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METAL—METAL BONDED COMPOUNDS

V *. COMPOUNDS WITH Ir(Rh)—Hg BONDS CONTAINING A BRIDGING AND A CHELATING TRIAZENIDO GROUP, WHICH INTERCONVERT INTRAMOLECULARLY

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Summary

The compounds $[(\text{Diene})(RN_3R')_2MHgCl]_2$ (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_3-C_6H_4; R' = p-$CH_3C_6H_4$) have been prepared by reaction of $[(\text{Diene})MCl]_2$ with $[Hg(RN_3R')_2]$ and by reaction of $[\{(\text{Diene})MCl\}(HgCl_2)]_2$ with $[Ag(RN_3R')]_n$. A crystal structure study of $[(\text{COD})(\text{EpTT})_2IrHgCl]_2$ shows that the complex is dimeric with two chloride atoms bridging the two mercury atoms. In each half of the dimer there is one triazenido group chelating to the Ir atom and one triazenido group bridging an iridium—mercury bond (2.62 Å). The complexes are monomeric in solution but have otherwise a configuration around the Ir(Rh) atom similar to that in the solid state. Fluxional processes, which occur for M = Rh but not for M = Ir, involve a novel dynamic process consisting of interchange of the bridging and chelating triazenido groups via monodentate intermediates.

Introduction

Our investigations into the stabilization of metal—metal bonds by means of triazenido, formamidino and carboxylato ligands have led to the development of a novel class of complexes and better understanding of the bonding characteristics of these ligands.

Reactions of $[L_2(CO)MX]$ with $[M'(RNYNR')]_n$ afforded $[L_2(CO)MM'$-$(RNYNR')X]$ (Y = N; M = Ir, Rh; M' = Cu, Ag; R = CH_3; R' = p-$CH_3C_6H_4$, CH_3;

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* For part IV see ref. 3.

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X = Cl, Br, I, O_2CCH_3; L = Ph_3P, Ph_3As, $PhMe_2P$ and Y = CH; M = Ir; M′ = Cu, Ag; R = p-$CH_3C_6H_4$; R′ = CH_3, C_2H_5, $CH(CH_3)_2$, $C(CH_3)_3$, C_6H_{11}; X = Cl; L = Ph_3P) in which a formal M-to-M′ donor bond is bridged by a triazenido or formamidino group [1,2,3]. In this five-membered bimetallic ring delocalization enhances the stability of the otherwise unstable M-to-M′ bond. A notable feature is that stabilization can also be affected by a bridging carboxylate or even a perchlorato group. On the other hand, reactions of [$(Ph_3P)_2$(CO)MX] (M = Ir, Rh; X = Cl, O_2CR) with [X′Hg(RN_3R')] and [Hg$(RN_3R')_2$] (X′ = Cl, I; R = CH_3; R′ = CH_3, p-$CH_3C_6H_4$) afforded a great variety of covalent M—Hg bonded complexes, in which, depending on X, X′ and R′, the triazenido group may bridge the M—Hg bond or may be converted into a chelating acyltriazenido group by CO insertion into the M—N bond [4]. However, no monodentate or chelating triazenido or formamidino groups were observed, although these coordination modes occur relatively frequently [5—8].

Since it is known that [{(COD)RhCl}(Hg(Cl_2))]$_2$ [9] (COD = 1,5-cyclooctadiene) contains a Rh-to-Hg donor bond it appeared to us of interest to investigate the reactions of [(Diene)MCl]$_2$ (M = Rh; Diene = 1,5-cyclooctadiene, bicyclo[2,2,1]hepta-2,5-diene and M = Ir; Diene = 1,5-cyclooctadiene) with triazenido and formamidino mercury compounds in order (a) to find out whether metal-to-metal donor bonds or covalent metal—metal bonds would be formed, (b) to determine the influence of the replacement of one CO group and two phosphines by a diene ligand on the coordination capacities of the triazenido and formamidino ligands.

In this paper we describe the preparation, structure, fluxional behaviour and chemical properties of covalent Ir(Rh)-Hg bonded complexes formed in the reaction of [(Diene)MCl]$_2$ with [Hg$(RN_3R')_2$].

Experimental

All preparations were carried out under nitrogen in dried solvents. The silver and mercury triazenes (AgMpTT, AgEpTT, AgDpTT and Hg$(DpTT)_2$ *) and diene—rhodium, iridium compounds ([CODIrCl]$_2$, [CODRhCl]$_2$ and [NORRhCl]$_2$ **) were prepared by published methods [10—14].

Preparation of [(Diene)$(RN_3R')_2$MHgCl]$_2$ (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-$CH_3C_6H_4$; R′ = p-$CH_3C_6H_4$

Method I. A solution of [Ag(RN_3R')]$_n$ (2/n mmol) in THF (10 ml) was added to a rapidly stirred solution of $HgCl_2$ (1 mmol) in THF (5 ml). After 20 min 0.5 mmol of [(Diene)MCl]$_2$ was added and stirring was continued for one hour. After filtration, concentration, addition of hexane, and cooling, red or orange crystals were obtained in 90% yield.

Method II. A solution of [AgRN_3R']$_n$ (2/n mmol) in CH_2Cl_2 (10 ml) was added during 20 min dropwise to a suspension of [{(Diene)MCl}($HgCl_2$)]$_2$ [9]

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* MpTT = CH_3-N_3-p-tolyl; EpTT = C_2H_5-N_3-p-$CH_3C_6H_4$; DpTT = p-$CH_3C_6H_4$-N_3-p-$CH_3C_6H_4$.

** COD = 1,5-cyclooctadiene; NOR = bicyclo[2,2,1]hepta-2,5-diene (norbornadiene).

(0.5 mmol) in CH_2Cl_2 (10 ml). The work-up procedure reaction was as described above.

