only then allowed to come to room temperature.

**Magnetization Transfer Experiments.** Estimates of the $^{13}C$ site $T_1$'s were obtained by standard inversion-recovery techniques using a composite 180° pulse and a three-parameter fit to the data. The $T_1$ values obtained at the lowest temperature that exchange could be detected were used as initial guesses in the magnetization transfer analysis and were at least consistent with $T_1$ measurements made at higher temperatures. The long $T_1$ of the acyl carbon necessitated a recycle delay of 150 s for the experiments involving $CH_3CO–Co(CO)_4$, and between 16 and 32 accumulations were acquired for each time point in a given experiment. Magnetization transfer experiments were initiated by a selective inversion pulse arranged to be between 1 and 6 ms by attenuation of the low power transmitter; spectra were acquired as a function of time from 20 ms up to 50 s following the initial perturbation. The time dependence of the integrated areas was obtained from standard Nicolet software, and these experimental intensities used as input for a general multisite analysis.

The evaluation of exchange and relaxation rate constants in an $n$-site system depends on the time evolution of $z$ magnetization according to a set of coupled differential equations (eq 5), where

$$d\mathbf{M}(t)/dt = (\mathbf{K} + \mathbf{R})\Delta\mathbf{M}(t) \tag{5}$$

$\Delta\mathbf{M}(t) = (\mathbf{M}(t) - \mathbf{M}^{eq})$ is an $n$ vector of deviations of the $(n)$ $z$ magnetizations $(\mathbf{M}(t))$ from thermal equilibrium $(\mathbf{M}^{eq})$. The diagonal relaxation matrix **R** contains the relaxation rate constants written as $-(1/T_1)_i$ for the individual sites, while the exchange matrix **K** contains terms $K_{ij}$ describing the rate of transfer from site $j$ to site $i$ (the diagonal terms $-K_{ii}$ describe the loss of magnetization from site $i$ to the other sites). The formal solution of eq 5 is expressed in terms of the diagonal matrix **D** (containing the eigenvalues $-\lambda_i$)

$$\mathbf{D} = \mathbf{T}^{-1}(\mathbf{K} + \mathbf{R})\mathbf{T} \tag{6}$$

where the diagonalizing matrix **T** is found by standard numerical procedures (our particular implementation involved the EISPACK routines). The time dependence of the $z$ magnetization is then given by eq 7, where $\mathbf{M}(0)$ describes the initial $(t = 0)$ site intensities.

$$\mathbf{M}(t) = \mathbf{T}(\exp{-\mathbf{D}t})\mathbf{T}^{-1}(\mathbf{M}(0) - \mathbf{M}^{eq}) + \mathbf{M}^{eq} \tag{7}$$

Best guesses for the initial and equilibrium magnetizations, the $T_1$'s, and the rate constants are iteratively adjusted to provide both the least-squares best fit to the experimental observations and the standard deviations for the parameter estimates.

The two-site exchange of CO with $Co_2(CO)_8$ is particularly simple and would not by itself require the general treatment given above (analytic solutions are available and have been presented by others[14,15]). The exchange processes involved in the $CH_3C$-$O–Co(CO)_4$ experiments are assumed to be described by eq 2 and 3 (i.e., there is no direct pathway for exchanging the acyl with free CO etc.), and include eq 1 because of the $Co_2(CO)_8$ impurity present. The sites are labeled 1 ($Co(CO)_4$), 2 ($CH_3CO–$), 3 (free CO), and 4 ($Co_2(CO)_8$); the required equilibrium ratios are $A = M^{eq}{}_1/M^{eq}{}_3$ and $B = M^{eq}{}_4/M^{eq}{}_3$. Making the identifications with the rate constants described in the Results, the exchange matrix **K** becomes eq 8. Since the exchange and relaxation rates involving $Co_2(CO)_8$ were well-determined in the first set of experiments, it is unimportant that the "selective" inversion pulse on the $Co(CO)_4$ resonance partly perturbs the $Co_2(CO)_8$ signal; the initial intensity $(\mathbf{M}_4(0))$ is simply another parameter in the fit, and the exchange contribution from $k_1$ is readily estimated.

