

## METAL—METAL BONDED COMPOUNDS

### II \*. TRIAZENIDO COMPOUNDS WITH METAL—MERCURY BONDS

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#### Summary

Reactions of  $[(\text{Ph}_3\text{P})_2(\text{CO})\text{MX}^2]$  ( $\text{M} = \text{Rh}^{\text{I}}, \text{Ir}^{\text{I}}; \text{X}^2 = \text{Cl}, \text{O}_2\text{CCF}_3$ ) with triazenido compounds  $[\text{X}^1\text{Hg}(\text{RN}_3\text{R}^1)]$  ( $\text{X}^1 = \text{Cl}, \text{I}; \text{R} = \text{CH}_3; \text{R}^1 = \text{CH}_3, p\text{-tolyl}$ ),  $[\text{Hg}(\text{RN}_3\text{R}^1)_2]$  and with  $\text{Hg}(\text{Ox})_2$  ( $\text{Ox} = \text{O}_2\text{CCF}_3, \text{O}_2\text{CCH}_3, \text{O}_2\text{CCH}(\text{CH}_3)_2$ ) afforded, in almost all cases, metal—mercury bonded compounds. The triazenido compounds gave a great variety of products. The type of structure formed is critically dependent on M, X and on the groups R and R<sup>1</sup>. The triazenido group can bond as (i) a metal—mercury bridging ligand, (ii) an acyltriazenido chelating group, or (iii) a chelate. In the case of the Ox groups only one type of structure was found, viz. that with the carboxylato ligand acting as monodentate.

#### Introduction

Previous publications have dealt with the preparation of novel  $\text{Rh}^{\text{I}}(\text{Ir}^{\text{I}})\text{-to-Cu}^{\text{I}}(\text{Ag}^{\text{I}})$  bonded compounds of the type  $[\text{L}_2(\text{CO})\text{MM}'(\text{RN}_3\text{R}')\text{X}]$  ( $\text{L} = \text{R}_3\text{P}, \text{R}_3\text{-As}; \text{M} = \text{Rh}^{\text{I}}, \text{Ir}^{\text{I}}; \text{M}' = \text{Cu}^{\text{I}}, \text{Ag}^{\text{I}}; \text{X} = \text{Cl}, \text{Br}, \text{I}$ ) and  $[\text{L}_2(\text{CO})\text{M}(\text{Ox})_2]$  ( $\text{L} = \text{Ph}_3\text{P}, p\text{-tol}_3\text{P}; \text{M} = \text{Rh}^{\text{I}}, \text{Ir}^{\text{I}}; \text{Ox} = \text{O}_2\text{CCF}_3, \text{ClO}_4$ ) in which, in all cases, the M-to-M<sup>1</sup> donor bond was bridged by either a triazenido group or a carboxylato group [1–5]. It was also found that acyltriazenido—metal compounds can be formed by CO insertion [2].

These results prompted us to investigate in more detail the coordination properties of the triazenido ligands and of related carboxylato groups. In this paper we show that reactions of  $[(\text{R}_3\text{P})_2(\text{CO})\text{MX}]$  ( $\text{M} = \text{Rh}^{\text{I}}, \text{Ir}^{\text{I}}; \text{X} = \text{Cl}, \text{O}_2\text{CCF}_3$ ) with triazenidomercury and carboxylatomercury compounds give a much greater variety of products than in the case of  $\text{Cu}^{\text{I}}$  and  $\text{Ag}^{\text{I}}$  compounds.

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## Experimental

All preparations were carried out under dry, oxygen free, nitrogen. The silver triazenido \* compounds were prepared by published methods [2,6,7].

*Preparation of [XHg(RN<sub>3</sub>R<sup>1</sup>)] and [Hg(RN<sub>3</sub>R<sup>1</sup>)<sub>2</sub>] (X = Cl, I; R = CH<sub>3</sub>, p-tol; R<sup>1</sup> = CH<sub>3</sub>, p-tol)*

A solution of [Ag(RN<sub>3</sub>R<sup>1</sup>)]<sub>n</sub> (1 or 2 mmol) in THF (10 ml) was slowly added to a solution of HgX<sub>2</sub> (X = Cl, I) (1 mmol) in THF (10 ml) with rapid stirring. After 15 min the resulting suspension of AgX and [XHg(RN<sub>3</sub>R<sup>1</sup>)] or [Hg(RN<sub>3</sub>R<sup>1</sup>)<sub>2</sub>] was used directly for the preparations below.

*Preparation of [(Ph<sub>3</sub>P)<sub>2</sub>(CO)Cl(Ox)MHg(Ox)] \*\* (M = Rh<sup>I</sup>, Ir<sup>I</sup>; Ox = O<sub>2</sub>CCF<sub>3</sub>, O<sub>2</sub>CCH<sub>3</sub>, O<sub>2</sub>CCH(CH<sub>3</sub>)<sub>2</sub>)*

Hg(Ox)<sub>2</sub> (1 mmol) was added to a stirred suspension of [(Ph<sub>3</sub>P)<sub>2</sub>(CO)MCl] (1 mmol) in THF (20 ml). After 20 min hexane (60 ml) was added and the white precipitate was filtered off and dried in vacuo (yield 95%).

*Reaction of [X<sup>1</sup>Hg(DMT)] with [(Ph<sub>3</sub>P)<sub>2</sub>(CO)MX<sup>2</sup>] (X<sup>1</sup> = Cl, I; X<sup>2</sup> = Cl, O<sub>2</sub>CCF<sub>3</sub>; M = Rh<sup>I</sup>, Ir<sup>I</sup>)*

[(Ph<sub>3</sub>P)<sub>2</sub>(CO)MX<sup>2</sup>] (1 mmol) was added to a stirred suspension of [X<sup>1</sup>Hg(DMT)] (1 mmol) in THF (20 ml) and the mixture was stirred for 10 min (M = Rh) and for 20 min (M = Ir). Thereafter the procedure was as in the next preparation described below. In the case of M = Rh three different types of compound were obtained viz. [(Ph<sub>3</sub>P)<sub>2</sub>(CO—DMT)RhCl<sub>2</sub>] (yield 40%), [(Ph<sub>3</sub>P)<sub>2</sub>(CO—DMT)ClRhHgI] (yield 60%) and [(Ph<sub>3</sub>P)<sub>2</sub>(CO—DMT)(O<sub>2</sub>CCF<sub>3</sub>)RhHgI] (yield 40%). In the case of M = Ir only one type of compound was isolated: [(Ph<sub>3</sub>P)<sub>2</sub>(CO—DMT)X<sup>1</sup>IrHgX<sup>2</sup>] (X<sup>1</sup> = Cl, I; X<sup>2</sup> = Cl; yield 70% and X<sup>1</sup> = O<sub>2</sub>CCF<sub>3</sub>, X<sup>2</sup> = I; yield 55%). No identifiable products were obtained for X<sup>1</sup> = O<sub>2</sub>CCF<sub>3</sub> and X<sup>2</sup> = Cl.

Analogous reactions with [XHg(DpTT)] did not give well defined products.