Preparation of $[(Diene)(RN_3R)_2RhHgCl]_2$ (Diene = NOR, COD; R = p-CH_3-C_6H_4)

To a solution of $[(Diene)RhCl]_2$ (0.5 mmol) in THF or CH_2Cl_2 (15 ml) was added 1 mmol of $Hg(DpTT)_2$, and the suspension was stirred until a clear red solution was formed. After concentration, addition of hexane and cooling red crystals were obtained in 90% yield.

Attempts to isolate the Ir compounds containing the di-*p*-tolyltriazenido group by the above methods were unsuccessful. We were also unable to replace the Cl atom by a F or Br atom by addition of the sodium salts to solutions of $[(Diene)MCl]_2$ or $[(Diene)(RN_3R')_2MHgCl]_2$ in acetone, THF and CH_2Cl_2. Reactions of $[M(RN_3R')]_n$ (M = Cu, Ag; R = CH_3, C_2H_5, *p*-$CH_3C_6H_4$; R' = *p*-$CH_3C_6H_4$) with $[(Diene)MCl]_2$ did not give metal—Ag(Cu) bonded complexes.

The exchange experiments involving the triazenido and diene ligands were monitored by ^1H NMR spectroscopy and were carried out by adding the free ligand to a solution of the appropriate compound.

Spectroscopic measurements and analytical data

^1H NMR spectra were recorded on a A60-D and XL-100 Varian spectrometer and ^{13}C NMR spectra on a WP 80 Bruker spectrometer. Molecular weights were recorded 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).

TABLE 1

ANALYTICAL DATA

Compound [a]	M.W. [b]	Analysis found (calcd.) (%)			Colour
		C	H	N	
$[COD(MpTT)_2IrHgCl]_2$	790	34.61	3.87	10.09	orange
	(833)	(34.88)	(3.90)	(9.90)	
$[COD(EpTT)_2IrHgCl]_2$	853	36.28	4.22	9.76	red
	(861)	(36.31)	(4.23)	(9.58)	
$[COD(MpTT)_2RhHgCl]_2$	739	38.77	4.34	11.30	orange
	(743)	(37.32)	(4.17)	(11.17)	
$[COD(EpTT)_2RhHgCl]_2$	777	40.47	4.70	10.89	orange
	(772)	(40.84)	(4.92)	(10.69)	
$[COD(DpTT)_2RhHgCl]_2$	810	48.27	4.50	9.38	orange
	(896)	(46.89)	(4.38)	(9.16)	
$[NOR(MpTT)_2RhHgCl]_2$	665	37.97	3.88	11.55	red
	(727)	(37.78)	(3.88)	(11.16)	
$[NOR(EpTT)_2RhHgCl]_2$	723	39.74	4.27	11.12	red
	(755)	(40.45)	(4.47)	(10.79)	
$[NOR(DpTT)_2RhHgCl]_2$	826	47.79	4.13	9.55	red
	(880)	(47.84)	(4.39)	(9.47)	

[a] COD = 1,5-cyclooctadiene; NOR = bicyclo[2.2.1]hepta-2,5-diene (norbornadiene); MpTT = CH_3—N_3—*p*-$CH_3C_6H_4$; EpTT = C_2H_5—N_3—*p*-$CH_3C_6H_4$; DpTT = *p*-$CH_3C_6H_4$—N_3—*p*-$CH_3C_6H_4$. [b] M.W. in $CHCl_3$, the experimental error is ± 10% (found (calcd.)).

Crystal Data of [(COD(EpTT)$_2$IrHgCl]$_2$

The red crystals are triclinic with the cell constants a 10.453(2); b 11.612(1); c 11.919(1) Å; α 82.69(1); β 88.07(1); γ 76.96(1)°; $Z = 2$; space group $P\bar{1}$.

Intensity Data

4750 independent reflections with $3° < \theta < 65°$ of which 4212 were above the significance level of 2.5σ (1) were measured on a Nonius Cad-4 automatic diffractometer (Cu-K_α). No absorption correction was applied.

Structure determination and refinement

The positions of the iridium, mercury and chloride atoms were determined from a sharpened, origin removed, Patterson function, the space group being $P\bar{1}$; the other non-hydrogen atoms were located in a difference Fourier synthesis. No attempt was made to determine the positions of the hydrogen atoms. The refinement has been carried out by means of a blockdiagonal least squares procedure, using anisotropic temperature parameters for the iridium, mercury and chloride atoms and isotropic factors for the remaining atoms. A final R value of 7.5% was obtained using a weighting scheme $W = 1.0/(15.0 + F_{obs} + 0.0071F_{obs}^2)$.

Results

The complexes [(Diene)(RN$_3$R')$_2$MHgCl]$_2$ (M = Rh; Diene = NOR, COD; R = CH_3, C_2H_5, p-$CH_3C_6H_4$; R' = p-$CH_3C_6H_4$ and M = Ir; Diene = COD; R = CH_3, C_2H_5; R' = p-$CH_3C_6H_4$) were prepared in almost quantitative yield according to equations 1 and 2.

$$[(\text{Diene})\text{MCl}]_2 + 2\,[\text{Hg}(\text{RN}_3\text{R}')_2] \rightarrow [(\text{Diene})(\text{RN}_3\text{R}')_2\text{MHgCl}]_2 \qquad (1)$$

$$[\{(\text{Diene})\text{MCl}\}_2(\text{HgCl}_2)_2] + \tfrac{4}{n}\,[\text{Ag}(\text{RN}_3\text{R}'\text{P}]_n \rightarrow [(\text{Diene})(\text{RN}_3\text{R}')_2\text{MHgCl}]_2 + 4\,\text{AgCl} \qquad (2)$$

The 1 : 2 mercury triazenido complexes were always obtained irrespective of the initial ratio of the reactants.