$$\mathbf{K} = \begin{pmatrix} -k_{acyl}/4 - k_2/4 & k_{acyl}\mathrm{A} & k_2\mathrm{A}/4 & 0 \\ k_{acyl}/4 & -k_{acyl}\mathrm{A} & 0 & 0 \\ k_2/4 & 0 & -k_2\mathrm{A}/4 - k_1\mathrm{B}/8 & k_1/8 \\ 0 & 0 & k_1\mathrm{B}/8 & -k_1/8 \end{pmatrix} \tag{8}$$

The activation parameters reported for the dissociation rate constants were determined by fitting the results to the Eyring equation by using a nonlinear least-squares program and assuming a 10% error in the absolute rate constant and a 2 °C error in the temperature. The error estimates in the activation parameters represent 95% confidence limits.

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# Some Platinum(II) and Iridium(III) Complexes with Direct Mercury–Hydrogen Bonds

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The preparation in solution and the NMR characterization of complexes of the types $[L_2(C_6Cl_5)Pt(\mu\text{-}H)HgR](CF_3SO_3)$ (for L = $PEt_3$, R = $n$-$C_{12}H_{25}$, $PhCH_2$, 2,4,6-$Me_3C_6H_2$, Ph, 4-$ClC_6H_4$; for L = $PMe_3$, R = $PhCH_2$, 2,4,6$Me_3C_6H_2$, Ph) and $[(triphos)(H_{3-x})Ir(\mu\text{-}H)_xHgR](CF_3SO_3)$ (triphos = $CH_3C(CH_2PPh_2)_3$, R = $n$-$C_{12}H_{25}$, $PhCH_2$, 2,4,6-$Me_3C_6H_2$, Ph, 4-$ClC_6H_4$, 2,4,6-$Cl_3C_6H_2$) are described. The values of the $^1J(^{199}Hg, ^1H)$ coupling constants range from 600 to 1000 Hz for the former class of compounds and from 126 to 475 Hz for the latter class of compounds. Although some of these species can be obtained in the solid state by low-temperature precipitation and can be stored indefinitely at ca. −20 °C, their solutions decompose above ca. −30 °C for the platinum complexes and ca. −60 °C for the iridium complexes.

## Introduction

Many attempts have been made to prepare compounds containing mercury–hydrogen bonds. Thus Wiberg and Henle[1] describe the synthesis of $HgH_2$ and report that it decomposes above −125 °C.

Much work has also been done on the reductive demercuration of alkyl- and arylmercury halides[2-6] by main-

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Table I. $^1$H NMR Data for Complexes $[L_2(C_6Cl_5)Pt(\mu\text{-}H)HgR]^{+}$[a]

| | L | R | $\delta$(H) | $^1J(^{195}Pt,^1H)$, Hz | $^1J(^{199}Hg,^1H)$, Hz | $^2J(^{31}P,^1H)$, Hz |
|---|---|---|---|---|---|---|
| **2a** | $PEt_3$ | $n\text{-}C_{12}H_{25}$ | –0.86 | 492 | 626 | 9.8 |
| **2b** | $PEt_3$ | $PhCH_2$[b] | –1.73 | 499 | 746 | 10.0 |
| **2c** | $PEt_3$ | 2,4,6-$Me_3C_6H_4$[c] | –0.78 | 483 | 947 | 9.6 |
| **2d** | $PEt_3$ | Ph[d] | –1.65 | 481 | 990 | 9.9 |
| **2e** | $PEt_3$ | 4-$ClC_6H_4$[e] | –1.83 | 477 | 1092 | 9.6 |
| **3b** | $PMe_3$ | $PhCH_2$[f] | –1.45 | 487 | 768 | 10.1 |
| **3c** | $PMe_3$ | 2,4,6-$Me_3C_6H_2$ | –0.63 | 495 | 961 | 9.9 |
| **3d** | $PMe_3$ | Ph | –1.42 | 495 | 1013 | 9.7 |