*Reaction of [X<sup>1</sup>Hg(MpTT)] with [(Ph<sub>3</sub>P)<sub>2</sub>(CO)MX<sup>2</sup>] (X<sup>1</sup> = Cl, I; M = Rh<sup>I</sup>, Ir<sup>I</sup>; X<sup>2</sup> = Cl, O<sub>2</sub>CCF<sub>3</sub>)*

[(Ph<sub>3</sub>P)<sub>2</sub>(CO)MX] (1 mmol) was added to a stirred suspension of [X<sup>1</sup>Hg(MpTT)] (1 mmol) in THF (20 ml). After 10 min the AgX was removed by filtration and the solution was concentrated to 5 ml under vacuum. Then 50 ml ether/hexane were added, and the precipitate was filtered off and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/ether/hexane. In the case of Rh no products could be isolated. In the case of Ir two different types of compound were obtained. Compounds of the first type were [(Ph<sub>3</sub>P)<sub>2</sub>(CO)ClIrHg(MpTT)Cl] (yield 70%) and [(Ph<sub>3</sub>P)<sub>2</sub>(CO)(O<sub>2</sub>CCF<sub>3</sub>)IrHg(MpTT)X] (X = Cl, I) (yield 70%). The second type of compound was represented by [(Ph<sub>3</sub>P)<sub>2</sub>(CO—MpTT)ClIrHgI] (yield 50%).

\* DMT = CH<sub>3</sub>N<sub>3</sub>CH<sub>3</sub>; MpTT = CH<sub>3</sub>N<sub>3</sub>-p-tol; DpTT = p-tol-N<sub>3</sub>-p-tol.

\*\* The compound [(Ph<sub>3</sub>P)<sub>2</sub>(CO)Cl(O<sub>2</sub>CCH<sub>3</sub>)IrHg(O<sub>2</sub>CCH<sub>3</sub>)] has been described [8], but was not completely characterized.

TABLE 1

## ANALYTICAL DATA

Compound <sup>a</sup>	Mol. weight <sup>b</sup>	Analysis found (calcd.) (%)				Colour
		C	H	Hg	N	
(Ph <sub>3</sub> P) <sub>2</sub> (CO)(OAc)ClIrHg(OAc)		44.84(44.81)	3.29(3.30)			white
(Ph <sub>3</sub> P) <sub>2</sub> (CO)(IB)ClIrHg(IB)	1168(1155)	46.45(46.79)	3.87(3.84)	17.11(17.37)		white
(Ph <sub>3</sub> P) <sub>2</sub> (CO)(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )ClIrHg(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )		39.99(40.81)	2.59(2.51)			white
(Ph <sub>3</sub> P) <sub>2</sub> (CO)(OAc)ClRhHg(OAc)		49.41(48.77)	3.69(3.59)			white
(Ph <sub>3</sub> P) <sub>2</sub> (CO)(IB)ClRhHg(IB)	1077(1066)	49.34(50.71)	3.83(4.16)			white
(Ph <sub>3</sub> P) <sub>2</sub> (CO)(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )ClRhHg(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )		43.62(44.05)	2.71(2.70)	18.85(17.94)	5.21(5.26)	white
(Ph <sub>3</sub> P) <sub>2</sub> (CO-DMT)RhCl <sub>2</sub>	871(798)	57.50(58.66)	4.70(4.54)		3.45(3.85)	yellow
(Ph <sub>3</sub> P) <sub>2</sub> (CO-DMT)ClRhHgI	1154(1091)	42.93(42.95)	3.22(3.33)	19.48(18.39)		yellow
(p-tol <sub>3</sub> P) <sub>2</sub> (CO-DMT)ClRhHgI		47.03(46.00)	4.33(4.12)			yellow
(Ph <sub>3</sub> P) <sub>2</sub> (CO-MpTT)ClRhHgI		42.38(43.04)	3.19(3.21)	18.12(15.97)	3.07(3.34)	white
(Ph <sub>3</sub> P) <sub>2</sub> (CO-DMT)(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )RhHgI	1179(1168)	41.91(42.16)	3.28(3.11)	17.03(17.01)	3.35(3.60)	yellow
(Ph <sub>3</sub> P) <sub>2</sub> (CO-DMT)ClRhHgCl	1135(1088)	43.06(43.04)	3.40(3.33)			yellow
(Ph <sub>3</sub> P) <sub>2</sub> (CO-DMT)IrHgCl	1292(1180)	39.52(39.70)	3.18(3.08)	17.57(17.00)	4.00(3.56)	yellow
(Ph <sub>3</sub> P) <sub>2</sub> (CO-DMT)(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )IrHgI		40.17(39.16)	2.98(2.89)			yellow
(Ph <sub>3</sub> P) <sub>2</sub> (CO)ClIrHg(MpTT)Cl	1124(1164)	45.92(46.41)	3.64(3.46)	17.89(17.23)	3.31(3.61)	yellow
(Ph <sub>3</sub> P) <sub>2</sub> (CO)(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )IrHg(MpTT)Cl	1272(1242)	44.82(45.45)	3.38(3.25)			yellow
(Ph <sub>3</sub> P) <sub>2</sub> (CO)(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )IrHg(MpTT)I		43.23(42.33)	3.25(3.02)			yellow
Ph <sub>3</sub> P(DMT)(CO-DMT)IrHgCl	907(863)	36.66(32.01)	3.40(3.15)	18.74(23.25)		yellow
p-tol <sub>3</sub> P(DMT)(CO-DMT)IrHgCl		40.01(34.51)	4.00(3.68)			yellow
Ph <sub>3</sub> P(DMT)(CO-DMT)RhHgCl	699(773)	40.52(34.56)	4.58(3.52)			yellow
Ph <sub>3</sub> P(MpTT)(CO-MpTT)RhHgCl	947(926)	45.29(45.42)	3.82(3.81)	21.43(21.67)	8.44(9.08)	orange
Ph <sub>3</sub> P(MpTT)(CO-MpTT)RhHg(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )		48.95(44.31)	3.17(3.52)	19.56(20.00)		orange

<sup>a</sup> OAc = O<sub>2</sub>CCH<sub>3</sub>, IB = O<sub>2</sub>CCH(CH<sub>3</sub>)<sub>2</sub>, O<sub>2</sub>C<sub>2</sub>F<sub>3</sub> = O<sub>2</sub>CCF<sub>3</sub>, DMT = dimethyltriazene, MpTT = methyl-p-tolytriazene. <sup>b</sup> The experimental error is ± 10%.

