METAL—METAL BONDED COMPOUNDS

VI *. RHODIUM—MERCURY BONDED COMPLEXES [(Diene){RNC(Y)NR'}$_2$RhHgCl]$_2$ CONTAINING INTERCHANGING METAL—METAL BRIDGING AND CHELATING AMIDINO GROUPS

P.I. VAN VLIET, G. VAN KOTEN and K. VRIEZE **

Anorganisch Chemisch Laboratorium, J.H. van 't Hoff Instituut, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam (The Netherlands)

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Summary

Complexes of the composition [(Diene){RNC(Y)NR'}$_2$RhHgCl] (Diene = 1,5-cyclooctadiene, norbornadiene; Y = H; R = R' = CH(CH$_3$)$_2$; R = CH$_3$, CH-(CH$_3$)$_2$, p-CH$_3$C$_6$H$_4$; R' = p-CH$_3$C$_6$H$_4$ and Y = CH$_3$, R = R' = p-CH$_3$C$_6$H$_4$) have been isolated in almost quantitative yields from the reaction of [(Diene)RhCl]$_2$ with [Hg{RNC(Y)NR'}$_2$]. The structure in the solid state is probably dimeric, while in solution the compounds are definitely monomeric. NMR data show that the molecular configuration consists of a rhodium atom coordinated by a bidentate diene, a bidentate amidino group, a HgCl ligand and a N atom of an amidino group, which bridges the Rh—Hg bond. Various isomers are possible for compounds containing asymmetric amidino groups, depending on the size of the alkyl (R) group. For bulky R groups (CH(CH$_3$)$_2$) the two N-aryl groups are bonded to Rh and situated *cis* to Hg. For small R groups (CH$_3$) two isomers are observed, one with the two NCH$_3$ groups bonded to Rh and *cis* to Hg, and one with a NCH$_3$ and a N-aryl group bonded to Rh and situated *cis* to Hg.

^{13}C NMR data show that for R' = p-CH$_3$C$_6$H$_4$ the complexes are fluxional. The process involves an interchange of the bridging and the chelating aminido groups via monodentate intermediates.

Introduction

In previous papers [1—7] we reported the preparation, structure and properties of a series of binuclear metal—metal bonded compounds. The main empha-

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* For part V see ref. 7.
** To whom correspondence should be addressed.

sis was on the stabilization of transition metal—post transition metal bonds by means of triazenido, amidino and carboxylato ligands. We restricted ourselves mainly to reactions of Rh^I and Ir^I with compounds of the elements of the iso-electronic series $Ag^I(Cu^I)$ [1—3,6], Hg^{II} [4,7] and Tl^{III} [5].

Our most recent work involved the preparation, structure determination and properties of $[(Diene)(RN_3R')_2MHgCl]_2$ (M = Ir; Diene = COD *; R = CH_3, C_2H_5; R' = p-$CH_3C_6H_4$ and M = Rh; Diene = COD, NOR **; R = CH_3, C_2H_5, p-$CH_3C_6H_4$). A crystal structure determination showed that the complex contained both a metal—metal bridging and a chelating triazenido group, which for M = Rh underwent in intramolecular interchange in solution [7].

In the course of these studies we were concerned with the differences and analogies in the behaviour of triazenido, amidino and carboxylato groups. It therefore appeared of interest to investigate whether the amidino ligand would also be able to stabilize the novel structure found for the complexes $[(Diene)$-$(RN_3R')_2MHgCl]_2$ [7].

In this paper we show that the analogous amidino complexes may be prepared, but only for M = Rh. NMR studies are presented which indicate the wider occurrence of the rather unusual intramolecular interchanges of bridging and chelating bidentate ligands.

Experimental

All preparations were carried out under nitrogen in dried solvents. The silver-formamidino complexes (AgDiPF, AgMpTF, AgiPpTF, AgDpTF and AgDpTA ***) and the diene-rhodium compounds ($[(COD)RhCl]_2$ and $[(NOR)$-$RhCl]_2$) were prepared according to literature methods [8—10].