[a] The spectra were recorded at –90 °C. The $PEt_3$ complexes were measured in acetone-$d_6$. [b] $\delta(^{31}P)$ 10.9 $[^1J(^{195}Pt,^{31}P) = 2219$ Hz]; $\delta(^{195}Pt)$ –4568 $[^2J(^{199}Hg,^{195}Pt) = 450$ Hz]. [c] $\delta(^{31}P)$ 9.0 $[^1J(^{195}Pt,^{31}P) = 2192$ Hz, $^3J(^{199}Hg,^{31}P) = 47$ Hz]. [d] $\delta(^{31}P)$ 10.5 $[^1J(^{195}Pt,^{31}P) = 2205$ Hz, $^3J(^{199}Hg,^{31}P) = 49$ Hz]; $\delta(^{195}Pt)$ –4619 $[^2J(^{199}Hg,^{195}Pt) = 547$ Hz]; $\delta(^{199}Hg)$ –1022 relative to $Me_2Hg$. [e] $\delta(^{31}P)$ 11.4 $[^1J(^{195}Pt,^{31}P) = 2199$ Hz]; $\delta(^{195}Pt)$ –4627 $[^2J(^{199}Hg,^{195}Pt) = 825$ Hz]. [f] $\delta(^{31}P)$ –19.2 ppm $[^1J(^{195}Pt,^{31}P) = 2204$ Hz]; $\delta(^{195}Pt)$ –4542 $[^2J(^{199}Hg,^{195}Pt) = 407$ Hz].

group metal hydrides, e.g., by reaction 1, and the intermediacy of RHgH has been generally postulated, which

$$RHgX + NaBH_4 \rightarrow RHgH \qquad (1)$$

subsequently decomposes to give metallic mercury and the parent hydrocarbon. The following pathways (2) and (3) have been postulated for this decomposition process.

$$RHgH \rightarrow R^{\bullet} + HgH \qquad (2a)^{2}$$

$$R^{\bullet} + HgH \rightarrow RH + Hg(0)$$

$$R^{\bullet} + RHgH \rightarrow RH + RHg \qquad (2b)$$

$$RHg \rightarrow R^{\bullet} + Hg(0)$$

$$RHgH \rightarrow RHg + H^{\bullet} \qquad (3)^{6}$$

$$RHg \rightarrow R^{\bullet} + Hg(0)$$

$$R^{\bullet} + RHgH \rightarrow RH + RHg$$

While the decomposition of the species RHg and HgH are expected to be facile because of their low estimated bond energies[7] (ca. 30 ± 1.2 (for R = alkyl) and ca. 35 kJ mol$^{-1}$, respectively), the cleavage of the first bond in RHgH, if of a similar order of magnitude as that in $R_2Hg$, is expected to be ca. 200 kJ mol$^{-1}$.

It is now well-established[8] that "unstable" terminal M–H bonds in complexes of the type $L_mM$–H can be stabilized by formation of three-center, two-electron assemblies, i.e., $L_mM$–H–$M'L'_n$. M–H bonds stabilized in complexes of this type include palladium,[9] silver, and gold.[10,11] Thus it appeared possible to obtain complexes of the type $L_mM$–H–HgR.

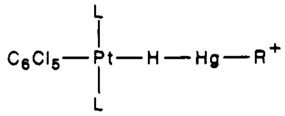
Several reactions of mercury compounds with transition-metal hydrides have been reported in the literature.[12–16] In particular the reaction of $[OsH_2(CO)(PR_3)_3]$ ($PR_3 = PMe_2Ph$ or $PEtPh_2$) with $HgCl_2$ has been reported[13] as giving $[OsH(HgCl)(CO)(PR_3)_3]$.