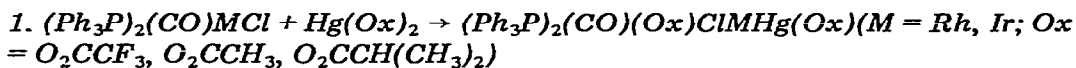
Reaction of  $[\text{Hg}(\text{RN}_3\text{R}^1)_2]$  with  $[(\text{Ph}_3\text{P})_2(\text{CO})\text{MX}]$  ( $\text{R} = \text{R}^1 = \text{CH}_3$ ;  $\text{M} = \text{Rh}^I$ ,  $\text{Ir}^I$ ;  $\text{X} = \text{Cl}$  and  $\text{R} = \text{CH}_3$ ;  $\text{R}^1 = p\text{-tol}$ ;  $\text{M} = \text{Rh}^I$ ;  $\text{X} = \text{Cl}$ ,  $\text{O}_2\text{CCF}_3$ )

In a typical experiment, the preparation of  $[(\text{Ph}_3\text{P})(\text{DMT})(\text{CO}-\text{DMT})\text{IrHgCl}]$  is given:  $[(\text{Ph}_3\text{P})_2(\text{CO})\text{IrCl}]$  (1 mmol) was added to a stirred suspension of  $[\text{Hg}(\text{DMT})_2]$  (1 mmol) in THF (20 ml). After 10 min the AgX was filtered off and the solution concentrated to 5 ml under vacuum. Hexane/ether (50 ml) was added, and the precipitate recrystallized from  $\text{CH}_2\text{Cl}_2$ /ether/hexane (yield 70%). Table 1 shows that only  $[(\text{Ph}_3\text{P}(\text{MpTT})(\text{CO}-\text{MpTT})\text{RhHgCl}]$  analyzed satisfactorily. All other compounds of this type clearly contained impurities. NMR spectra, however, showed that the complexes  $[(\text{R}_3\text{P})(\text{RN}_3\text{R}^1)(\text{CORN}_3\text{R}^1)\text{MHgX}]$  were present in solution as the most important product.

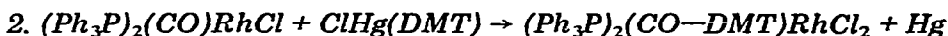
Elemental analysis (C, H) were carried out in this laboratory and Hg and N in the Organic Chemistry Laboratory (TNO) in Utrecht) colours and molecular weights are listed in Table 1.  $^1\text{H}$  NMR spectra were recorded with an HA 100 Varian spectrometer, and  $^{31}\text{P}$  NMR spectra with a Varian XL-100 spectrometer. IR spectra were recorded with a Beckman IR 4250 spectrometer and molecular weights measured with a Hewlett Packard vapour pressure osmometer Model 302 B.

## Results

The reactions and structural characterizations are discussed below according to the type of structure. The  $^{31}\text{P}$ -,  $^1\text{H}$ -NMR and IR data are given in Tables 2, 3 and 4.



The complexes contain a M—Hg bond, as has been proposed for  $[(\text{Ph}_3\text{P})_2(\text{CO})\text{O}_2\text{CCH}_3]\text{ClIrHg}(\text{O}_2\text{CCH}_3)]$  by Nyholm and Vrieze [8].  $^{31}\text{P}$  NMR data (Table 2) show that the phosphines are equivalent, with a  $^{31}\text{P}-^{105}\text{Rh}$  coupling constant of about 85 Hz, indicating that the phosphine groups are *trans* to each other [9]. It should be noted that there is coupling of 292–361 Hz between the  $^{31}\text{P}$  nuclei and the  $^{199}\text{Hg}$  nucleus.  $^1\text{H}$  NMR data show that the carboxylato (Ox) groups are inequivalent, while IR data indicate that they are both monodentate. The Rh—Cl and Ir—Cl stretching frequencies lie at about  $305\text{ cm}^{-1}$ , as expected for Cl *trans* to CO [10]. The structure shown in Fig. 1 therefore seems the most likely.



$^{31}\text{P}$  NMR data show the presence of equivalent  $\text{Ph}_3\text{P}$  groups *trans* to each other. The stretching frequency of the CO group lies in the region of a ketonic carbonyl group ( $\nu(\text{CO}) = 1729\text{ cm}^{-1}$ ), and so an acyltriazenido group appears to be present, as in the case of  $[(\text{Ph}_3\text{P})(\text{CO})_2\text{Ir}(\text{CO}-\text{DpTT})]$  [2].

The  $\text{CH}_3$  resonance at 2.00 ppm (Table 3) shows small couplings with  $^{31}\text{P}$  and  $^{105}\text{Rh}$  and was therefore assigned to the N— $\text{CH}_3$  group bonded to Rh, so that the resonance at 3.00 ppm for which no couplings were observed, has to be assigned to the N— $\text{CH}_3$  group bonded to CO. The two Rh—Cl stretching frequencies of  $308$  and  $342\text{ cm}^{-1}$  were tentatively assigned to the bonds *trans* to CO and *trans* to N respectively [11,12]. The structure is thus that shown in Fig. 2.

TABLE 2  
 31P NMR DATA (PPM RELATIVE TO 85% H<sub>3</sub>PO<sub>4</sub>)

Compound <sup>a</sup>	Structure <sup>b</sup>	Solvent	P-atom(s) bonded to		Coupling constants (Hz)			
			Ir	Rh	J(P-Hg) <sup>c</sup>	J(P-Rh)	J(P-P)	
Ph <sub>3</sub> P			+ 4.95 <sup>d</sup>					
(Ph <sub>3</sub> P) <sub>2</sub> (CO)IrCl		C <sub>6</sub> D <sub>6</sub>	-24.43					
(Ph <sub>3</sub> P) <sub>2</sub> (CO)RhCl		C <sub>6</sub> D <sub>6</sub>		-29.58d			129	
(Ph <sub>3</sub> P) <sub>2</sub> (CO)(OAc)ClIrHg(OAc)	1	C <sub>6</sub> D <sub>6</sub>	+ 1.23		330			
(Ph <sub>3</sub> P) <sub>2</sub> (CO)(IB)ClIrHg(IB)	1	C <sub>6</sub> D <sub>6</sub>	+ 2.48		327			
(Ph <sub>3</sub> P) <sub>2</sub> (CO)(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )ClIrHg(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )	1	C <sub>6</sub> D <sub>6</sub>	+ 0.68		292			
(Ph <sub>3</sub> P) <sub>2</sub> (CO)(OAc)ClRhHg(OAc)	1	C <sub>6</sub> D <sub>6</sub>		-26.01d	361		85	
(Ph <sub>3</sub> P) <sub>2</sub> (CO)(IB)ClRhHg(IB)	1	C <sub>6</sub> D <sub>6</sub>		-25.90d	355		85	
(Ph <sub>3</sub> P) <sub>2</sub> (CO)(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )ClRhHg(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )	1	C <sub>6</sub> D <sub>6</sub>		-26.10d	314		80	
(Ph <sub>3</sub> P) <sub>2</sub> (CO-DMT)RhCl <sub>2</sub>	2	C <sub>6</sub> D <sub>6</sub>		- 9.69d			95	
(Ph <sub>3</sub> P) <sub>2</sub> (CO-DMT)ClRhHgI	3	CDCl <sub>3</sub>		-25.54d	357		105	
(p-tol <sub>3</sub> P) <sub>2</sub> (CO-DMT)ClRhHgI	3	C <sub>6</sub> D <sub>6</sub>		-24.08d	355		105	
(Ph <sub>3</sub> P) <sub>2</sub> (CO-MpTT)ClRhHgI	3	C <sub>6</sub> D <sub>6</sub>	+ 6.05		422			
(Ph <sub>3</sub> P) <sub>2</sub> (CO-DMT)(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )RhHgI <sup>e</sup>	4	C <sub>6</sub> D <sub>6</sub>		-26.75q;			136;	19
		C <sub>6</sub> D <sub>6</sub>		-14.41q			103	
(Ph <sub>3</sub> P) <sub>2</sub> (CO-DMT)ClRhHgCl	5	C <sub>6</sub> D <sub>6</sub>	+18.54d; 21.16d		397; 3879			15
(Ph <sub>3</sub> P) <sub>2</sub> (CO-DMT)IrRhHgCl	5	C <sub>6</sub> D <sub>6</sub>	+18.08d; 19.60d		468; 3670			14
(Ph <sub>3</sub> P) <sub>2</sub> (CO-DMT)(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )IrHgCl	5	C <sub>6</sub> D <sub>6</sub>	+11.33d; 12.33d		499; 3498			15
(Ph <sub>3</sub> P) <sub>2</sub> (CO)ClRhHg(MpTT)Cl	6	C <sub>6</sub> D <sub>6</sub>	+ 9.49		305			
(Ph <sub>3</sub> P) <sub>2</sub> (CO)(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )IrHg(MpTT)Cl	6	C <sub>6</sub> D <sub>6</sub>	+ 5.33		354			
(Ph <sub>3</sub> P) <sub>2</sub> (CO)(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )IrHg(MpTT)I	6	C <sub>6</sub> D <sub>6</sub>	+ 5.37		366			
Ph <sub>3</sub> P(DMT)(CO-DMT)IrHgCl	7	CDCl <sub>3</sub>	+ 4.14		451			
p-tol <sub>3</sub> P(DMT)(CO-DMT)IrHgCl	7	C <sub>6</sub> D <sub>6</sub>	+ 0.08		538			
Ph <sub>3</sub> P(DMT)(CO-DMT)RhHgCl <sup>e</sup>	7	CDCl <sub>3</sub>		-32.38d			135	
Ph <sub>3</sub> P(MpTT)(CO-MpTT)RhHgCl <sup>e</sup>	7	CDCl <sub>3</sub>		-36.98d			133	
Ph <sub>3</sub> P(MpTT)(CO-MpTT)RhHg(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )	7	CDCl <sub>3</sub>		-36.72d	583		133	