Preparations of $[(Diene)\{RNC(Y)NR'\}_2RhHgCl]_2$ (Diene = COD, NOR; Y = H; R = R' = $(CH_3)_2CH$; R = CH_3, $(CH_3)_2CH$, p-$CH_3C_6H_4$, R' = p-$CH_3C_6H_4$ and Y = CH_3; R = R' = p-$CH_3C_6H_4$)

Method 1. A solution of $[Ag\{RNC(Y)NR')\}]_n$ (2/n mmol) in THF (10 ml) was added with rapid stirring to a solution of $HgCl_2$ (1 mmol) in THF (5 ml). After 10 min 0.5 mmol of $[(Diene)RhCl]_2$ was added and stirring was continued for one hour. After filtration, concentration, addition of hexane and cooling, red, orange or yellow crystals were obtained in 90% yield.

Method II. A solution of $[Ag\{RNC(Y)NR'\}]_n$ (2/n mmol) in CH_2Cl_2 (10 ml) was added dropwise to a stirred suspension of $[\{(Diene)RhCl\}(HgCl_2)]_2$ [11] (0.5 mmol) in CH_2Cl_2 (10 ml) over during 20 min. The workup was as above.

Reactions of $[(Diene)\{RNC(Y)NR'\}_2RhHgCl]_2$ with HCl (Diene = COD, NOR; Y = H; R = R' = $(CH_3)_2CH$; R = CH_3, $(CH_3)_2CH$, p-$CH_3C_6H_4$; R' = p-$CH_3C_6H_4$ and Y = CH_3; R = R' = p-$CH_3C_6H_4$)

A solution of $[(Diene)\{(RNC(Y)NR'\}_2RhHgCl]_2$ (1 mmol) in a mixture of CH_2Cl_2 and ethanol (20 ml) was placed under a HCl atmosphere and stirred for

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* COD = 1,5-cyclooctadiene.
** NOR = bicyclo[2,2,1]hepta-2,5-diene(norbornadiene).
*** DiPF = $(CH_3)_2CHNC(H)NCH(CH_3)_2$; MpTF = $CH_3NC(H)N$-p-$CH_3C_6H_4$; iPpTF = $(CH_3)_2CHNC(H)N$-p-$CH_3C_6H_4$; DpTF = p-$CH_3C_6H_4NC(H)N$-p-$CH_3C_6H_4$; DpTA = p-$CH_3C_6H_4NC(CH_3)N$-p-$CH_3C_6H_4$.

TABLE 1

ANALYTICAL DATA

Compound [a]	M.W. [b]	Analysis found (calcd.)(%)			Colour
		C	H	N	
[COD(DiPF)$_2$RhHgCl]$_2$	702	37.06	5.87	7.70	yellow
	(683)	(37.67)	(6.03)	(7.99)	
[COD(MpTF)$_2$RhHgCl]$_2$	742	41.53	4.29	7.39	orange
	(762)	(42.11)	(4.62)	(7.56)	
[COD(iPpTF)$_2$RhHgCl]$_2$	798	45.78	5.24	6.94	yellow
	(721)	(45.17)	(5.31)	(7.02)	
[COD(DpTF)$_2$RhHgCl]$_2$	894	50.63	4.66	6.27	red
	(830)	(51.07)	(4.74)	(6.27)	
[COD(DpTA)$_2$RhHgCl]$_2$	922	51.80	4.87	5.96	orange
	(910)	(52.12)	(5.03)	(6.08)	
[NOR(DiPF)$_2$RhHgCl]$_2$	686	36.89	5.52	7.88	orange
	(707)	(36.79)	(5.59)	(8.17)	
[NOR(MpTF)$_2$RhHgCl]$_2$	726	41.23	4.20	7.53	orange
	(701)	(41.39)	(4.17)	(7.72)	
[NOR(iPpTF)$_2$RhHgCl]$_2$	782	45.66	5.27	6.93	orange
	(793)	(44.57)	(4.90)	(7.17)	
[NOR(DpTF)$_2$RhHgCl]$_2$	878	50.34	4.42	6.17	red
	(855)	(50.63)	(4.36)	(6.38)	
[NOR(DpTA)$_2$RhHgCl]$_2$	902	51.98	4.79	5.86	red
	(851)	(51.72)	(4.67)	(6.19)	