The molecular structure of [(COD)(EpTT)$_2$IrHgCl]$_2$

Although the complexes are monomeric in solution (Table 1) the crystal structure of [(COD)(EpTT)$_2$IrHgCl]$_2$ indicates that the complexes are chloride-bridged dimers in the solid state. For the complex studied a centre of symmetry exists between the two mercury atoms analogous to the earlier reported structure of [(Ph$_3$P)$_2$(CO)ClXIrHgX]$_2$ (X = Cl, Br) [15]. The molecular structure is depicted in Fig. 1, which also gives the numbering of the atoms. Fig. 2 shows the coordination of the metal atoms in the central part of the molecule. Table 2 contains the fractional coordinates; Tables 3 and 4 the bond angles and bond distances. Finally, Table 5 gives the distances of some atoms from the corresponding least square plane.

The bonding mode of the chelating triazenido group is analogous to that of triazenido compounds [(C_5H_5)(CO)$_2$Mo(DFT)] (DFT = 3,5-di(CF_3)phenyl-N$_3$-

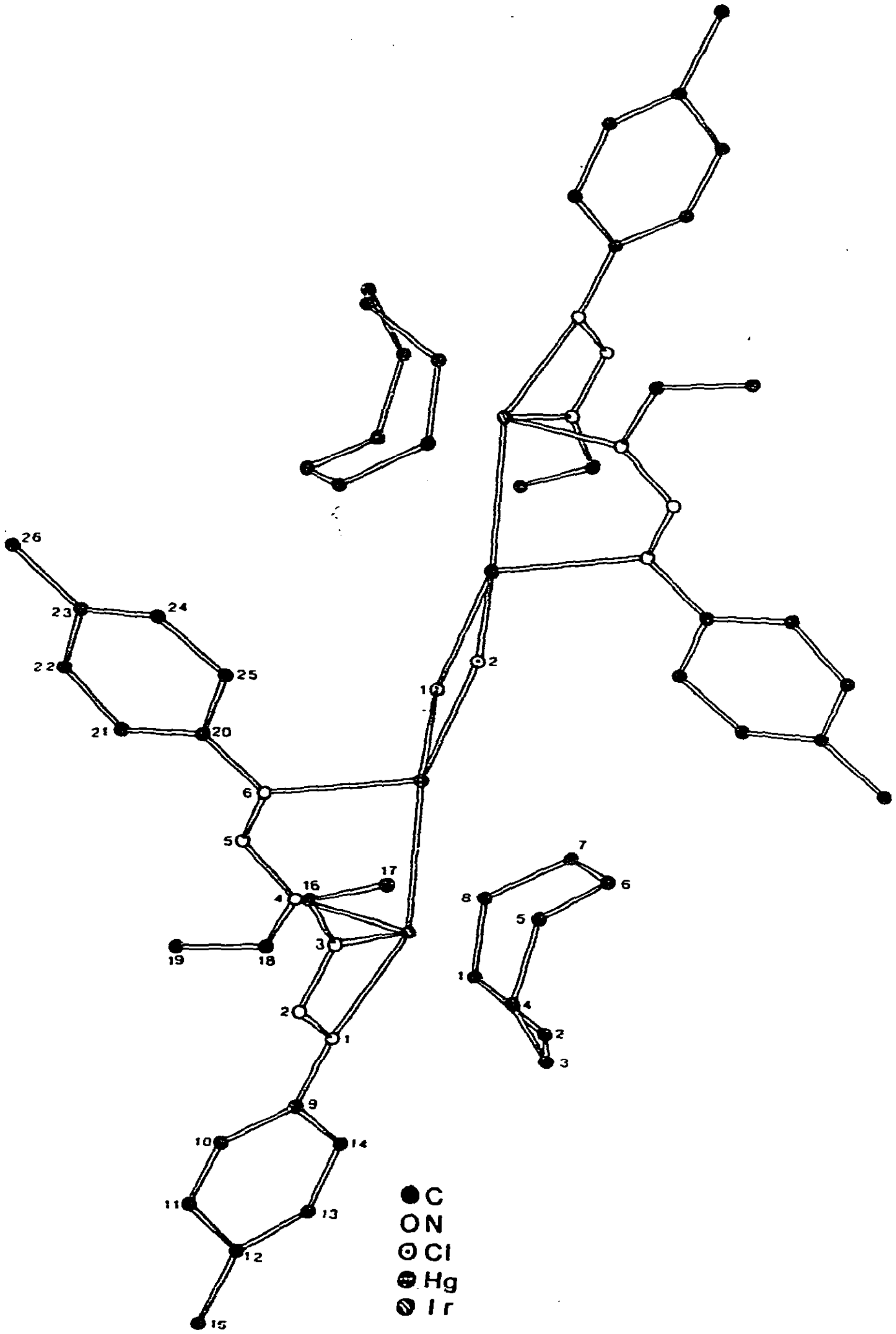

Fig. 1. Molecular structure of [COD(EpTT)$_2$IrHgCl]$_2$.

3,5-di(CF$_3$)phenyl), Co(DPT)$_3$ and [(Ph$_3$P)(CO)HRu(DPT)] (DPT = C_6H_5—N_3—C_6H_5) [7,16,17]. The Ir atom and the three N atoms of the four-membered ring and the carbon atoms directly bonded to the N atoms are planar (Table 5),