<sup>a</sup> See Table 1. <sup>b</sup> Number of the reaction in which the compound is formed. <sup>c</sup> Coupling of 31P with 199Hg (I = 1/2), natural abundance 16.86%. <sup>d</sup> Not bonded to Ir, Rh or Hg. <sup>e</sup> J(P-Hg) is not known; due to decomposition of the compound during recording the spectra.

TABLE 3  
<sup>1</sup>H NMR DATA IN CDCl<sub>3</sub> (PPM RELATIVE TO TMS)

Compound <sup>a</sup>	Structure <sup>b</sup>	Resonances of OAc, IB			Resonances of L	J(CH-CH <sub>3</sub> ) (Hz)
		CH <sub>3</sub>	CH	CH		
(Ph <sub>3</sub> P) <sub>2</sub> (CO)(OAc)ClIrHg(OAc)	1			1.34; 1.37	7.48m; 7.74m	
(Ph <sub>3</sub> P) <sub>2</sub> (CO)(IB)ClIrHg(IB)	1			0.63; 0.54d	7.42m; 7.74m	7
(Ph <sub>3</sub> P) <sub>2</sub> (CO)(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )ClIrHg(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )	1				7.45m; 7.74m	
(Ph <sub>3</sub> P) <sub>2</sub> (CO)(OAc)ClRhHg(OAc)	1			1.30; 1.27	7.44m; 7.76m	
(Ph <sub>3</sub> P) <sub>2</sub> (CO)(IB)ClRhHg(IB)	1			0.62; 0.54d	7.43m; 7.78m	8
(Ph <sub>3</sub> P) <sub>2</sub> (CO)(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )ClRhHg(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )	1				7.44m; 7.74m	
Compound <sup>a</sup>	Structure <sup>b</sup>	Methyl protons on the side of			Aryl protons of the Resonances of L	J(P-CH <sub>3</sub> ) (Hz)
		CO	Rh, Ir	Hg	triazenido group	
(Ph <sub>3</sub> P) <sub>2</sub> (CO-DMT)RhCl <sub>2</sub>	2	3.00	2.00 <sup>d</sup>			7.33m; 7.82m
(Ph <sub>3</sub> P) <sub>2</sub> (CO-DMT)ClRhHgI	3	2.84	2.45 <sup>d</sup>			7.31m; 7.66m
( <i>p</i> -tol <sub>3</sub> P) <sub>2</sub> (CO-DMT)ClRhHgI	3	2.89	2.40 <sup>d</sup>			7.13m; 7.60m; 2.30 <sup>f</sup>
(Ph <sub>3</sub> P) <sub>2</sub> (CO-MpTT)ClIrHgI	3	2.27	2.41 <sup>d</sup>		6.27; 6.97	7.36m; 7.70m
(Ph <sub>3</sub> P) <sub>2</sub> (CO-DMT)(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )RhHgI	4	3.36	2.64 <sup>d</sup>			7.29m
(Ph <sub>3</sub> P) <sub>2</sub> (CO-DMT)ClIrHgCl	5	3.30	3.14d			7.28m
(Ph <sub>3</sub> P) <sub>2</sub> (CO-DMT)IrHgCl	5	3.29	3.14d			7.26m
(Ph <sub>3</sub> P) <sub>2</sub> (CO-DMT)(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )IrHgI	5	3.35	2.43d			7.28m
(Ph <sub>3</sub> P) <sub>2</sub> (CO)ClIrHg(MpTT)Cl	6		2.37 <sup>d</sup>	2.27	6.95; 7.15	7.34m; 7.53m
(Ph <sub>3</sub> P) <sub>2</sub> (CO)(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )IrHg(MpTT)Cl	6		3.25 <sup>d</sup>	2.33	7.02; 7.22	7.36m; 7.56m
(Ph <sub>3</sub> P) <sub>2</sub> (CO)(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )IrHg(MpTT)	6		3.23 <sup>d</sup>	2.31	7.04; 7.24	7.38m; 7.50m
Ph <sub>3</sub> P(DMT)(CO-DMT)IrHgCl	7	3.57	2.57 <sup>e</sup> ; 2.85 <sup>e</sup> ; 3.95d <sup>f</sup>			7.32m
<i>p</i> -tol <sub>3</sub> P(DMT)(CO-DMT)IrHgCl	7	3.57	2.55 <sup>e</sup> ; 2.91 <sup>e</sup> ; 3.95d <sup>f</sup>			7.26m; 2.30 <sup>f</sup>
Ph <sub>3</sub> P(DMT)(CO-DMT)RhHgCl	7	3.48	2.06 <sup>e</sup> ; 3.48 <sup>e</sup> ; 3.97d <sup>f</sup>			7.33m
Ph <sub>3</sub> P(MpTT)(CO-MpTT)RhHgCl	7	3.60	2.20 <sup>g</sup> ; 2.38 <sup>g</sup> ; 2.62 <sup>h</sup>		6.17; 6.69; 7.21;	7.27m
					7.21	
Ph <sub>3</sub> P(MpTT)(CO-MpTT)RhHg(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )	7	3.54	2.19 <sup>g</sup> ; 2.33 <sup>g</sup> ; 2.60 <sup>h</sup>		6.20; 6.71; 7.17;	7.28m
					7.17	

<sup>a</sup> See Table 1. <sup>b</sup> See Table 2. <sup>c</sup> dm = double multiplet. <sup>d</sup> A complex pattern of small coupling constants (J(P-CH<sub>3</sub>); J(Rh-CH<sub>3</sub>)) is observed which indicates that this N-CH<sub>3</sub> group is bonded to Ir or Rh. <sup>e</sup> A small methyl-methyl coupling of the chelate DMT-group is observed. <sup>f</sup> Resonance of the methyl group *trans* to phosphorus. <sup>g</sup> Resonance of the tolylmethyl group. <sup>h</sup> Resonance of the chelate methyl group. <sup>i</sup> Methyl resonance of the tolyl group.