[a] COD = 1,5-cyclooctadiene; NOR = bicyclo[2.2.1]hepta-2,5-diene (norbornadiene); DiPF = $(CH_3)_2$CH-NC(H)N-CH$(CH_3)_2$; MpTF = CH$_3$-NC(H)N-p-CH$_3$C$_6$H$_4$; IPpTF = $(CH_3)_2$CH-NC(H)N-p-CH$_3$C$_6$H$_4$ DpTF = p-CH$_3$C$_6$H$_4$-NC(H)N-p-CH$_3$C$_6$H$_4$; DpTA = p-CH$_3$C$_6$H$_4$-NC(CH$_3$)N-p-CH$_3$C$_6$H$_4$. [b] M.W. in CDCl$_3$, the experimental error is ±10% (found(calcd.)).

10 min. After cooling red crystals of [{(Diene)RhCl}(HgCl$_2$)]$_2$ were obtained in 40% yield. Further crystallization of the filtrate afforded [RN(H)C(Y)N-(H)R′]Cl (yield 20—60%).

Attempts to obtain the corresponding Ir compounds by the above methods failed, as did attempts to make the rhodium compounds with R = R′ = C(CH$_3$)$_3$. The exchange experiments involving the triazenido, formamidino and diene ligands were followed by ^{1}H NMR, and were carried out by adding the free ligand to solutions of the various compounds described above.

Reaction of Hg-carboxylato complexes with [(Diene)RhCl]$_2$ complexes afforded compounds with a metal-to-metal donor bond and a structure analogous to the known [{(Diene)RhCl}(HgCl$_2$)]$_2$ complexes [11].

^{1}H NMR spectra were recorded on a A60-D and XL-100 Varian spectrometer and ^{13}C NMR spectra were recorded on a WP 80 Bruker spectrometer. Molecular weights were determined with a Hewlett Packard vapour pressure osmometer Model 320 B (Table 1). C, H and N analyses were carried out at the Organic Laboratory of the TNO in Utrecht (Table 1).

Results

As in the case of the analogous triazenido complexes [7], the compounds [(Diene){RNC(Y)NR′}$_2$RhHgCl]$_2$ (Diene = COD, NOR; Y = H; R = R′ = (CH$_3$)$_2$CH; R = CH$_3$, (CH$_3$)$_2$CH, p-CH$_3$C$_6$H$_4$; R′ = p-CH$_3$C$_6$H$_4$ and Y = CH$_3$; R =

TABLE 2

^{13}C NMR DATA (IN $CDCl_3$ RELATIVE TO TMS AT $-30°$ C)

Compound	amidino resonances [a]							COD or NOR resonances			
	p-tolyl					allyl			olefinic [b]	aliphatic	
	CH_3	C_1	C_2	C_3	C_4	C(H) or C(CH_3)	CH_3	CH	CH	CH	CH_3
[COD(DiPF)$_2$RhHgCl]$_2$						158.94	27.28; 25.73; 26.77; 24.46(br); 25.86; 24.22	53.59; 52.20	93.10(d); 80.93(d); 86.61(d); 76.06(d)		35.51; 29.90; 32.53; 27.80
[COD(MpTF)$_2$RhHgCl]$_2$ [c]	20.52	147.17; 145.47; 145.23	120.79; 120.11	129.57; 120.45	131.82; 131.51; 131.33	161.19(br)	44.13		88.80(d); 86.79(d); 88.36(d); 85.73(d); 87.79(d); 85.18(d)		32.39; 30.11; 31.02; 29.38(br); 30.84
[COD(IPpTF)$_2$RhHgCl]$_2$	20.57	147.42	123.44	128.04	132.30	160.28	22.25; 25.13	55.17	86.88(d); 85.36(d)		30.65; 29.87
[COD(DpTF)$_2$RhHgCl]$_2$	20.52	147.41; 145.05	124.05; 120.53	129.63; 129.15	133.82; 132.30	158.76	42.73		89.79(d); 86.33(d)		30.78; 29.74
[COD(DpTA)$_2$RhHgCl]$_2$ [d]	20.76	147.11; 146.38	125.99; 124.23	129.45	133.88; 132.24	163.44	40.61		88.60(d); 85.30(d)		30.47; 29.44
[NOR(diPF)$_2$RhHgCl]$_2$						158.46	26.28; 25.50; 25.98(br); 25.80	54.26; 52.62	63.12(d); 62.55(d); 62.63(d); 61.99(d)	51.47; 50.13	62.21
[NOR(MpTF)$_2$RhHgCl]$_2$ [c]	20.64	146.74	120.59	129.57	132.00	160.58	42.85		67.46(d); 63.64(d); 66.11(d); 61.97(d); 64.77(d); 61.03(d)	52.26; 51.35; 51.77; 50.88	64.01(br)
[NOR(IPpTF)$_2$RhHgCl]$_2$	20.52	146.11	123.20	129.03	132.55	159.49	26.04; 25.61	54.80	63.51(d); 62.77(d)	51.47; 50.560	63.15
[NOR(DpTF)$_2$RhHgCl]$_2$	20.70; 20.58	146.50; 145.17	123.75; 120.41	129.69; 129.21	133.88; 132.24	157.91	41.70		66.51(d); 64.12(d)	51.20(br)	64.41
[NOR(DpTA)$_2$RhHgCl]$_2$ [e]	20.70	146.56; 145.65	125.99; 124.33	129.33	133.82; 132.06	163.37	40.85		64.37(d); 63.61(d)	51.17; 50.01	64.21