TABLE 2

FINAL POSITIONAL ISOTROPIC AND ANISOTROPIC PARAMETERS

Atom	x	y	z	10^2U	Atom	x	y	z	10^2U
C(1)	−0.028(1)	0.372(1)	0.448(1)	4.77	C(20)	0.382(1)	0.323(1)	0.048(1)	4.86
C(2)	−0.135(2)	0.324(1)	0.515(1)	5.91	C(21)	0.504(2)	0.343(2)	0.065(2)	8.01
C(3)	−0.137(2)	0.197(1)	0.495(1)	6.08	C(22)	0.592(2)	0.349(2)	−0.029(2)	9.25
C(4)	−0.085(2)	0.166(1)	0.381(1)	6.35	C(23)	0.563(2)	0.324(2)	−0.131(2)	6.60
C(5)	−0.125(2)	0.241(2)	0.271(2)	7.58	C(24)	0.444(2)	0.303(2)	−0.145(2)	6.86
C(6)	−0.232(2)	0.361(2)	0.265(2)	8.66	C(25)	0.351(2)	0.299(2)	−0.057(2)	6.95
C(7)	−0.180(2)	0.469(1)	0.281(2)	8.94	C(26)	0.667(2)	0.327(2)	−0.228(2)	8.56
C(8)	−0.046(1)	0.438(1)	0.343(1)	5.98	ME1 [a]	−0.037(2)	0.405(2)	0.395(2)	
C(9)	0.236(1)	0.085(1)	0.553(1)	4.64	ME2 [b]	−0.105(2)	0.202(2)	0.326(2)	
C(10)	0.349(2)	−0.005(1)	0.577(1)	5.79	N(1)	0.186(1)	0.118(1)	0.445(1)	4.45
C(11)	0.396(2)	−0.037(2)	0.687(2)	6.86	N(2)	0.232(1)	0.049(1)	0.369(1)	4.58
C(12)	0.330(2)	0.019(1)	0.779(1)	6.49	N(3)	0.178(1)	0.103(1)	0.275(1)	4.73
C(13)	0.220(2)	0.111(1)	0.753(1)	5.98	N(4)	0.243(1)	0.323(1)	0.316(1)	4.45
C(14)	0.173(2)	0.142(1)	0.644(1)	5.22	N(5)	0.323(1)	0.336(1)	0.230(1)	4.41
C(15)	0.386(2)	−0.016(2)	0.895(2)	9.32	N(6)	0.288(1)	0.314(1)	0.135(1)	4.82
C(16)	0.216(2)	0.041(1)	0.176(1)	5.84	Cl(1)	−0.0297(4)	0.3779(4)	−0.0776(4)	
C(17)	0.102(2)	0.001(2)	0.128(2)	10.77	Ir	0.06986(5)	0.25870(4)	0.32494(4)	
C(18)	0.290(1)	0.358(1)	0.421(1)	5.37	Hg	0.05289(5)	0.35071(6)	0.11223(5)	
C(19)	0.432(2)	0.344(2)	0.438(2)	9.86					

Atom	10^2U_{11}	10^2U_{22}	10^2U_{12}	10^2U_{13}	10^2U_{23}	10^2U_{23}
Cl	5.35	8.68	4.38	−2.03	−0.48	0.01
Ir	3.35	4.66	3.24	−1.48	0.71	−0.40
Hg	3.81	7.99	3.70	−1.01	0.41	0.59

[a] ME1 = middle of the C(1)—C(8) bond. [b] ME2 = middle of the C(4)—C(5) bond.

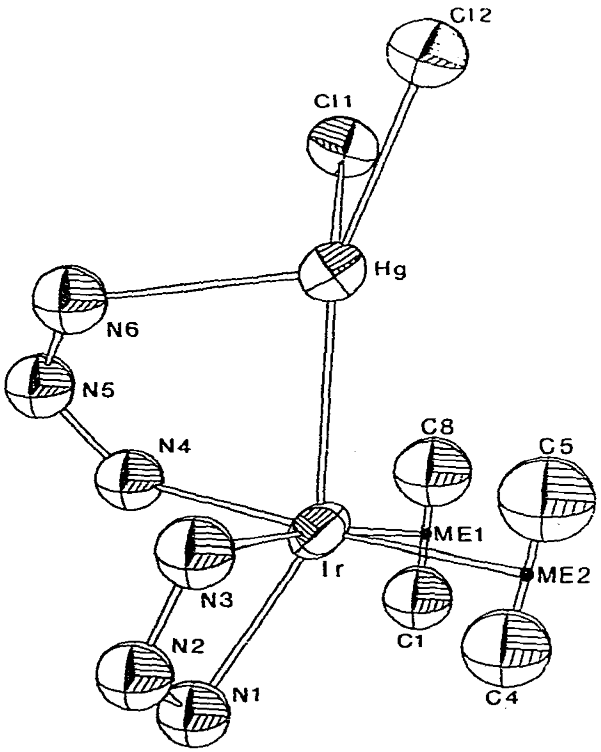

Fig. 2. Coordination of the metal atoms in the central part of the molecule.

while the N—N distances (1.30 Å) are almost equal and intermediate between the single (1.34 Å) and double bond (1.28 Å) values [7]. Furthermore, it is of interest to note that the middle of the C(1)—C(8) bond (ME1) also lies in the plane of the chelating triazenido group. In the case of the metal—metal bridging triazenido group it is of interest to note that, in contrast to the structures of the previously reported Cu(Ag)-to-Rh(Ir) bonded compounds bridged by a triazenido group [18,19,20], the five-membered ring is not planar. The Ir atom, three nitrogen atoms and the carbon atoms directly bonded to nitrogen lie in one plane while the mercury atom lies out of this plane by 1.27 Å. Study of a molecular model of $[(COD)(EpTT)_2IrHgCl]_2$, based on the available crystal data, unambiguously reveals that this deformation is caused by steric hindrance between the mercury atom and the ethyl group of the chelating triazenido ligand. Furthermore, comparison of the N—N bond distances (1.27 Å and 1.31 Å) with those present in $[(Ph_3P)_2Pt(DPT)_2]$ (N=N 1.28 Å and N—N 1.34 Å) and $[(Ph_3P)(CO)HRu(DPT)]$ (N—N 1.32 Å) show that the double bond is delocalised to only a small extent.