TABLE 4  
IR DATA (NUJOLL MULL, CM<sup>-1</sup>)

Compound <sup>a</sup>	Struc- ture <sup>b</sup>	$\nu(\text{CO})$	$\nu(\text{HgCl})$	$\nu(\text{M}-\text{Cl})$	$\nu_{\text{as}}(\text{tri-azetidco})^c$	$\nu_{\text{as}}(\text{OAc, IB, O}_2\text{C}_2\text{F}_3)^d$
ClHgDMT					1325	
IHgDMT					1315	
ClHgMpTT					1318	
IHgMpTT					1312	
Hg(DMT) <sub>2</sub>					1312	
Hg(MpTT) <sub>2</sub>					1318	
(Ph <sub>3</sub> P) <sub>2</sub> (CO)(OAc)ClIrHg(OAc)	1	2022		302		1623; 1601
(Ph <sub>3</sub> P) <sub>2</sub> (CO)(IB)ClIrHg(IB)	1	2020		303		1620; 1589
(Ph <sub>3</sub> P) <sub>2</sub> (CO)(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )ClIrHg(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )	1	2038		305		1685(br)
(Ph <sub>3</sub> P) <sub>2</sub> (CO)(OAc)ClRhHg(OAc)	1	2030		307		1615; 1598
(Ph <sub>3</sub> P) <sub>2</sub> (CO)(IB)ClRhHg(IB)	1	2020		305		1602; 1588
(Ph <sub>3</sub> P) <sub>2</sub> (CO)(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )ClRhHg(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )	1	2048		305		1680; 1690
(Ph <sub>3</sub> P) <sub>2</sub> (CO-DMT)RhCl <sub>2</sub>	2	1729		308; 342	1319	
(Ph <sub>3</sub> P) <sub>2</sub> (CO-DMT)ClRhHgI	3	1649		332? <sup>e</sup>	1313	
( <i>p</i> -tol <sub>3</sub> P) <sub>2</sub> (CO-DMT)ClRhHgI	3	1640		333? <sup>e</sup>	1309	
(Ph <sub>3</sub> P) <sub>2</sub> (CO-MpTT)ClRhHgI	3	1679		267	1308	
(Ph <sub>3</sub> P) <sub>2</sub> (CO-DMT)(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )RhHgI	4	1643			1315	1676
(Ph <sub>3</sub> P) <sub>2</sub> (CO-DMT)ClRhHgCl	5	1640	287		1337	
(Ph <sub>3</sub> P) <sub>2</sub> (CO-DMT)IrHgCl	5	1639	267		1328	
(Ph <sub>3</sub> P) <sub>2</sub> (CO-DMT)(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )IrHgI	5	1638			1328	1685
(Ph <sub>3</sub> P) <sub>2</sub> (CO)ClIrHg(MpTT)Cl	6	1996	257	287	1360	
(Ph <sub>3</sub> P) <sub>2</sub> (CO)(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )IrHg(MpTT)Cl	6	2030	307		1354	1685
(Ph <sub>3</sub> P) <sub>2</sub> (CO)(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )IrHg(MpTT)I	6	2025			1351	1683
Ph <sub>3</sub> P(DMT)(CO-DMT)IrHgCl	7	1616	281		1321(br)	
<i>p</i> -tol <sub>3</sub> P(DMT)(CO-DMT)IrHgCl	7	1596	280? <sup>e</sup>		1318(br)	
Ph <sub>3</sub> P(DMT)(CO-DMT)RhHgCl	7	1655	269? <sup>e</sup>		1316(br)	
Ph <sub>3</sub> P(MpTT)(CO-MpTT)RhHgCl	7	1647	263		1303; 1290	
Ph <sub>3</sub> P(MpTT)(CO-MpTT)RhHg(O <sub>2</sub> C <sub>2</sub> F <sub>3</sub> )	7	1669			1302; 1280	1682

<sup>a</sup> See <sup>a</sup> Table 1. <sup>b</sup> See <sup>b</sup> Table 2. <sup>c</sup> Vibrations between 1595–1750 cm<sup>-1</sup> belong to the CO of an acyltriazenido group, vibrations above 1345 cm<sup>-1</sup> to a bridging triazenido group, vibrations between 1280–1345 to an acyltriazenido group or a bidentate group (see also refs. 1, 2 and 3). <sup>d</sup> In the case of O<sub>2</sub>CCF<sub>3</sub> vibrations between 1675–1690 cm<sup>-1</sup> are characteristic for a unidentate group. <sup>e</sup> A tentative assignment was made.

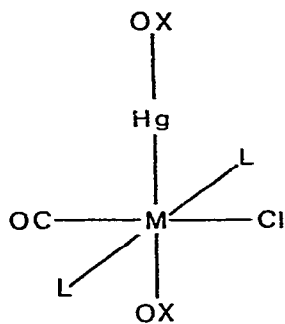


Fig. 1. Proposed structure for  $[(\text{Ph}_3\text{P})_2(\text{CO})(\text{Ox})\text{Cl}]\text{M}(\text{Hg}(\text{Ox}))$  ( $\text{L} = \text{Ph}_3\text{P}$ ;  $\text{Ox} = \text{O}_2\text{CCH}_3, \text{O}_2\text{CCF}_3, \text{O}_2\text{CCH}(\text{CH}_3)_2$ ;  $\text{M} = \text{Rh}, \text{Ir}$ )

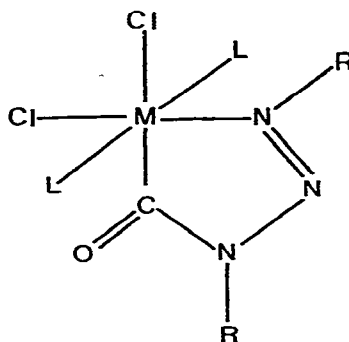


Fig. 2. Proposed structure for  $[(\text{Ph}_3\text{P})_2(\text{CO}-\text{DMT})\text{MCl}_2]$  ( $\text{L} = \text{Ph}_3\text{P}$ ;  $\text{R} = \text{CH}_3$ ;  $\text{M} = \text{Rh}$ ).