[a] The C_1 atom is bound to nitrogen. [b] The ^{13}C–^{103}Rh coupling is ±10 Hz. [c] This compound has two isomers. [d] The CH_3 resonance is at 19.43 ppm. [e] The CH_3 resonance is at 19.00 ppm.

$R' = p\text{-}CH_3C_6H_4$) were prepared in quantitative yield according to reactions 1 and 2

$$[(\text{Diene})\text{MCl}]_2 + 2[\text{Hg}\{\text{RNC}(Y)\text{NR}'\}_2] \rightarrow 2[(\text{Diene})\{\text{RNC}(Y)\text{NR}'\}_2\text{RhHgCl}]_2 \ (1)$$

$$[\{(\text{Diene})\text{MCl}\}(\text{HgCl}_2)]_2 + \tfrac{4}{n}[\text{Ag}\{\text{RNC}(Y)\text{NR}'\}]_n \rightarrow$$
$$[(\text{Diene})\{\text{RNC}(Y)\text{NR}'\}_2\text{RhHgCl}]_2 + 4 \text{ AgCl} \ (2)$$
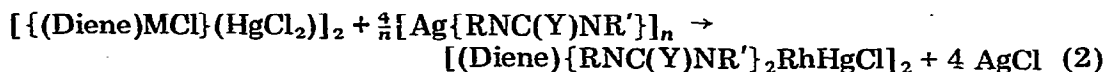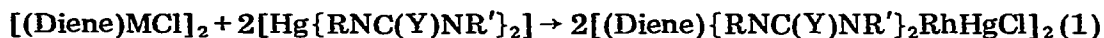
Molecular weight measurements show that all the described compounds are monomeric in solution. In view of the close analogy to the triazenido compounds they are very probably dimeric in the solid state.

Structure and properties of the [(Diene){RNC(Y)NR'}₂RhHgCl]₂ compounds in solution

^{13}C NMR results

The ^{13}C NMR data (Table 2) for the $[(\text{Diene})\{\text{RNC}(Y)\text{NR}'\}_2\text{RhHgCl}]_2$ compounds containing the symmetric di-*p*-tolyl amidino groups show the presence of two pairs of inequivalent *p*-tolyl groups and also two resonances for the olefinic carbon atoms (Fig. 1a).