Finally, $[ReH_7L_2]$ and $[OsH_6L_2]$ (L = PPh-$i$-$Pr_2$) react with $HgCl_2$[14] giving compounds that have been formulated as $[HgCl_2(ReH_7L_2)]$ and $[HgCl_2(OsH_6L_2)]$, respectively. The $^1$H NMR spectra of these species show $^{199}$Hg satellites that, in the case of the rhenium compound, give a $J(^{199}Hg,^1H)$ value of 94 Hg while the corresponding value in the osmium complex is 45 Hz. These authors conclude that "there exists no unequivocal NMR evidence for a strong Lewis acid metal–hydride interaction". In this context it is noteworthy that for $[(\eta^5\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_2(\mu\text{-}HgBr)(CO)_9]$ a $^2J(^{199}Hg,^1H)$ value of 50 Hz has been reported.[16]

As it was recently observed in our laboratory that *trans*-$[PtH(C_6Cl_5)(PEt_3)_2]$ and $[IrH_3(triphos)]$ (triphos = $CH_3C(CH_2PPh_2)_3$) easily give compounds containing stable M–H–M′ units,[10] attempts were made to prepare and characterize complexes containing Hg–H bonds by using the above complexes.

## Results and Discussion

**Platinum Complexes.** Colorless solutions of cations $RHg^+$ were prepared in situ by reacting $R_2Hg$ (R = $n$-dodecyl, $PhCH_2$ 2,4,6-$Me_3C_6H_2$, Ph, 4-$ClC_6H_4$) with $HgI_2$ in acetone and abstracting with $AgCF_3SO_3$ the iodine from the RHgI.[17] These were reacted at –80 °C with acetone solutions of *trans*-$[PtH(C_6Cl_5)L_2]$ (**1**) and the resulting colorless solutions examined by multinuclear NMR. The products can be formulated as shown below on the basis of the data given in Table I.



**2a**: L = $PEt_3$; R = $n$-dodecyl
**b**: L = $PEt_3$; R = $PhCH_2$
**c**: L = $PEt_3$; R = 2,4,6-$Me_3C_6H_2$
**d**: L = $PEt_3$; R = Ph
**e**: L = $PEt_3$; R = 4-$ClC_6H_4$
**3b**: L = $PMe_3$; R = $PhCH_2$
**c**: L = $PMe_3$; R = 2,4,6-$Me_3C_6H_2$
**d**: L = $PMe_3$; R = Ph

Figure 1 shows the $^1$H NMR spectrum of compound **2e**. An enlargement of the high-field region of the hydride resonances is shown in the inset. This spectrum is the superimposition of the subspectra given by the following isotopomers: (A) *Pt–H–*Hg, 55.1%; (B) $^{195}$Pt–H–*Hg, 28.1%; (C) *Pt–H–$^{199}$Hg, 11.1%; (D) $^{195}$Pt–H–$^{199}$Hg 5.7%. The asterisk denotes those isotopes that do not have nuclear spins $I$, of $^1/_2$; the resonances corresponding to these isotopomers are marked with the appropriate number. As can be seen in Figure 1, the integration of the aryl protons and of the central signal due to the hydride ligand give a relative intensity ratio of 4.0;0.5 compared with the calculated values for the proposed structure of 4.0;0.55.