3.  $\text{L}_2(\text{CO})\text{RhCl} + \text{IHg}(\text{DMT}) \rightarrow \text{L}_2(\text{CO}-\text{DMT})\text{ClRhHgI}$  ( $\text{L} = \text{Ph}_3\text{P}, (p\text{-tol})_3\text{P}$ );  
 $(\text{Ph}_3\text{P})_2(\text{CO})\text{IrCl} + \text{IHg}(\text{MpTT}) \rightarrow (\text{Ph}_3\text{P})_2(\text{CO}-\text{MpTT})\text{ClIrHgI}$

In the case of Rh and Ir, the  $^1\text{H}$  NMR data (Table 3) and IR data (Table 4) indicate the presence of an acyltriazenido group. The phosphine groups are equivalent and *trans* to each other. In the case of the rhodium complexes, the tentative assignment of the band around  $330\text{ cm}^{-1}$  to a Rh—Cl stretch seems to indicate that the Cl atom is *trans* to N, so that the HgI group must be *trans* to the ketonic CO group. The P—Hg coupling constants are similar to those of the carboxylato compounds of Fig. 1. The most likely structure is shown in Fig. 3.

In the case of  $[(\text{Ph}_3\text{P})_2(\text{CO}-\text{MpTT})\text{ClIrHgI}]$  an IR band was formed at  $267\text{ cm}^{-1}$  (Table 4), which is in the region of Hg—Cl stretching frequencies [13,14]. If the  $267\text{ cm}^{-1}$  band is indeed due to a metal—halide stretch, it is possible that Cl and I have exchanged positions, which is possible in view of the similar migration observed in  $[\text{L}_2(\text{CO})\text{MM}^1(\text{RN}_3\text{R}^1)\text{X}]$  [1–3].

4.  $(\text{Ph}_3\text{P})_2(\text{CO})\text{Rh}(\text{O}_2\text{CCF}_3) + \text{IHg}(\text{DMT}) \rightarrow (\text{Ph}_3\text{P})_2(\text{CO}-\text{DMT})(\text{O}_2\text{CCF}_3)\text{RhHgI}$

In contrast to the results for the complexes discussed above, it was found that the phosphine groups are inequivalent with a  $J(\text{P}-\text{P})$  coupling of 19 Hz, as is usual for *cis*-phosphines [15]. Two P—Rh coupling constants of 103 and 136 Hz were also observed.  $^1\text{H}$  NMR methyl resonances (Table 3) and the appearance of a ketonic carbonyl stretching frequency at  $1643\text{ cm}^{-1}$  indicate the presence of an acyltriazenido group. The structure shown in Fig. 4 thus seems the only possible one.

5.  $(\text{Ph}_3\text{P})_2(\text{CO})\text{IrX}^a + \text{X}^b\text{Hg}(\text{DMT}) \rightarrow (\text{Ph}_3\text{P})_2(\text{CO}-\text{DMT})\text{X}^1\text{IrHgX}^2$  ( $\text{X}^a = \text{Cl}, \text{O}_2\text{CCF}_3$ ;  $\text{X}^b = \text{Cl}, \text{I}$ ;  $\text{X}^1 = \text{Cl}, \text{I}$ ;  $\text{X}^2 = \text{Cl}$  and  $\text{X}^1 = \text{O}_2\text{CCF}_3$ ;  $\text{X}^2 = \text{I}$ )

The  $^{31}\text{P}$  NMR data show two P—Hg coupling constants which greatly differ in size. This indicates that one  $\text{Ph}_3\text{P}$  group is *cis* to Hg while the other, which has the bigger coupling constant, is *trans* to the Hg atom. A similar situation has been found in  $\text{Pt}(\text{SnMe}_3)_2$  (diphos) in which  $J(\text{Sn}-\text{P}) = 143\text{ Hz}$  (*cis*) and  $J(\text{Sn}-\text{P}) = 1554\text{ Hz}$  (*trans*) [16].



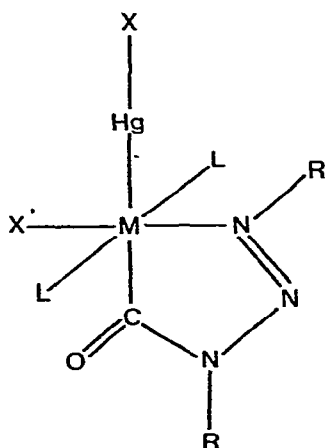


Fig. 3. Proposed structure for  $[L_2(CO-DMT)ClMHgI]$  ( $L = Ph_3P, p\text{-tol}_3P$ ;  $X = I$ ;  $X^1 = Cl$ ;  $M = Rh$ ;  $R = R^1 = CH_3$ ) and  $[(Ph_3P)_2(CO-MpTT)ClMHgI]$  ( $L = Ph_3P$ ;  $X = I$ ;  $X^1 = Cl$ ;  $M = Ir$ ;  $R^1 = CH_3$ ;  $R = p\text{-tol}$ )

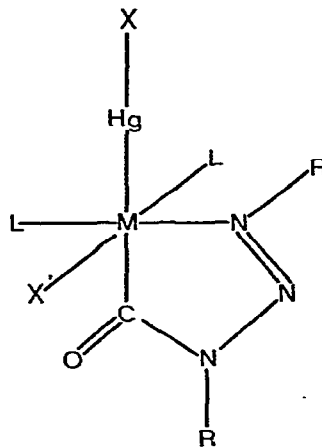


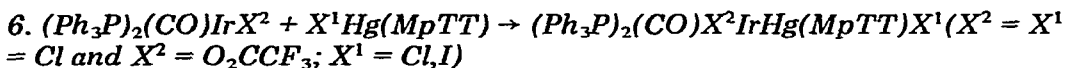
Fig. 4. Proposed structure for  $[(Ph_3P)_2(CO-DMT)(O_2CCF_3)MHgI]$  ( $L = Ph_3P$ ;  $X = I$ ;  $X^1 = O_2CCF_3$ ;  $M = Rh$ ;  $R = CH_3$ ).

The appearance of ketonic carbonyl stretching frequencies ( $\sim 1640\text{ cm}^{-1}$ ) again show the presence of an acyltriazenido group.

$^1H$  NMR data (Table 3) show a band at 3.14 ppm in the case of  $[(Ph_3P)_2(CO-DMT)XIrHgCl]$  ( $X = Cl, I$ ), and one at 2.14 ppm in the case of  $[(Ph_3P)_2(CO-DMT)(O_2CCF_3)IrHgI]$ , both bands showing a clear doublet of 1.5 Hz which indicates that this  $N-CH_3$  is bonded *trans* to  $Ph_3P$ . The other resonances, which lie between 3.29 and 3.35 ppm, must therefore be assigned to the  $N-CH_3$  bonded to the ketonic CO group. It should be noted that the introduction of a trifluoroacetato group has a large upfield influence on the  $N-CH_3$  resonance when this group is *cis* to Hg.

In the case of  $[(Ph_3P)_2(CO-DMT)XIrHgCl]$  one IR  $Ir-Cl$  band was found at 287 and 267  $cm^{-1}$  (for  $X = Cl$  and  $I$  resp.). These values indicate that in both cases the mercury is bonded to a chloride ligand.

In view of these data the structure shown in Fig. 5 seems the most likely.