Variable temperature and concentration studies showed no change in the observed signals. In view of the analogy of these data with those of the recently reported corresponding triazenido compounds [7] the structure and properties of the amidino compounds are probably completely analogous to those of the triazenido compounds. The data show that the aminido groups and two pairs of the olefinic carbon atoms are at the fast exchange limit on the NMR time scale.
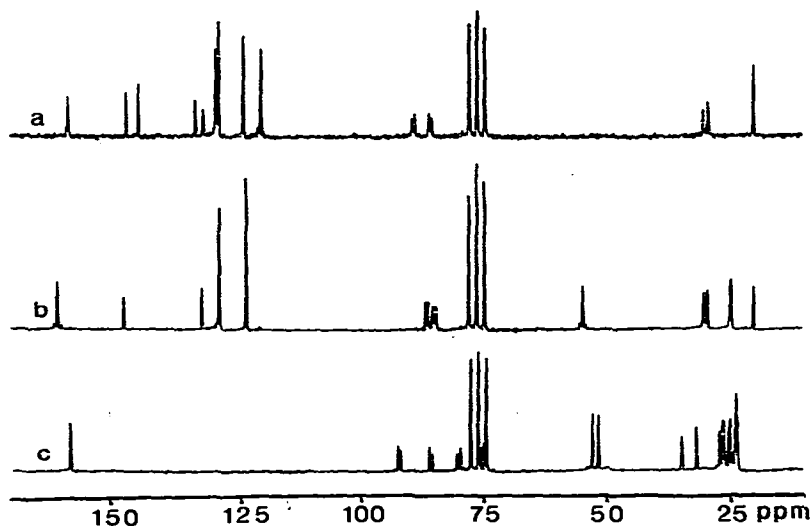

Fig. 1a. ^{13}C NMR spectrum of [(COD){*p*-CH₃C₆H₄NC(H)N*p*-CH₃C₆H₄}₂RhHgCl]₂ in CDCl₃ at −30°C.

Fig. 1b. ^{13}C NMR spectrum of [(COD){(CH₃)₂CHNC(H)N*p*-CH₃C₆H₄}₂RhHgCl]₂ in CDCl₃ at −30°C.

Fig. 1c. ^{13}C NMR spectrum of [(COD){(CH₃)₂CHNC(H)N(CH₃)₂CH}₂RhHgCl]₂ in CDCl₃ at −30°C.
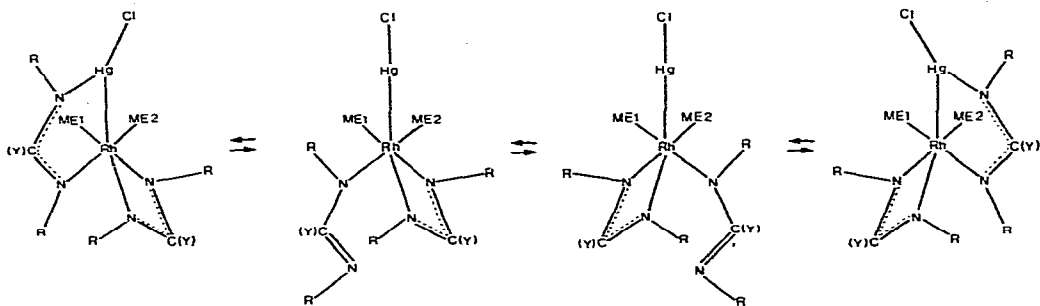
Fig. 2. Proposed mechanism for the interchange of the chelating and bridging amidino group (for R, see text), ME_1 and ME_2 are the midpoints of the olefinic bonds in the COD and NOR ligands).

This means that a plane of symmetry is observed on the NMR time scale, arising from fluxional intramolecular processes. In the light of these results we suggest that the complexes have a structure with both a chelating and a bridging amidino ligand, which interchange according to the equilibrium shown in Fig. 2.