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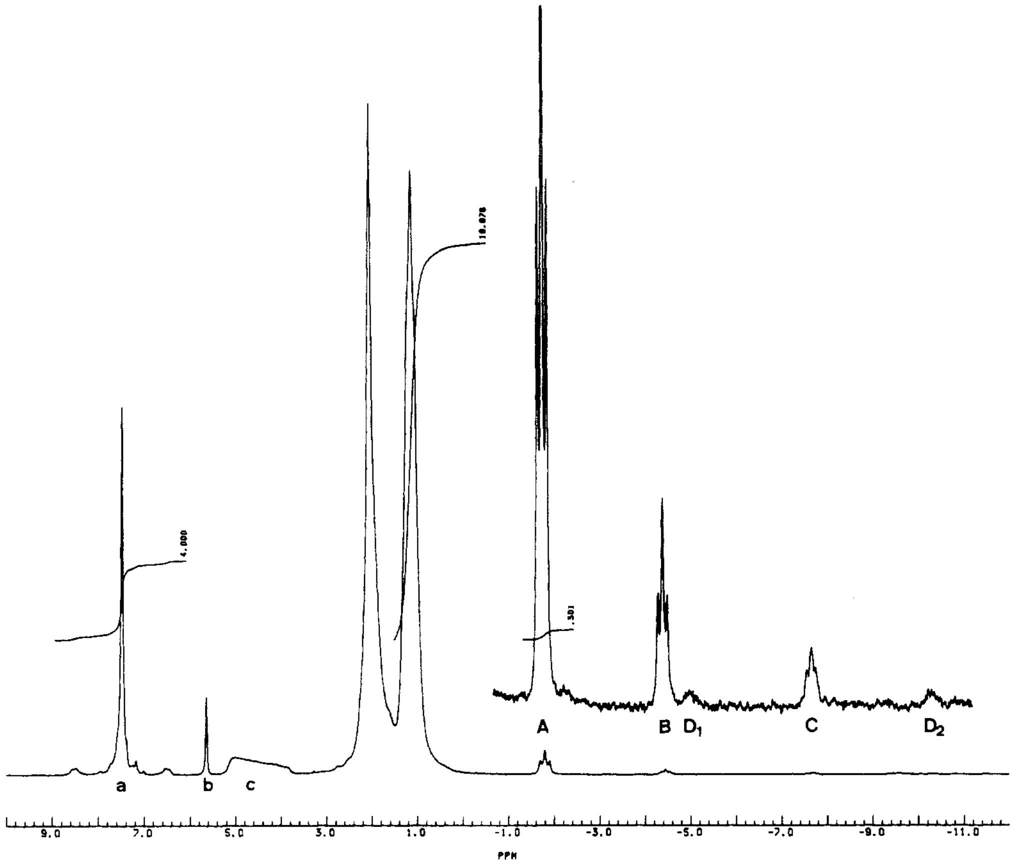

**Figure 1.** 90-MHz $^1H$ NMR spectrum of $[(PEt_3)_2(C_6Cl_5)Pt(\mu\text{-}H)Hg(4\text{-}ClC_6H_4)]^+$ (**2e**). (The assignment of the resonances denoted by the letters A to D is given in the text. The resonance denoted as a is due to the aryl protons, that corresponding to b is caused by the $CHDCl_2$ in the solvent, and the region marked as c arises from water.)

**Table II.** $^1$**H and** $^{31}$**P NMR Data for Complexes** $[(triphos)(H_{3-x})Ir(\mu\text{-}H)_xHgR]^{+\,a}$

| | R | $\delta(^1H)^b$ | $J_{obsd}$,$^c$ Hz | $^1J(^{199}Hg,^1H)$ Hz | $\delta(^{31}P)^d$ |
|---|---|---|---|---|---|
| **4a** | $n\text{-}C_{12}H_{25}$ | -6.84 | 62.3 | 126.0 | -5.2 |
| **4b** | $PhCH_2$ | -7.42 | 60.6 | 198.1 | *e* |
| **4c** | $2,4,6\text{-}Me_3C_6H_2$ | -7.03 | 61.0 | 281.2 | *e* |
| **4d** | Ph | -7.50 | 60.0 | 312.0 | -5.5 |
| **4e** | $4\text{-}ClC_6H_4$ | -7.60 | 59.4 | 326.7 | -6.1 |
| **4f** | $2,4,6\text{-}Cl_3C_6H_2$ | -7.85 | 60.3 | 478.8 | *e* |