$^{31}P$  NMR data show that the phosphine groups are bonded to Ir, equivalent and *trans* to each other.  $^1H$  NMR data, the terminal carbonyl stretching frequencies, which lie at 1996  $cm^{-1}$  for  $[(Ph_3P)_2(CO)ClIrHg(MpTT)Cl]$  and at about 2030  $cm^{-1}$  for  $[(Ph_3P)_2(CO)(O_2CCF_3)IrHg(MpTT)X]$  ( $X = Cl, I$ ), and the asymmetric NNN vibration at about 1355  $cm^{-1}$  clearly show that there is no acyltriazenido group present [1-3], but, instead, a bridging azenido group. The small couplings for the  $N-CH_3$  group indicate that this group is bonded to Ir, analogous to the crystal structure of  $[(Ph_3P)_2(CO)IrAg(Me-N_3-p\text{-tol})(O_2CCH(CH_3)_2)]$  [ $HO_2CCH(CH_3)_2$ ] [5]. The precise location of the CO and  $O_2CCF_3$  groups in the case of the trifluoroacetato compounds is not known. It should

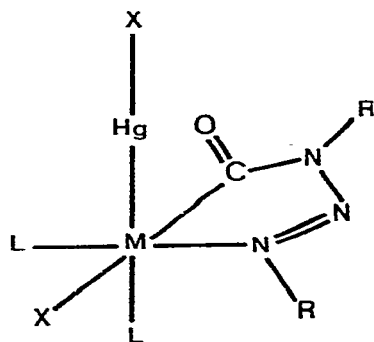


Fig. 5. Proposed structure for  $[(\text{Ph}_3\text{P})_2(\text{CO}-\text{DMT})\text{XMHgX}^1]$  ( $\text{L} = \text{Ph}_3\text{P}$ ;  $\text{M} = \text{Ir}$ ;  $\text{R} = \text{CH}_3$ ;  $\text{X} = \text{Cl}$ ,  $\text{I}$ ;  $\text{X}^1 = \text{Cl}$  and  $\text{X} = \text{O}_2\text{CCF}_3$ ;  $\text{X}^1 = \text{I}$ ).

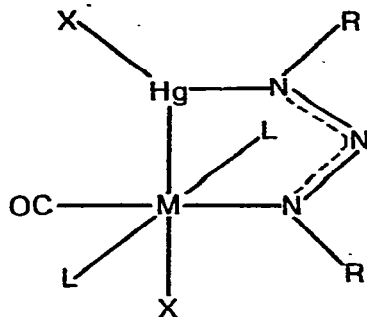


Fig. 6. Proposed structure for  $[(\text{Ph}_3\text{P})_2(\text{CO})\text{XMHg}(\text{MpTT})\text{X}^1]$  ( $\text{L} = \text{Ph}_3\text{P}$ ;  $\text{R} = p\text{-tol}$ ;  $\text{R}^1 = \text{CH}_3$ ;  $\text{X} = \text{X}^1 = \text{Cl}$  and  $\text{X} = \text{O}_2\text{CCF}_3$ ;  $\text{X}^1 = \text{Cl}$ ,  $\text{I}$ ;  $\text{M} = \text{Ir}$ ).

be noted, however, that the trifluoroacetato group now has a downfield influence on the N-CH<sub>3</sub> group, indicating that this latter group is situated differently from that in the structure shown in Fig. 5.

A possible structure is shown in Fig. 6, although another alternative, in which the O<sub>2</sub>CCF<sub>3</sub> and CO groups have exchanged positions, is not excluded.

7.  $\text{L}_2(\text{CO})\text{MX} + \text{HgT}_2 \rightarrow \text{L}(\text{T})(\text{CO}-\text{T})\text{MHgX} + \text{L}$  ( $\text{L} = \text{Ph}_3\text{P}$ ,  $p\text{-tol}_3\text{P}$ ;  $\text{M} = \text{Ir}$ ;  $\text{T} = \text{DMT}$ ;  $\text{X} = \text{Cl}$  and  $\text{L} = \text{Ph}_3\text{P}$ ;  $\text{M} = \text{Rh}$ ;  $\text{T} = \text{DMT}$ ;  $\text{X} = \text{Cl}$  and  $\text{L} = \text{Ph}_3\text{P}$ ;  $\text{M} = \text{Rh}$ ;  $\text{T} = \text{MpTT}$ ;  $\text{X} = \text{Cl}$ ,  $\text{O}_2\text{CCF}_3$ )

From the <sup>31</sup>P NMR spectra it can be concluded that only one phosphine group is bonded to Rh in the light of the size of the coupling constants between

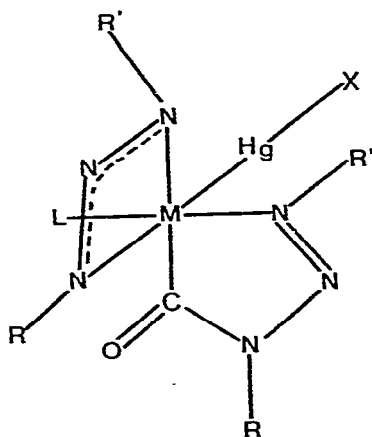


Fig. 7. Proposed structure for  $[\text{L}(\text{T})(\text{CO}-\text{T})\text{MHgX}]$  ( $\text{L} = \text{Ph}_3\text{P}$ ,  $\text{tol}_3\text{P}$ ;  $\text{R} = \text{R}^1 = \text{CH}_3$ ;  $\text{M} = \text{Ir}$ ;  $\text{X} = \text{Cl}$  and  $\text{L} = \text{Ph}_3\text{P}$ ;  $\text{R} = \text{CH}_3$ ;  $\text{R}^1 = p\text{-tol}$ ,  $\text{CH}_3$ ;  $\text{M} = \text{Rh}$ ;  $\text{X} = \text{Cl}$ ,  $\text{O}_2\text{CCF}_3$ ).

P and Hg or Rh (Table 2). Combination of the  $^1\text{H}$  NMR and IR data seem to indicate that there is one acyltriazenido group and one chelating triazenido group. A possible structure, in which the halide atom has migrated from the Rh(Ir) atom to Hg, is shown in Fig. 7 ( $\nu(\text{Hg}-\text{Cl}) = \sim 270 \text{ cm}^{-1}$ ).

It should be noted that satisfactory analyses were only obtained for  $[(\text{Ph}_3\text{P})-(\text{MpTT})(\text{CO}-\text{MpTT})\text{RhHgCl}]$ . In the other cases the C and H analyses were too high, while the Hg analysis was too low. This indicates the possible presence of some extra  $\text{R}_3\text{P}$ , which might be coordinated to the Hg atom. Nonetheless  $^1\text{H}$  and  $^{31}\text{P}$  NMR indicate that the main component is  $[(\text{R}_3\text{P})(\text{T})(\text{CO}-\text{T})\text{MHgX}]$ .

