been extensively investigated [18–20]. Interest in these reactions stems from the formation of compounds of the type $[\text{Rh}(\text{CO})_2(\text{N-N})^+\text{X}^-]$ for which a polymeric structure has been proposed involving metal-metal interaction [20]. Furthermore, some of these complexes are claimed to exhibit interesting biological activity [18].

The reactions between $[(\text{CO})_2\text{Rh}(\mu\text{-Cl})_2\text{Rh}(\text{CO})_2]$ and bipy or phen are immediate and always give rise to the formation of ionic products irrespective of the ligand to rhodium ratio. The low solubility of these ionic products as well as of their precursors has hampered investigations in solution. The structure in the solid state is very complex due to polymorphism and the influence of impurities [17–20]. However, there seems to be consensus that the ionic structure consists of ionic $[\text{Rh}(\text{CO})_2(\text{N-N})^+]$ and $[\text{RhCl}_2(\text{CO})_2]^-$ species.

Gillard *et al.* [18] reported that the reaction of $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]$ with phen in a 1/2 molar ratio in benzene afforded $[\text{RhCl}(\text{CO})_2(\text{phen})]$. Investigations on the structure of this compound in less polar solvents showed a weak interaction between a $[\text{Rh}(\text{CO})_2(\text{phen})]^+$ and Cl^- ion resulting in coordination to the 'vacant' fifth position of the cation. In both $[\text{RhCl}(\text{CO})_2(\text{phen})]^+$ and $[\text{Rh}(\text{CO})_2(\text{phen})]^+$ complexes the phen ligand acts as a $\sigma,\sigma\text{-N,N}'$ chelate. In previous papers we have given a rationale for this predominant $\sigma,\sigma\text{-N,N}'$ chelating coordination behaviour [1, 10].

Relevant for the discussion of the Rh complexes described in this paper is our observation that in platinum-R-dim chemistry the five-co-ordinate geometry

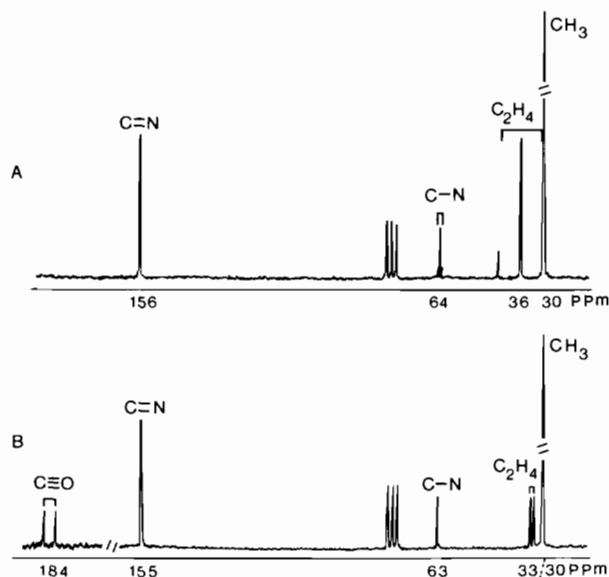


Fig. 4. Comparison of the ^{13}C NMR spectra (CDCl_3) of five-co-ordinate Rh^{I} and Pt^{II} ethylene α -diimine complexes; $[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)(t\text{-Bu-dim})]$ (34°C) A and $[\text{RhCl}(\text{CO})(\eta^2\text{-C}_2\text{H}_4)(t\text{-Bu-dim})]$ (-55°C) B.

could be stabilized by bulky alkyl groupings (R) and suitable co-ligands, *e.g.* $[\text{PtX}_2(\eta^2\text{-olefin})(\text{R-dim})]$ [8].

The reactions of $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]$ and $[\{\text{Rh}(\text{CO})(\eta^2\text{-C}_2\text{H}_4)\text{Cl}\}_2]$ using different Rh to R-dim ratios revealed that bridge splitting reactions occurred. The products are in equilibrium, and the equilibria can be shifted to some extent to form either the ionic products containing four-co-ordinate Rh centres (see references 9–11) or the five-co-ordinate neutral Rh species (this paper).