[a] As the systems appear to remain dynamic even at -90 °C and the three H ligands remain "equivalent", the actual number of H atoms bonded to mercury in a static structure could not be determined. [b] Measured at -90 °C in $CH_2Cl_2\text{-}d_2$. [c] $J_{obsd} = (^2J(^{31}P,^1H)_{trans} + 2^2J(^{31}P,^1H)_{cis})$. [d] Measured at -60 °C in $CH_2Cl_2\text{-}d_2$. [e] Not recorded.

The nuclearity of these compounds is unambiguously given by the number and relative intensities of the satellites arising from $^{195}Pt$ (33.8%) and $^{199}Hg$ (16.8%). These correspond to a Pt:Hg ratio of 1:1. Thus, these data and the above integration give an $H_{hydride}$:Pt:Hg ratio of 1:1:1.

The triplet splitting of each set signals is due to the $^{31}P$ nuclei, and its magnitude (ca. 10 Hz) is typical for compounds of the type $L_2XPt\text{-}H\text{-}ML_n$ containing the unit *trans*-$[PtHR(PR'_3)_2]$,[10,18] showing the typical decrease (ca. 8 Hz) from the corresponding value for the mononuclear units *trans*-$[PtHXL_2]$.[19]

The $^1J(^{195}Pt,^1H)$ values (477–499 Hz) closely correspond to those found for compounds $[(PEt_3)_2RPt(\mu\text{-}H)PtR(PEt_3)_2]^+$ (R = Ph, $2\text{-}MeC_6H_4$, and $2,4\text{-}Me_2C_6H_3$; 445–447 Hz)[20] and $[(PMe_3)_2(C_6X_5)Pt(\mu\text{-}H)Pt(C_6X_5)(PMe_3)_2]^+$ (X = Cl and F; 453 and 512 Hz, respectively).[21] The $^1J(^{199}Hg,^1H)$ values (626–1092 Hz) are quite large and could be taken as an indication of strong Hg–H interactions. These are also confirmed by the observation of the satellites for the $^{199}Hg\text{-}^{195}Pt$ isotopomer ($D_1$ and $D_2$). The signals due to the isotopomers C and D are normally quite broad, and in many cases it is difficult to identify their triplet structure. This effect is likely to be due to fast $^{195}Pt$ and $^{199}Hg$ relaxations arising from "chemical shift anisotropy" (CSA).[22]

The magnitude of the Hg–H coupling constants for compounds of types **2** and **3** is about 1 order of magnitude larger than the $^2J(^{199}Hg,^1H)$ value in $[(\eta^5\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_2(\mu\text{-}HgBr)(CO)_9]$ (50 Hz).[16]

Furthermore, examination of coupling constant data[23] shows that the values of $^1J(^{195}Pt,^xX)$, and $^1J(^{199}Hg,^xX)$, at parity of X, are of comparable magnitudes, the latter being somewhat larger than the former; e.g., the $^1J(^{195}Pt,^{13}C)$ values for compounds containing $Pt\text{-}CH_3$ bonds range from 500 to 700 Hz while the $^1J(^{199}Hg,^{13}C)$ values for compounds containing $Hg\text{-}C_{alkyl}$ bonds fall between 650 and 1500 Hz. This relationship exists also for $^2J(^{195}Pt,^1H_{alkyl})$ and $^2J(^{199}Hg,^1H_{alkyl})$ coupling constants. These are 40–90 Hz in the former compounds and 100–300 Hz in the latter compounds. Thus one would expect $^1J(^{199}Hg,^1H)$ values of the order of 500 Hz for compounds

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of types **2** and **3**. The observed values (620–1100 Hz) are consistent with the postulated direct H–Hg bond.