## Discussion

Recent work on triazenidometal compounds has shown that the triazenido group occasionally acts as monodentate [17–19] or bidentate [17,20,21], although it generally binds as a ligand bridging two metal centers [1–5,22–27]. One example is known in which a chelate acyltriazenido is formed by CO insertion [2]. It has also been observed that otherwise unstable metal–metal bonds such as the  $\text{Rh}^{\text{I}}(\text{Ir}^{\text{I}})$ -to- $\text{Cu}^{\text{I}}(\text{Ag}^{\text{I}})$  donor bonds may be stabilized by triazenido groups, by amidino groups (which are very similar to the triazenido groups [28,29]), by carboxylato, and even by  $\text{ClO}_4$  and  $\text{NO}_3$  groups [3]. In each case the stabilization clearly involved the formation of a five membered bimetallic ring. In view of these results it is remarkable that reactions of  $[(\text{Ph}_3\text{P})_2(\text{CO})\text{MX}]$  ( $\text{M} = \text{Rh}^{\text{I}}, \text{Ir}^{\text{I}}$ ) with  $\text{Hg}(\text{Ox})_2$ ,  $[\text{Hg}(\text{RN}_3\text{R}^1)_2]$  and with  $[\text{XHg}(\text{RN}_3\text{R}^1)]$  give quite different results.

In the case of the reactions with  $\text{Hg}(\text{Ox})_2$  ( $\text{Ox} = \text{O}_2\text{CCH}_3, \text{O}_2\text{CCH}(\text{CH}_3)_2, \text{O}_2\text{CCF}_3$ ) only one type of compound was formed which contained monodentate carboxylato groups in addition to a metal–mercury bond. The structure is therefore similar to that of  $[(\text{Ph}_3\text{P})_2(\text{CO})\text{Cl}_2\text{IrHgCl}]$  [8]. It is interesting that Rh–Hg bonded compounds could be made since reaction of  $[(\text{Ph}_3\text{P})_2(\text{CO})\text{RhCl}]$  with  $\text{HgCl}_2$  did not yield a compound with a Rh–Hg bond [8].

Compounds containing Ir–Hg and Rh–Hg bonds were formed by reaction of  $[(\text{Ph}_3\text{P})_2(\text{CO})\text{MX}^2]$  ( $\text{M} = \text{Rh}^{\text{I}}, \text{Ir}^{\text{I}}; \text{X}^2 = \text{Cl}, \text{O}_2\text{CCF}_3$ ) with  $[\text{X}^1\text{Hg}(\text{RN}_3\text{R}^1)]$  ( $\text{X}^1 = \text{Cl}, \text{I}; \text{R} = \text{CH}_3, \text{R}^1 = \text{CH}_3$  and  $\text{R} = \text{CH}_3, \text{R}^1 = p\text{-tol}$ ), although the rhodium compounds were generally less stable in solution. These reactions resulted in a great variety of products, the formation and stability of which are clearly critically dependent on M,  $\text{X}^1$ ,  $\text{X}^2$ , R and  $\text{R}^1$ .

In the case of rhodium, reaction of  $[(\text{Ph}_3\text{P})_2(\text{CO})\text{RhCl}]$  with  $[\text{ClHg}(\text{DMT})]$  afforded  $[(\text{Ph}_3\text{P})_2(\text{CO}-\text{DMT})\text{RhCl}_2]$  with formation of metallic mercury. However reaction of  $[\text{IHg}(\text{DMT})]$  with  $[(\text{Ph}_3\text{P})_2(\text{CO})\text{RhCl}]$  and  $[(\text{Ph}_3\text{P})_2(\text{CO})\text{Rh}(\text{O}_2\text{CCF}_3)]$  yielded  $[(\text{Ph}_3\text{P})_2(\text{CO}-\text{DMT})\text{ClRhHgI}]$  and  $[(\text{Ph}_3\text{P})_2(\text{CO}-\text{DMT})(\text{O}_2\text{CCF}_3)\text{RhHgI}]$  in which the phosphine ligands are *trans* to each other in the first case and *cis* in the other (Figs. 3 and 4). The compounds slowly decomposed to form Hg and  $[(\text{Ph}_3\text{P})_2(\text{CO}-\text{DMT})\text{RhXI}]$  ( $\text{X} = \text{Cl}, \text{O}_2\text{CCF}_3$ ). In all compounds the triazenido group is present as a chelated acyltriazenido group, which forms a five-membered ring with Rh.

In the case of iridium the structure shown in Fig. 3 was only formed from the reaction of  $[(\text{Ph}_3\text{P})_2(\text{CO})\text{IrCl}]$  with  $[\text{IHg}(\text{MpTT})]$ . Different structures were found for the other iridium complexes, since reaction of  $[(\text{Ph}_3\text{P})_2(\text{CO})\text{IrX}^2]$

( $X^2 = \text{Cl}, \text{O}_2\text{CCF}_3$ ) with  $[\text{X}^1\text{Hg}(\text{DMT})]$  ( $X^1 = \text{Cl}, \text{I}$ ) gave compounds in which the phosphine groups are *cis*, while one of these phosphine groups is *trans* to Hg. (Fig. 5). Exchange may have occurred of  $X^1$  and  $X^2$ .

In the case of the methyl-*p*-tolyltriazenido ligand it is found that reaction of  $[\text{ClHg}(\text{MpTT})]$  with  $[(\text{Ph}_3\text{P})_2(\text{CO})\text{IrX}^2]$  ( $X^2 = \text{Cl}, \text{O}_2\text{CCF}_3$ ) and of  $[\text{IHg}(\text{MpTT})]$  with  $[(\text{Ph}_3\text{P})_2(\text{CO})\text{Ir}(\text{O}_2\text{CCF}_3)]$  did not produce the structure shown in Fig. 3, but instead that shown in Fig. 6, in which the triazenido group acts as a bridging ligand as in  $\text{Cu}^{\text{I}}$  and  $\text{Ag}^{\text{I}}$  compounds [1-5].

The great difference between the Hg metal and the  $\text{Cu}^{\text{I}}(\text{Ag}^{\text{I}})$  metal compounds is that formation of the Hg metal bond is easy and not very dependent on the presence of stabilizing bridging ligands. Consequently the azenido group may bridge, although it can also prefer other bonding modes, such as the acyltriazenido one.

The mechanism by which these different compounds are formed is not very clear. It seems quite possible that the first step involves the formation of a metal-to- $\text{Hg}^{\text{II}}$  donor bond [13,14,30,31], which is a well established mode of bonding. In this type of addition complex the  $\text{Rh}^{\text{I}}(\text{Ir}^{\text{I}})$  atom is five-coordinate, so that Berry pseudorotations may easily occur. This and the migration of X ligands from  $\text{Rh}^{\text{I}}(\text{Ir}^{\text{I}})$ -to- $\text{Hg}^{\text{II}}$  and vice versa might then account for the formation of so many different types of product.

Finally, it is not at all clear why small differences in X, R and M give rise to such different structures, as is clearly apparent from the difference in reactions between  $[\text{IHg}(\text{MpTT})]$  with  $[(\text{Ph}_3\text{P})_2(\text{CO})\text{IrCl}]$  (Fig. 3), and  $[\text{ClHg}(\text{MpTT})]$  with  $[(\text{Ph}_3\text{P})_2(\text{CO})\text{IrCl}]$  (Fig. 6).

Very little is understood about the reactions of  $[(\text{Ph}_3\text{P})_2(\text{CO})\text{MX}]$  with  $[\text{Hg}(\text{RN}_3\text{R}^1)_2]$ . From NMR it is clear that the main product is the same in all cases, but since a pure compound was obtained in only one case, further discussion is unwarranted. However, it seems clear that both a chelate azenido and a chelate acyltriazenido group seem always to be present (Fig. 7).

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