The coordination of the iridium atom can be described as strongly octahedrally distorted. The bond vectors from the Ir atom to N(3), N(4), ME1 and ME2 (ME1 = middle of the C(1)—C(8) bond; ME2 middle of the C(4)—C(5) bond) lie in one plane (Table 5) while the mutual bond angles are about 90° (Table 3). The distortion arises from the chelating triazenido group having a

TABLE 3

BOND ANGLES (IN DEG.) WITH STANDARD DEVIATIONS

Hg—Ir—N(1)	143.7(3)	Ir—N(1)—C(9)	147.8(9)	N(1)—C(9)—C(14)	120(1)
Hg—Ir—N(3)	88.6(3)	N(2)—N(1)—C(9)	117(1)	C(10)—C(9)—C(14)	118(1)
Hg—Ir—N(4)	82.3(3)	N(1)—N(2)—N(3)	106(1)	C(9)—C(10)—C(11)	120(2)
Hg—Ir—ME1	98.40(2)	Ir—N(3)—N(2)	101.5(8)	C(10)—C(11)—C(12)	121(2)
Hg—Ir—ME2	94.94(2)	Ir—N(3)—C(16)	142.5(9)	C(11)—C(12)—C(13)	117(2)
N(1)—Ir—ME1	115.1(3)	N(2)—N(3)—C(16)	116(1)	C(11)—C(12)—C(15)	119(2)
N(1)—Ir—ME2	100.5(3)	Ir—N(4)—N(5)	129(1)	C(13)—C(12)—C(15)	124(2)
N(1)—Ir—N(3)	58.2(4)	Ir—N(4)—C(18)	118.7(8)	C(12)—C(13)—C(14)	122(2)
N(1)—Ir—N(4)	82.6(4)	N(5)—N(4)—C(18)	112(1)	C(9)—C(14)—C(13)	122(1)
N(3)—Ir—ME1	173.0(3)	N(4)—C(5)—N(6)	117(1)	N(3)—C(16)—C(17)	113(2)
N(3)—Ir—Me2	93.1(4)	Hg—N(6)—N(5)	114.0(8)	N(4)—C(18)—C(19)	117(1)
N(3)—Ir—N(4)	88.4(5)	Hg—N(6)—C(20)	126.3(9)	N(6)—C(20)—C(21)	123(1)
N(4)—Ir—ME1	92.9(3)	N(5)—N(6)—C(20)	114(1)	N(6)—C(20)—C(25)	116(1)
N(4)—Ir—ME2	176.9(3)	C(2)—C(1)—C(8)	124(1)	C(21)—C(20)—C(25)	119(2)
ME1—Ir—ME2	85.9(3)	C(1)—C(2)—C(3)	113(1)	C(20)—C(12)—C(22)	119(2)
Ir—Hg—Cl(1)	154.5(1)	C(2)—C(3)—C(4)	114(1)	C(21)—C(22)—C(23)	122(2)
Ir—Hg—C(12)	113.53(8)	C(3)—C(4)—C(5)	125(1)	C(22)—C(23)—C(24)	118(2)
Ir—Hg—N(6)	80.7(3)	C(4)—C(5)—C(6)	121(2)	C(22)—C(23)—C(26)	119(2)
Cl(1)—Hg—N(6)	117.5(3)	C(5)—C(6)—C(7)	115(2)	C(24)—C(23)—C(26)	123(2)
C(12)—Hg—N(6)	91.5(3)	C(6)—C(7)—C(8)	113(2)	C(23)—C(24)—C(25)	124(2)
Cl(1)—Hg—Cl(2)	85.2(1)	C(1)—C(8)—C(7)	123(2)	C(20)—C(25)—C(24)	118(2)
Ir—N(1)—N(2)	94.4(7)	N(1)—C(9)—C(10)	123(1)		

small N—Ir—N angle (58°) which is usual for chelating triazenido groups.

The coordination geometry of the mercury atom is severely distorted. The small N(6)—Hg—Ir angle (81°) induced by the bridging triazenido group and the Cl—Hg—Cl angle (85°) are no doubt the reason for the strong deviation from a normal planar or tetrahedral coordination geometry. Finally, the iridium—mercury bond length (2.62 Å) is almost equal to those in the compounds $[(Ph_3P)_2(CO)XClIrHgX]$ (X = Cl; 2.57 Å and X = Br; 2.58 Å [15]), which indicates that the bridging triazenido group does not influence the Ir—Hg bond length.

Structure and properties of the compounds in solution

A. ^1H NMR results. The ^1H NMR spectra of the compounds described in this paper are rather complicated because of hydrogen—hydrogen couplings, and in

TABLE 4

BOND LENGTHS (IN Å) WITH STANDARD DEVIATIONS

Ir—Hg	2.618(1)	Hg—Cl(1)	2.41(1)	C(1)—C(8)	1.38(2)	C(12)—C(13)	1.39(2)
Ir—N(1)	2.19(1)	Hg—Cl(2)	3.08(1)	C(2)—C(3)	1.53(2)	C(12)—C(15)	1.50(3)
Ir—N(3)	2.06(1)	N(1)—N(2)	1.30(2)	C(3)—C(4)	1.51(2)	C(13)—C(14)	1.38(2)
Ir—N(4)	2.10(1)	N(2)—N(3)	1.29(1)	C(4)—C(5)	1.49(2)	C(20)—C(21)	1.38(2)
Ir—ME1	2.07(1)	N(4)—N(5)	1.31(2)	C(5)—C(6)	1.58(3)	C(29)—C(25)	1.38(3)
Ir—ME2	2.07(1)	N(5)—N(6)	1.27(2)	C(6)—C(7)	1.51(4)	C(21)—C(22)	1.42(3)
Ir—C(1)	2.17(1)	N(1)—C(9)	1.37(2)	C(7)—C(8)	1.55(3)	C(22)—C(23)	1.34(3)
Ir—C(4)	2.19(2)	N(3)—C(16)	1.45(2)	C(9)—C(10)	1.40(2)	C(23)—C(24)	1.34(3)
Ir—C(5)	2.22(2)	N(4)—C(18)	1.50(2)	C(9)—C(14)	1.41(2)	C(23)—C(26)	1.56(3)
Ir—C(8)	2.19(2)	N(6)—C(20)	1.42(2)	C(10)—C(11)	1.40(3)	C(24)—C(25)	1.41(3)
Hg—N(6)	2.42(1)	C(1)—C(2)	2.52(2)	C(11)—C(12)	1.42(3)		