As can be seen from the data given in Table I, the $^1J(^{199}Hg,^1H)$ values increase with decreasing electron-donor capacity of the R group bound to mercury. If one considers the formation of the bimetallic complex as resulting from the combination of the Lewis acid, $RHg^+$ in this case, and a Lewis base, *trans*-$[PtH(C_6Cl_5)L_2]$ here, one can suppose that the stronger the Lewis acid the stronger will be its interaction with the Lewis base.

The sets of $PMe_3$ and $PEt_3$ complexes show similar trends. However, the values of the $^1J(^{199}Hg,^1H)$ coupling constants are ca. 20 (5) Hz larger for complexes of the former phosphine, which could be taken as an indication of stronger Pt–H–Hg interactions. This effect could be of steric origin as it has been observed[21] that while *trans*-$[PtH(C_6Cl_5)(PMe_3)_2]$ can form the binuclear hydrido-bridged complex $[(PMe_3)_2(C_6Cl_5)Pt(\mu\text{-}H)Pt(C_6Cl_5)(PMe_3)_2]^+$, the corresponding compound with $PEt_3$ is not formed.

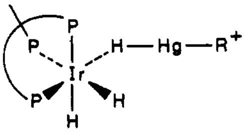
As found for other systems, e.g., the complexes with Pt–H–Au moieties mentioned earlier,[10] the $\delta$ ($^1H$) of the parent hydride *trans*-$[PtH(C_6Cl_5)(PEt_3)_2]$ (−9.8 ppm[19]) appears at higher field. However, while in the Pt–H–Au case this difference is ca. 5 ppm, in the case of the P–H–Hg complexes this ranges from 7.5 to 9 ppm. While the values of the $\delta$ ($^{31}P$) and of the corresponding $^1J(^{195}Pt,^{31}P)$ constants show changes that are typical for hydrido-bridged complexes,[20] the $^2J(^{199}Hg,^{195}Pt)$ and $^3J(^{199}Hg,^{31}P)$ values deserve some comment. Although no values of $^1J(^{199}Hg,^{195}Pt)$ appear to have been reported in the literature, extrapolation from physical constants and empirical data leads one to expect values of the order of several kilohertz[23] and comparable with Pt–Pt coupling constants. Thus, one might also expect Hg–H–Pt coupling constants to be comparable in magnitude to Pt–H–Pt coupling constants. The $^2J(^{199}Hg,^{195}Pt)$ values ranging from 400 and 825 Hz for compounds **2b,d,e** and **3b** are in agreement with this expectation.[24] Values of $^3J(^{199}Hg,^{31}P)$ for comparable compounds are not available. However, values of $^2J(^{199}Hg,^{31}P)$ for several types of platinum–mercury–phosphine complexes,[25] e.g., $[(PPh_3)_2(R)Pt(\mu\text{-}Hg)Pt(R)(PPh_3)_2]$ (R = aryl group), are about 200 Hz for phosphines in the cis positions relative to mercury. Thus, the value of 49 Hz for $^3J(^{199}Hg,^{31}P)$ in **2d** is reasonable.

The thermal stability of these compounds is relatively low. Thus, in solution, the most stable of them, **2d** and **2e**, decompose above −30 °C. However, they can be obtained as colorless amorphous solids by mixing ethereal solutions of the components precooled to −78 °C and by sucking off the supernatant liquid phase. These solids are stable when stored at −20 °C. Thus the $^1H$ NMR spectrum of a solution of **2d**, prepared from a solid that had been stored at this temperature for about 4 weeks, was identical with that of a freshly prepared solution.

There appears to be a direct correlation between the thermal stability in solution of the $PMe_3$ compounds **3b–d** and their $^1J(^{199}Hg,^1H)$ values. This, however, is not the case for the corresponding $PEt_3$ compounds **2a–e** where, at a qualitative level, the ease of decomposition seems to be related to the ability of the R group to give the corresponding radical. Thus it is possible that the two sets of compounds decompose by different pathways.