$[\text{RhCl}(\text{CO})(\eta^2\text{-C}_2\text{H}_4)(\text{R-dim})]$ (R = *t*-Bu (*1a*), EtMe_2C (*1b*))

Similar to the reactions found for R-dim with Zeise's dimer, $([\text{Pt}(\eta^2\text{-C}_2\text{H}_4)\text{Cl}_2]_2)$, the bridge splitting reactions of $[(\eta^2\text{-C}_2\text{H}_4)(\text{CO})(\text{Rh}(\mu\text{-Cl})_2\text{Rh}(\text{CO})(\eta^2\text{-C}_2\text{H}_4))]$ with R-dim results in the direct formation of five-co-ordinate products *1a,b*. No evidence for the intermediate formation of species containing for example a 2/1 Rh to R-dim ratio was found. A further striking similarity with the Pt-R-dim complexes ($[\text{PtCl}_2(\eta^2\text{-olefin})(\text{R-dim})]$) is the almost identical ^1H and ^{13}C NMR chemical shift positions found for the C_2H_4 and R-dim skeleton. This is demonstrated in Fig. 4 for *1a* and its platinum analogue $[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)(t\text{-Bu-dim})]$.

This remarkable resemblance indicates that these compounds have similar structural features. We can

TABLE II. ^{13}C NMR Spectra^a of Four- and Five-co-ordinate Rh^{I} -Olefin-Carbonyl Complexes.

| | | $\eta^2\text{-C}_2\text{H}_4$ | | CO | |
|---|------|-------------------------------|---------------------|--------------------|---------------------|
| | | (<i>trans</i> -N) | (<i>trans</i> -Cl) | (<i>trans</i> -N) | (<i>trans</i> -Cl) |
| $[\text{RhCl}(\text{CO})_2(2,4,6\text{-Me}_3\text{py})]$ | (5) | | | 178.82 [73] | 182.94 [67] |
| $[\text{RhCl}(\text{CO})_2(\text{t-Bu-dim})]$ | (3a) | | | | 181.08 [71] |
| $[\text{RhCl}(\text{CO})(\eta^2\text{-C}_2\text{H}_4)(\text{t-Bu-dim})]$ | (1a) | 33.20 [14] | | | 183.76 [69] |
| $[\text{RhCl}(\text{CO})(\eta^2\text{-C}_2\text{H}_4)(2,4,6\text{-Me}_3\text{py})]^b$ | (4a) | 55.93 [13] | | | 183.82 [68] |
| $[\text{RhCl}(\text{CO})(\eta^2\text{-C}_2\text{H}_4)(2,4,6\text{-Me}_3\text{py})]^b$ | (4b) | | 63.26 [11] | 179.91 [74] | |
| $[\text{RhCl}(\eta^2\text{-C}_2\text{H}_4)_2(2,4,6\text{-Me}_3\text{py})]$ | | 57.63 [14] | 67.20 [11] | | |

^aSpectra recorded in CDCl_3 at -50°C ; δ in ppm relative to TMS; $^1\text{J}(^{103}\text{Rh}-^{13}\text{C})$ in brackets [Hz]. ^bMeasured on a mixture of two isomers. Note that the assignments are opposite to those reported in ref. 15.

therefore infer that the Rh-Cl interaction is strong, resulting in a trigonal bipyramidal geometry having the $\eta^2\text{-C}_2\text{H}_4$ and $\sigma,\sigma\text{-N,N'}$ -R-dim ligand in the equatorial plane. The tremendous upfield shift of the C_2H_4 carbon resonances (~ 90 ppm) with respect to the free ethylene should be compared to related four-co-ordinate $[\text{RhCl}(\text{CO})(\eta^2\text{-C}_2\text{H}_4)(2,4,6\text{-Me}_3\text{py})]$ and $[\text{RhCl}(\eta^2\text{-C}_2\text{H}_4)(2,4,6\text{-Me}_3\text{py})]$ in which this shift amounts to ~ 65 ppm (see Table II). This distinctive shift behaviour has been observed in corresponding four- and five-co-ordinate platinum-ethylene complexes [8].