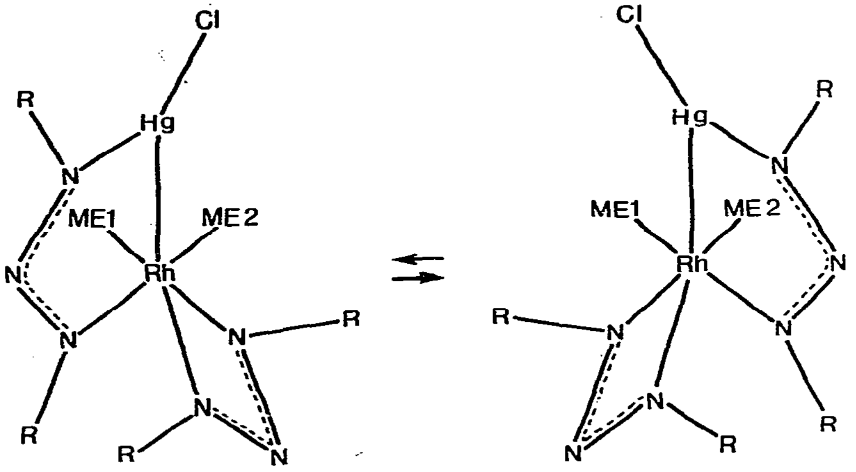

Fig. 3. Exchange between the chelating and bridging triazenido group.

the case of the Rh complexes intramolecular exchange processes also. The resonances of the triazenido ligands can be assigned directly. Assignments of the diene resonances can be made by comparing the resonances of the Ir and Rh compounds and the resonances of the COD and NOR ligands in the Rh compounds. The data obtained at −30° C in $CDCl_3$ are given (Table 6).

B. ^{13}C NMR results. In contrast to the ^{1}H NMR data, the ^{13}C NMR data (Table 7) give more insight into the configuration and behaviour of the monomeric compounds (Table 1) in solution.

The ^{13}C NMR data for the Rh compounds containing the symmetric di-*p*-tolyl triazenido groups in a temperature range from +30° C to −90° C show the presence of two pairs of inequivalent *p*-tolyl groups and also two resonances for the olefinic carbon atoms, indicating a plane of symmetry. In contrast to this there are four inequivalent resonances for the aliphatic carbon atoms of the COD group, which indicates a completely asymmetric molecule. This contradiction can be explained by the fact that the *p*-tolyl groups, the two olefinic carbon atoms at the side of mercury and the two olefinic carbon atoms at the opposite side are at the fast exchange limit on the NMR time scale, while the aliphatic carbon atoms are still undergoing slow exchange. This indicates the presence of an equilibrium as shown in Fig. 3.

Of particular interest is the large downfield shift of about 37 ppm for one of the aliphatic carbon atoms. Model studies of the monomer, based on the crystal structure, show that one CH_2 group of the COD ligands is close to the chloride atom as a result of the coordination geometry (see Fig. 3). This small distance explains the observed downfield shift. Attempts to confirm this suggestion by substitution of the chloride atom by bromide or fluoride atoms unfortunately failed (see Experimental).

For the Rh compounds containing two asymmetric triazenido groups, the ^{13}C NMR data show the presence of two isomers. Temperature and concentration dependent measurements showed no change in the relative integrals and shifts of the observed signals, indicating that the exchange between the two iso-

(continued on p. 424)

TABLE 5

DISTANCES (IN Å) OF SOME ATOMS TO MOLECULAR PLANES

Plane defined by				Plane defined by				Plane defined by			
N(4), N(5), N(6), C(18), C(20), Ir				N(1), N(2), N(3), C(9), C(16), Ir				N(3), N(4), ME1, ME2, Ir			
N(4)	0.010	C(20)	−0.037	N(1)	−0.052	C(16)	0.026	N(3)	0.095	ME2	−0.083
N(5)	−0.013	Ir	−0.019	N(2)	−0.018	Ir	0.016	N(4)	−0.079	Ir	−0.029
N(6)	0.060	Hg	1.261	N(3)	−0.015	Hg	0.777	ME1	0.096		
C(18)	−0.001	ME2	0.049	C(9)	0.044	ME1	−0.040				

TABLE 6

^{1}H NMR DATA (IN $CDCl_3$ RELATIVE TO TMS AT −30°C)

Compound	triazene resonances (ppm)				NOR or COD resonances (ppm)		
	p-tolyl		alkyl		olefinic CH	aliphatic	
	aryl	CH_3	CH_3	CH_2		CH	CH
[COD(MpTT)$_2$IrHgCl]	7.63; 7.16; 7.25	2.38 2.35	3.71 3.35		5.45 (vbr) 4.72 (vbr) 4.10 (vbr)		2.70 (vbr) 1.68 (vbr)
[COD(EpTT)$_2$IrHgCl]	7.61; 7.16; 7.28	2.38 2.35	1.07 ^{a}	4.01 ^{a} 3.41 ^{a}	5.40 (vbr) 4.27 (vbr) 4.11 (vbr)		2.73 (vbr) 1.58 (vbr)
[COD(MpTT)$_2$RhHgCl]	8.18; 7.27; 7.60; 7.15	2.38 2.32	3.83 3.72 3.51		4.51 (vbr)		2.72 (vbr) 1.89 (vbr)
[COD(EpTT)$_2$RhHgCl]	8.13; 7.26; 7.63; 7.18	2.40 2.32	1.42 ^{a} 0.81 ^{a}	4.05 ^{a} 3.92 ^{a}	4.58 (vbr)		2.71 (vbr) 1.88 (vbr)
[COD(DpTT)$_2$RhHgCl]	7.68; 7.19; 7.38; 7.05	2.37 2.35			4.28 (vbr) 2.92 (vbr)		3.80 (vbr) 1.92 (vbr)
[NOR(MpTT)$_2$RhHgCl]	8.17; 7.13; 7.57; 7.30	2.38 2.33	3.76 3.70 3.50		4.72 (vbr) 4.62 (vbr)	4.23 (vbr)	1.42 (vbr)
[NOR(EpTT)$_2$RhHgCl]	8.13, 7.25; 7.58, 7.23	2.37 2.31	1.42 ^{a} 1.35 ^{a} 0.99 ^{a}	4.00 ^{a} 3.75 ^{a}	4.68 (vbr) 4.62 (vbr)	4.23 (br) 4.15 (br)	1.38 (vbr)
[NOR(DpTT)$_2$RhHgCl]	7.61, 7.13; 7.43	2.35 2.32			4.62 (vbr)	4.24 (br) 4.11 (br)	1.36 (vbr)