For the compounds containing two asymmetric formamidino groups, the ^{13}C NMR data show the presence of two isomers for the MpTF compounds and of only one isomer for the iPpTF compounds. For the MpTF compounds the structures of the isomers are analogous to those of the corresponding triazenido compounds [7]. The first isomer is coordinated symmetrically (two doublets for the olefinic carbon atoms) with two $N-CH_3$ groups bonded to Rh cis to Hg. The second isomer has an asymmetric coordination with one $N-CH_3$ and one $N-p-CH_3C_6H_4$ group bonded to Rh cis to Hg. Comparison of the NMR data with those of the symmetric di-p-tolyl amidino compounds clearly show that the first isomer is involved in an equilibrium (Fig. 2), and although it seems very likely that the second isomer is also involved in such an equilibrium, a rigid conformation cannot be excluded. The iPpTF compounds show a ^{13}C NMR spectrum (Fig. 1b) with two formamidino groups in the fast exchange limit and two doublets for the olefinic carbon atoms clearly indicating the presence of the equilibrium shown in Fig. 2. Of special interest is the influence of the size of the alkyl group, which prevents the formation of an asymmetric isomer with one N-alkyl and one N-aryl group bonded to Rh cis to Hg. Since it seems very unlikely that both N-alkyl groups are bonded to Rh cis to Hg, we suggest for these compounds a structure with the two N-aryl groups bonded to Rh cis to Hg, while the equilibrium shown in Fig. 2 is also present.

The DiPF compounds show (Fig. 1c) four doublets for the olefinic carbon atoms, for the alkyl substituents two resonances for the CH carbon atoms and a multiplet for the CH_3 carbon atoms, and one resonance for the other CH carbon atoms. Temperature and concentration dependent measurements showed no change in the observed resonances. From these data we suggest that these compounds possess a rigid conformation, as shown in Fig. 3, in which the observed ^{13}C NMR resonances of the CH carbon atom of the alkyl substituents and of the other CH carbon atoms coincide by chance.

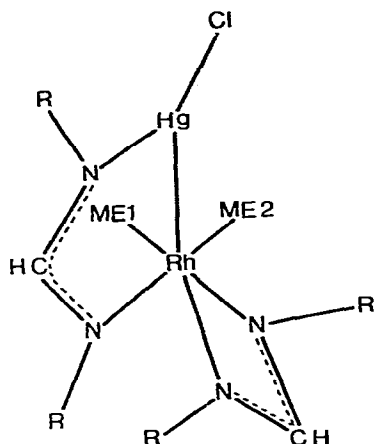Although a rigid conformation seems the most likely, an equilibrium as

Fig. 3. Structure of [(Diene){RNC(H)NR}₂RhHgCl]₂ in solution (R = (CH₃)₂CH). ME₁ and ME₂ are the midpoints of the olefinic bonds in the COD and NOR ligands.

shown in Fig. 2 with the COD or NOR and CH_3 ^{13}C resonances in the slow exchange limit on the NMR time scale and the two different CH resonances, having an initial small chemical shift difference at the fast exchange limit on the NMR time scale, cannot be excluded.

^1H NMR results

The ^1H NMR spectra of the new complexes are very complicated due to intramolecular exchange processes and hydrogen—hydrogen couplings. It was possible to assign the observed resonances comparing the spectra of all compounds, but no further information could be obtained. For this reason only the data at —30°C in CDCl₃ are given (Table 3).

Chemical properties of the compounds

The compounds are stable for days in solvents such as CH_2Cl_2, THF and CHCl₃ in air.

The diene ligands do not exchange with free diolefins, but the formamidino groups can be rapidly replaced by a more acidic triazenido or amidino group. The order of substitution is DpTT > MpTT > DpTF ~ DpTA > MpTF ~ i-PpTF > DiPF. With strong acids the compounds react to give the starting material according to reaction 3.

$$[(Diene)\{RNC(Y)NR'\}_2RhHgCl]_2 + 8\ HCl \rightarrow [\ \{(Diene)RhCl\}(HgCl_2)]_2$$

$$+ 4[RN(H)C(Y)N(H)R']Cl \tag{3}$$
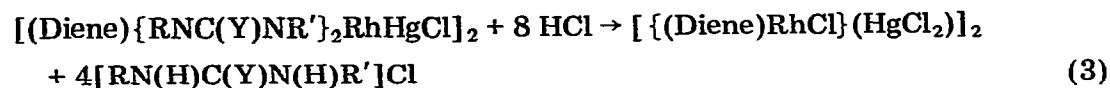
The compounds do not react with donor ligands such as Ph₃P, Ph₃As or pyridine. Treatment with CO resulted in a change of colour from red to yellow and the formation of metallic Hg, but no products could be isolated.