The bonding in the five-co-ordinate Pt^{II} -olefin complexes as well as the rotation of the olefin have been extensively discussed [8]. Similar arguments can be put forward for the bonding and rotation in the isoelectronic (18 e) $[\text{RhCl}(\eta^2\text{-C}_2\text{H}_4)(\text{CO})(\text{R-dim})]$ complexes *1a,b*. The differences in chemical shifts and coupling constants are too small to allow a worthwhile comparison with regards to the influence of the central metal atom on these data.

An interesting aspect however is the exchange reactions of the complexes *1a,b* with other ligands. The ^{13}C and ^1H NMR solution spectra of *1a,b* showed that these species have stable five-co-ordinate structures on the NMR time scales even in the presence of large excess of the corresponding R-dim ligand. However, spin saturation experiments (involving the ^1H resonances of free and co-ordinated imine) on solutions of *1a* and excess t-Bu-dim established that intermolecular t-Bu-dim exchange occurs on the laboratory time scale.

In scheme 1 various exchange reactions of *1a,b* with monodentate ligands are shown.

The exchange with 2,4,6-Me₃-pyridine affords quantitatively $[\text{RhCl}(\text{CO})(\eta^2\text{-C}_2\text{H}_4)(2,4,6\text{-Me}_3\text{py})]$ (*4*) which is present in two stereo-isomers having the N-donor ligand either *trans* to CO or *trans* to the η^2 -bonded C_2H_4 ligand. However this reaction is reversible and addition of excess R-dim to these stereo-isomers shifts the equilibrium towards *1a,b*.

Since the isomers reacted with R-dim at -50°C at different rates it was possible to assign the ^{13}C NMR resonances to two separate species (see Table II). By comparison of this data with $[\text{RhCl}(\eta^2\text{-C}_2\text{H}_4)_2(2,4,6\text{-Me}_3\text{py})]$, $[\text{RhCl}(\text{CO})_2(2,4,6\text{-Me}_3\text{py})]$ and five-co-ordinate $[\text{RhCl}(\text{CO})(\eta^2\text{-C}_2\text{H}_4)(\text{t-Bu-dim})]$ (which latter contains Cl *trans* to CO and C_2H_4 opposite to $\sigma,\sigma\text{-N,N'}$ R-dim in a trigonal bipyramid) it is possible to assign the resonances of *4* to their respective *cis*- and *trans*-isomers, see Table II.

The identity of *4* was further substantiated by quantitative formation of *cis*- $[\text{RhCl}(\text{CO})_2(2,4,6\text{-Me}_3\text{py})]$ (*5*) when its solution was treated with CO. A full description of these types of four-co-ordinate Rh^{I} complexes has been recently reported by Poilblanc *et al.* [15].

Since the Rh- C_2H_4 dissociation is irreversible (see route ii, scheme 1) and leads to four-co-ordinate $[\text{RhCl}(\text{CO})(\text{R-dim})]$ (*2a,b*) it is plausible to propose that the exchange mechanism follows the route earlier put forward for the ligand exchange reaction of the five-co-ordinate Pt^{II} analogues* [22]. This involves a reversible rearrangement of the Rh-R-dim interaction from $\sigma,\sigma\text{-N,N'}$ chelate to $\sigma\text{-N}$ monodentate, thus providing a free co-ordination site at the Rh-centre for exchange reaction.