[a] $J(CH_3—CH_2)$ is 7 Hz.

TABLE 7

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

Compound	Triazene resonances[a]							COD or NOR resonances				
	p-tolyl				Alkyl			olefinic[b] CH		aliphatic		
	C(1)	C(2)	C(3)	C(4)	CH_3	CH_2	CH_2			CH	CH_2	
[COD(MpTT)$_2$IrHgCl]	146.55	119.12	129.77	132.68	20.72	50.00		79.71	70.68		40.63	31.16
	145.79	114.99	129.52	132.52				71.17	70.24		31.36	26.94
[COD(EpTT)$_2$IrHgCl]	146.87	119.20	129.75	132.55	20.70	17.91	57.66	79.45	69.92		40.60	31.02
	145.67	114.58	129.45			15.60	55.84	71.07	69.55		31.20	27.13
[COD(MpTT)$_2$RhHgCl][c]	146.87 *	118.52 *	129.63	132.55 *	20.58	46.55 *		92.92(d)*	90.67(d)		31.93	29.93
	149.91	119.26	129.39	132.67		49.04		88.73(d)	88.37(d)		31.80	29.50
	146.99	118.71		133.19		45.28		93.22(d)	85.51(d)		30.71	
[COD(EpTT)$_2$RhHgCl][c]	146.75 *	118.71 *	129.63	133.40	20.70	16.51*	53.17*	92.22(d)	90.67(d)		31.05	29.99
	147.85	119.26	129.39	132.49	20.58	16.15	55.23	88.24(d)*	87.75(d)		30.65	29.74
	146.87	118.53				15.85	42.62	93.13(d)	85.66(d)		30.41	
[COD(DpTT)$_2$RhHgCl][c]	147.66 *	123.32*	129.75*	135.34*	20.82*			93.46(d)*			67.85*	29.62*
	146.44*	119.62*	128.75*	133.88*	20.72*			88.13(d)*			30.90*	25.37*
[NOR(MpTT)$_2$RhHgCl][c]	146.75*	118.71	130.48	132.36*	20.82	45.46*		72.74(d)*	69.15(d)	53.05(br)	65.73(br)	
	147.35	118.22	129.69	133.70	20.64	47.70		70.81(d)*	65.73(d)	52.35(vbr)		
	146.87			132.49		47.52		69.78(d)	64.79(d)	51.22(br)		
[NOR(EpTT)$_2$RhHgCl][c]	147.47*	118.77	129.63	133.76	20.82	16.88*	54.20	69.86(d)*	70.52(d)	52.68(br)	65.55*	
	147.05	118.53	129.51	132.24	20.64	16.39		65.03(d)*	69.49(d)	52.02(br)	65.79	
	146.87	118.28				16.09		71.71(d)	68.46(d)	51.23(br)		
[NOR(DpTT)$_2$RhHgCl][c]	146.38*	119.50*	129.82*	133.88*	20.88*			71.25(d)*		51.95*	65.29*	
		122.90*	129.21*	133.58*	20.76*			67.03(d)*		51.53*		

[a] The C(1) atom is bound to nitrogen. [b] The Rh compounds have a ^{13}C—^{103}Rh coupling of ±9 Hz. [c] The resonances marked with * are assigned to an isomer with two equivalent N—R groups bonded to Rh *cis* to Hg.

mers is slow. The first isomer shows two doublets for the olefinic carbon atoms of the diene ligand, which indicates the presence of a plane of symmetry analogous to the compounds with DpTT. For the triazenido groups only one set of resonances is observed, indicating the presence of a fast exchange between these groups. The second isomer shows four doublets for the olefinic carbon atoms and the presence of two inequivalent triazenido groups. This indicates that there is no plane of symmetry in this isomer. Of special interest is the fact that in the case of MpTT the two doublets of the olefinic carbon atoms dominate, and in the case of EpTT the four doublets of the olefinic carbon atoms. This, clearly, indicates the importance of the size of the alkyl groups of the triazenido ligands. From these data we suggest for the first isomer a structure containing two *N*-alkyl groups bonded to the Rh atom *cis* to the Hg atom while the bridging and chelating triazenido groups are in the fast exchange. The second isomer has an asymmetric structure with one *N*-alkyl group and one *N*-*p*-tolyl group bonded to Rh *cis* to Hg.

Although it seems very likely that this isomer is also involved in an equilibrium, as shown in Fig. 3, a rigid conformation cannot be excluded.

The resonances of the iridium compound, show the presence of two inequivalent triazenido groups, four inequivalent olefinic carbon atoms and four inequivalent aliphatic carbon atoms of the COD ligand. In view of our results on formamidino compounds [21], the configuration for the triazenido groups and the COD ligand will be rigid and analogous to that observed in the solid state of the dimer. However, the presence of an equilibrium, as shown in Fig. 3, having one *N*-alkyl and one *N*-aryl group bonded to Ir *cis* to Hg cannot be excluded.