TABLE 3

^{1}H NMR DATA (IN CDCl$_3$ RELATIVE TO TMS at -30°C)

| Compound | amidino resonances | | | | | COD or NOR resonances | | |
| | p-tolyl | | alkyl | | | olefinic | eliphatic | |
	CH$_3$	aryl	CH or CH$_3$	CH$_3$	CH	CH	CH	CH$_2$
[COD(DiPF)$_2$RhHgCl]$_2$ ^{a}			7.78(br); 1.4	1.47(d), 1.41(d), 1.37(d), 1.28(d)	3.90(s), 3.62(s)	4.19(br)		2.99(br), 2.49(br), 2.06(br), 1.68(br)
[COD(MpTF)$_2$RhHgCl]$_2$ ^{b}	2.44, 2.39	7.74,7.33; 7.19	8.08, 7.91	3.53, 3.38, 2.80		4.36(br), 4.23(br)		3.03(vbr), 2.00(br)
[COD(iPpTF)$_2$RhHgCl]$_2$ ^{a}	2.36	6.92	7.88	1.56(d)	4.14(s), 4.02(s)	4.33(br)		3.11(br);2.01(vbr), 2.66(br)
[COD(DpTF)$_2$RhHgCl]$_2$	2.44	7.21; 7.12,7.02	8.04			4.58(br)		3.13(br);2.30(br), 2.81(br);2.01(br)
[COD(DpTA)$_2$RhHgCl]$_2$	2.44	7.20,7.04; 7.16				4.62(br), 3.94(br)		2.96(br), 2.12(br0
[NOR(DiPF)$_2$RhHgCl]$_2$ ^{a}			7.62, 7.60	1.47(d), 1.43(d), 1.27(d), 1.19(d)	3.80(s), 3.55(s)	4.31(br), 4.26(br), 4.11(br)	4.09(br), 3.80(br)	1.45(br)
[NOR(MpTF)$_2$RhHgCl]$_2$ ^{b}	2.43, 2.39	7.71,7.31; 7.19	7.96, 7.81	3.54, 3.26, 2.86		4.59(br), 4.48(br), 4.37(br)	4.13(br), 3.96(br), 3.88(br)	1.40(br), 1.33(br)
[NOR(i-PpTF)$_2$RhHgCl]$_2$ ^{a}	2.38	6.97	7.74	1.58(d), 1.53(d)	4.08(s), 5.86(s)	4.45(br)	4.15(br), 4.02(br)	1.35(br)
[NOR(DpTF)$_2$RhHgCl]$_2$	2.44	7.37; 7.29,7.14	7.97			4.60(br), 4.32(br)	4.60(br), 4.32(br)	1.43(br)
[NOR(DpTA)$_2$RhHgCl]$_2$	2.46, 2.43	7.21; 7.19,6.91	1.76			4.51(br), 3.61(br)	4.13(br), 3.76(br)	1.33(br)

^{a} J(CH$_3$—CH) = 6 Hz. ^{b} This compound has two isomers.

Discussion

From the available evidence it is clear that the amidino compounds [(Diene)-{RNC(Y)NR'}$_2$RhHgCl]$_2$ are analogous in structure (i.e. one chelating and one metal—metal bridging amidino group) and behaviour (Fig. 2) to the recently reported triazenido compounds [(Diene)(RN$_3$R')$_2$MHgCl]$_2$ (M = Rh, Ir) [7]. A surprising feature is that we were unable to obtain the iridium complexes, especially since it is apparent from earlier work [1—6] that the iridium complexes are generally more stable and more easily formed than the corresponding rhodium compounds. The analogy between both series of complexes is further demonstrated by the chemical inertness towards bulky donor ligands such as pyridine, Ph$_3$P and Ph$_3$As. The smaller carbon monoxide reacts, but no products could be isolated. Also, no decomposition occurred when the complexes were treated with the free formamidines, while the formamidines can exchange with other groups which are derived from stronger acids, i.e. the substitution order is di-*p*-tolyltriazene > methyl-*p*-tolyltriazene > di-*p*-tolylformamidine ~ di-*p*-tolyl-acetamidine > i-propyl-*p*-tolylformamidine > di-i-propylformamidine. Of particular interest is the reaction with HCl, which was only observed for the formamidino complexes and which involves the conversion of [(Diene)-{RNC(Y)NR'}$_2$RhHgCl]$_2$ into the starting material [{(Diene)RhCl}(HgCl$_2$)]$_2$ with a concomitant reduction of Rh^{II} to Rh^{I}.