The reaction of *1a,b*, with triphenylphosphine (1/2 molar ratio) occurs stepwise resulting ultimately in release of both ethylene and the R-dim ligand and the irreversible formation of *trans*- $[\text{RhCl}(\text{CO})\text{-}(\text{PPh}_3)]_2$.

*For the $[\text{RhCl}(\text{CO})(\eta^2\text{-C}_2\text{H}_4)(\text{t-Bu-dim})]$ complex evidence for olefin-olefin exchange has also been found. In this way the styrene analogue was prepared which, however, has low stability; ^{13}C NMR data, -50°C : δ CO, 184.18 (72 Hz); δ CH₃, 29.73, 30.33; C-N, 63.09; HC=N, 155.39, 155.69 and C=C, 54.54 (13 Hz), ~ 30 ppm, indicates that styrene rotation is blocked on the NMR time scale [23].

$[\text{RhCl}(\text{CO})_2(\text{R-dim})]$ ($\text{R} = t\text{-Bu}$ (3a), EtMe_2C - (3b))

Two routes for the preparation of 3a,b are shown in scheme 1. The $\text{C}_2\text{H}_4/\text{CO}$ exchange with 1a,b is quantitative and is in fact the preferred route. The bridge splitting reaction of $[(\text{CO})_2\text{Rh}(\mu\text{-Cl})_2\text{Rh}(\text{CO})_2]$ with R-dim is clearly an equilibrium reaction as is fully described in references 9 and 10. Depending on the Rh/R-dim ratios various mixtures of dinuclear Rh species (7a,b) and five-co-ordinate $[\text{RhCl}(\text{CO})_2(\text{R-dim})]$ (3a,b) are observed. Complex 3a could only be isolated from solutions containing excess of R-dim.

In comparison to $[\text{RhCl}(\text{CO})(\eta^2\text{-C}_2\text{H}_4)(\text{R-dim})]$ the $[\text{RhCl}(\text{CO})_2(\text{R-dim})]$ ($\text{R} = t\text{-Bu}$, EtMe_2C -) complexes are less stable in solution. Dissolution of 3a in CDCl_3 gives rise to an equilibrium mixture containing 3a, 7a and free $t\text{-Bu-dim}$ (see Experimental).

The structure of 3a,b in solution (CDCl_3 , acetone- d_6 or C_6D_6) cannot be deduced with certainty from the NMR spectra because the resonance patterns can support both a square pyramidal and a trigonal bipyramidal geometry. A second possibility is a square pyramidal ground state structure having the Cl atom in apical and the two CO and $\sigma,\sigma\text{-N,N}'$ R-dim ligands in the basal positions. In this structure the two CO ligands are equivalent as well as the two R-NC=H halves of the R-dim ligand. However, in view of the trigonal bipyramidal structures found for $[\text{RhCl}(\text{CO})(\eta^2\text{-C}_2\text{H}_4)(\text{R-dim})]$ and the PF_3 complex (*vide infra*) it seems likely that $[\text{RhCl}(\text{CO})_2(\text{R-dim})]$ also has this geometry. Such a geometry would give rise to two different ^{13}C NMR resonances while only one is observed. Moreover, in contrast to 1b, in complex 3b no dissymmetry could be detected by the resonance pattern of the prochiral groupings in the EtMe_2C -substituents. This implies the occurrence of a rapid stereoisomerization process with a low activation barrier (spectra unchanged RT to -110°C ; acetone/dichloromethane mixture as solvent), rendering the axial and equatorial CO ligands equivalent and destroying the expected dissymmetry at the Rh-centre with respect to the alkyl grouping in $\sigma,\sigma\text{-N,N}'$ chelate bonded EtMe_2C -dim ligand. Such processes (e.g. Berry pseudo rotation or Turnstile mechanism) can be very fast on the NMR time scale as was indicated by the fact that in $[\text{Fe}(\text{CO})_3(\text{R-dim})]$, likewise containing a $\sigma,\sigma\text{-N,N}'$ chelate bonded R-dim ligand, the CO groups are also equivalent even at -110°C [24].