Chemical properties of the compounds

The compounds are stable for days in solvents such as CH_2Cl_2, THF and $CHCl_3$ open to the air.

The diene ligands do not exchange while the triazenido groups can be rapidly replaced by a more acidic triazenido group. The order of reactivity is DpTT > EpTT ≈ MpTT. With stronger acids such as HOAc and HCl the compounds rapidly decompose into a mixture of unidentified products.

Surprisingly, none of the compounds reacted with donor ligands such as Ph_3P, Ph_3As or pyridine. Treatment with CO resulted in a change of colour of the solution from red to yellow, while at the same time metallic mercury was formed, but no pure products could be isolated.

Discussion

Complexes $[(\text{Diene})(RN_3R')_2MHgCl]_2$ (M = Ir; Diene = COD; R = CH_3, C_2H_5; $R' = p\text{-}CH_3C_6H_4$ and M = Rh; Diene = COD, NOR; R = CH_3, C_2H_5, $p\text{-}CH_3C_6H_4$; $R' = p\text{-}CH_3C_6H_4$) have been prepared by reactions 1 and 2, which are very likely similar, since the reacting species in both cases undoubtedly involve $[Hg(RN_3R')_2]$. The structure details of $[(COD)(EpTT)_2IrHgCl]_2$ have been mentioned in the results section, and are shown in Fig. 1 and Fig. 2. A feature of interest is that this complex contains both a chelating and a metal—mercury bridging triazenido group, which has not been observed before. We have previously reported complexes with a metal—mercury bridging triazenido group, with a chelating triazenido ligand and/or with an acyltriazenido group as a result of the presence of coordinated CO. In the above reactions there is no coordinated CO and therefore the configuration as shown in Fig. 1 becomes possible. A second point of interest is that for the bridging triazenido group two inequivalent N—N bond distances are found, in contrast to the situation observed for $[(Ph_3P)_2(CO)RhCu(MeN_3Me)Cl]$ and for $[PhMe_2P)_2(CO)IrAg(MeN_3Me)Cl]$ [18,19]. On the other hand differing N—N bond distances have been determined for $[(\eta^3\text{-}C_4H_7)Pd(MeN_3Me)]_2$ [20], in which the MeN_3Me groups bridge two non-bonded Pd atoms. The reasons for this variation in behaviour are not clear and will not be discussed further.

When we consider the molecular configuration around Ir and Hg, it could be argued that the metal—mercury bond may be viewed upon as an Ir^I-to-Hg^{II} metal donor bond, as in $[\{(COD)RhCl\}(HgCl_2)]_2$ [9] or as a covalent Ir^{II}—Hg^I bond, as in $[(Ph_3P)_2(CO)Cl_2IrHgCl]_2$ [15,22], depending on how one wishes to regard the electron distribution in the five-membered bimetallic ring. Such a discussion is fruitless, but may serve to indicate that the present structure may be regarded as an intermediate in the sequence of steps to of metal—mercury bonded complexes. No doubt the first step involves an addition complex between $[(Diene)MCl]_2$ and $[Hg(RN_3R')_2]$ with a M^I-to-Hg^{II} metal-donor bond. Subsequent steps involve the transfer of Cl from M to Hg and of stepwise transfers of the triazenido groups from Hg to M. The final step is the complete transfer of a triazenido group to M with concomitant formation of a covalent M^{II}—Hg^I bond as was observed in the reaction of $[L_2(CO)MX]$ with $[Hg(RN_3R')_2]$ (see Fig. 7 of ref. 4). It should further be noted that bridging triazenido groups need not necessarily be formed to stabilize the metal—metal bond as is the case for the Cu(Ag)—Rh(Ir) bonded compounds [1,2] since many stable non-bridged metal—mercury bonds are known [9,15,22—25]. However, a metal—metal bridging group may well contribute to a further stabilization of the metal—metal bond. This is indicated by the unusual stability of the compounds, which do not even react with Ph_3P, Ph_3As or pyridine and do not decompose in solution exposed to air [4,22].

NMR studies show that the structures of the complexes in solution are probably very similar to those in the solid state, but the molecular weights show that in solution the complexes are all monomeric. This implies that the bridge between the two mercury atoms is very weak. The formal difference between the coordination of mercury in the dimer (four) and in the monomer (three) should be noted, but is chemically not interesting.

A final point is the very unusual fluxional process which is observed for the complexes of Rh (but not those of Ir), which involves interchange between the chelating and bridging triazenido groups. It is concluded that this process involves rupture of the Hg—N bond and of the Rh—N bond *trans* to Hg; no bond rupture occurs on the NMR time scale between the Rh atom and the N—R groups *cis* to Hg. It is not possible to define a detailed mechanism, but it is very likely that the first step involves a rupture of the Hg—N bond resulting in a six-coordinated Rh compound with one monodentate and one chelating triazenido group. Subsequently the Rh—N bond *trans* to Hg is broken, after which a five-coordinated intermediate is formed with two monodentate triazenido groups. Finally, the triazenido group, which was originally in the bridging position may now take up the chelating position. The rigidity of the Ir complexes can be explained by assuming that the Ir—N bond *trans* to Hg is stronger than the corresponding Rh—N bond.

Fluxional processes of triazenido complexes have been observed before and to our knowledge always involve monodentate bonded groups which undergo interchange of the point of coordination via a chelating intermediate [26—29]. The above mechanism would be the first example for which it is shown not only that the reverse process can also occur, but also that bridging triazenido groups can become temporarily monodentate, as was recently demonstrated for $[M(RNC(H)NR')]_n$ (M = Cu, Ag) [30]. Intramolecular interchange of chelating and bridging groups is thereby possible.

In a subsequent paper the preparation, properties and fluxional behaviour of analogous formamidino complexes will be discussed.

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