When we consider the structural features in more detail we find that the size of the R substituents determines the type of configuration around the metal atoms, as in the case of the triazenido complexes. Di-arylamidino complexes can be formed, which shows that there is sufficient room to accomodate two N-aryl groups bonded to Rh *cis* to Hg. The t-butyl group is clearly too large, since no di-t-butylformamidino compounds could be obtained. Use of unsymmetrically substituted alkyl, aryl formamidino groups gave us the opportunity to investigate further the role of the size of the R substituents. It was observed that methyl-*p*-tolylformamidino ligands, for example, may give rise to two isomers, one with both N-methyl groups bonded to Rh *cis* to Hg and one with a N-methyl and a N-aryl group *cis* to Hg. Increasing the size of the alkyl group to i-propyl prevented the formation of both these isomers, and instead the isomer with both N-aryl groups bonded to Rh *cis* to Hg was formed. The observed order of bulkiness t-butyl > i-propyl > *p*-tolyl > methyl, agrees as far as the order i-propyl > *p*-tolyl is concerned, with that observed by Brunner et al. for several [(C$_5$H$_5$)(CO)MoSC(CH$_3$)NR] complexes [12].

The fluxional processes are analogous to those which were first observed for the corresponding triazenido complexes [7]. The first step probably involves a cleavage of the Hg—N bond followed by an interchange of the chelating amidino group with the intermediate monodentate amidino group, after which the Hg—N bond may be reformed again. It is clear from the available data that the R—N bonds *cis* to Hg and *trans* to the olefinic groups are not broken on the NMR time scale. Thus we concludes that the Rh—N bond *trans* to Hg is cleaved. Clearly, the *trans*-influence of the HgCl group with respect to Rh—N bond rupture is larger than that of the olefinic groups.

In this respect, it is of interest to refer to the work of Creswell et al. [13], who observed interchange of monodentate and chelating acetate groups for

[(Ph$_3$P)$_2$(CO)M(O$_2$CCH$_3$)$_2$] (M = Ru, Os). They noted that the Ru—O bonds *trans* to Ph$_3$P, but not *trans* to CO, were cleaved at low temperatures, demonstrating the importance of the *trans*-influence in these exchange processes. They also found that the metal can have a strong effect, the ruthenium being more labile than the osmium complexes, and this is analogous to our earlier work, in which we found that the rhodium compounds are more labile than the corresponding iridium compounds [7].

References

1 J. Kuyper, P.I. van Vliet and K. Vrieze, J. Organometal. Chem., 96 (1975) 289.
2 J. Kuyper, P.I. van Vliet and K. Vrieze, J. Organometal. Chem., 105 (1976) 379.
3 J. Kuyper and K. Vrieze, J. Organometal. Chem., 107 (1976) 129.
4 P.I. van Vliet, J. Kuyper and K. Vrieze, J. Organometal. Chem., 122 (1976) 99.
5 P.I. van Vliet and K. Vrieze, J. Organometal. Chem., 139 (1977) 337.
6 P.I. van Vliet, G. van Koten and K. Vrieze, J. Organometal. Chem., 182 (1979) 105.
7 P.I. van Vliet, M. Kokkes, G. van Koten and K. Vrieze, J. Organometal. Chem., 187 (1980) 413.
8 P.I. van Vliet, G. van Koten and K. Vrieze, J. Organometal. Chem., 179 (1979) 89.
9 W. Bradley and I. Wright, J. Chem. Soc., (1956) 640.
10 J. Chatt and L.M. Venanzi, J. Chem. Soc. (1957) 4735.
11 J.L. Dawes and R.D.W. Kemmitt, J. Chem. Soc. (A), (1968) 2093.
12 H. Brunner, E. Bauer and J. Wachter, Chem. Ber., 111 (1978) 379.
13 C.J. Creswell, A. Dobson, M. Moore and S.D. Robinson, Inorg. Chem., 18 (1979) 2055.