A dynamic trigonal bipyramidal structure for $[\text{RhCl}(\text{CO})_2(\text{R-dim})]$ seems also to be supported by the observation of $\delta^{13}\text{C}$ at 181.1 ppm which is at the average position of the chemical shift and $^1\text{J}^{(10^3)\text{Rh}-^{13}\text{C}}$ values found for the CO ligands *trans* to the N-donor ligand and the chlorine atom in 5 (178.8 (73 Hz), 182.9 (67 Hz), respectively (see also Table II).

It is interesting that the use of PF_3 instead of CO ligands results in the stabilization of the trigonal bipyramidal structure in $[\text{RhCl}(\text{PF}_3)_2(\text{R-dim})]$ ($\text{R} = t\text{-Bu}$ (6a), EtMe_2C - (6b)). The presence of one PF_3 in an axial position may be related not only to electronic factors but also to the fact that this ligand is bulkier than CO. ^1H , ^{13}C , ^{19}F and ^{31}P NMR data indicated that this five-co-ordinate species is stable on the NMR time scales.

The equilibrium between the species 3a,b and 7a,b can be influenced by addition of monodentate ligands (see Scheme 1). For example, addition of excess 2,4,6- Me_3py to a solution of 3a,b in chloroform afforded quantitatively *cis*- $[\text{RhCl}(\text{CO})_2(2,4,6\text{-Me}_3\text{py})]$ while the 1/1 reaction of 7a,b with 2,4,6- Me_3py gave rise to a approximately 1/1 mixture of four-co-ordinate $[\text{RhCl}(\text{CO})_2(2,4,6\text{-Me}_3\text{py})]$ (5) and five-co-ordinate $[\text{RhCl}(\text{CO})_2(\text{R-dim})]$ (3a,b). These equilibria could be readily followed by ^1H NMR spectrometry using the chemical shifts of the R-dim protons (see Tables I and II and Experimental).

Like 1a,b, complexes 3a,b and 7a,b react stepwise with triphenylphosphine to afford $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$. In the case of 7a,b the intermediate formation of the five-co-ordinate complex 3a,b could be established by ^1H NMR spectrometry.

Influence of the R imine substituent R-N=CH-

The reactions discussed in this paper have been carried out for a series of different R-dim ligands but resulted for $t\text{-Bu}$ - and EtMe_2C -dim only in the formation of $[\text{RhCl}(\text{CO})(\eta^2\text{-C}_2\text{H}_4)(\text{R-dim})]$ which are stable in the solid state and in solution on the NMR time scale. The fact that the Rh-olefin complexes have stability in solution only with R-dim ligands in which R is connected to the N atom via a triply branched C^α atom is not surprising. Similar behaviour was apparent in the corresponding platinum-olefin complexes in which the stability decreased on going from triple to double branching at C^α and from double to single branching at C^β [8].

The stabilizing effect of these $t\text{-Bu}$ - and EtMe_2C -dim ligands most probably arises from the steric constraints introduced by the bulkiness of these groups in the equatorial plane. This results in an increased kinetic stability because decomposition of the five-co-ordinate complex generates a four-co-ordinate square planar complex (see for example eq. ii in Scheme 1) in which all ligands are in the same plane.

This effect of constraint in the equatorial plane increasing the kinetic stability of this type of five-co-ordinate complexes is evident in $[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)(6\text{-R}'\text{-py-2-CH=N-R})]$ which become more stable when a methyl group is introduced in the 6-R' position [25]. Recently, Deeming *et al.* [26] reported stable five-co-ordinate quinoline-2-carboxalde-

hyde-N-imine rhodium complexes in which the σ, σ -N,N' chelate co-ordination mode is favoured over monodentate σ -N co-ordination via the imine N-atom. In this case five-co-ordination also arises from the bulkiness of the substituents located at suitable positions on the pyridine-N donor ligand.

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