Two other points are worthy of note: (1) the complexes containing $PMe_3$ are generally less thermally stable than the corresponding complexes with $PEt_3$; (2) the $PhHg^+$ cation reacts with *trans*-$[PtHPh(PEt_3)_2]$ at −90 °C with immediate formation of metallic mercury. It can be presumed that the higher electron density of the hydride ligand in this mononuclear complex gives a very strong interaction with the Hg–Lewis acid which leads to electron transfer from the Pt–H to the Hg–R unit, with irreversible decomposition of the intermediate thus formed. It is noteworthy that the products of this decomposition reaction are, in addition to metallic mercury, the parent hydrocarbon, RH, and the platinum solvento cation $[Pt(C_6Cl_5)(solvent)L_2]^+$.

**Iridium Complexes.** Solution of the cations $RHg^+$ (R = *n*-dodecyl, $PhCH_2$, 2,4,6-$Me_3C_6H_2$, Ph, 4-$ClC_6H_4$, and 2,4,6-$Cl_3C_6H_2$) in $CD_2Cl_2$ were reacted at −80 °C with $CD_2Cl_2$ solution of $[IrH_3(triphos)]$,[26] and the solutions were examined by $^1H$ NMR. The products are formulated as shown in **4a–f**. (The monohydrido-bridged formulation is assumed by analogy with that found for the corresponding platinum complexes—see discussion later.)



**4a**: R = *n*-dodecyl
**b**: R = $PhCH_2$
**c**: R = 2,4,6-$Me_3C_6H_2$
**d**: R = Ph
**e**: R = 4-$ClC_6H_4$
**f**: R = 2,4,6-$Cl_3C_6H_2$

The evidence for this formulation rests mainly with the $^1H$ NMR spectral data that are summarized in Table II. The $^1H$ NMR spectrum of $[IrH_3(triphos)]$ gives rise to an AA′A″XX′X″ spin system with a $\delta$ ($^1H_{hydride}$) of −10.6.[26] On addition of the mercury reagent this spectral pattern is maintained but shifted to lower field and $^{199}Hg$ satellites are observed. Furthermore the calculated $^2J(^{31}P,^1H)_{trans}$ and $^2J(^{31}P,^1H)_{cis}$ values for the parent hydride (119.5 and −12.0 Hz, respectively) decrease significantly on Ir–H–Hg bridge formation as ($^2J(^{31}P,^1H)_{trans} + 2\,^2J(^{31}P,^1H)_{cis}$) becomes of the order of 60 Hz.

It is noteworthy that the $^1J(^{199}Hg,^1H)$ values fall in the range 126–478 Hz. It is unlikely that, in a static structure, there is a triple Ir–H–Hg bridge as the coordination number of mercury in the $RHg^+$ cation seldom becomes greater than 2.[27] If one assumes that this preferred coordination number is maintained in complexes of type **4**, i.e., a single Ir–H–Hg bridge is formed at the static limit, then the observed spectra indicate the presence of a very dynamic system even at −90 °C as all three hydride ligands appear to be equivalent. Thus, one can speculate that the $^{199}Hg$,$^1H$ coupling constant for a static Ir–H–Hg single bridge could range from ca. 380 to 1430 Hz, values which are of comparable magnitute with those of the corresponding Pt–H–Hg compounds (see Table I). It is also noteworthy that the variations for $^1J(^{199}Hg,^1H)$ with changes of R in the iridium compounds parallel those of the platinum compounds.

The thermal stability of solutions containing cations **4** is comparable with that of compounds of types **2** and **3**. However, unlike the platinum systems, where decomposition occurs with the formation of metallic mercury, the

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[27] Reference 17 p 866 and pp 907/908 (Table 10).

iridium complexes "decompose" into other species without the formation of any precipitate. These reactions could be related to those reported for reactions of other hydrides, e.g., $[IrHCl_2(CO)(PPh_3)_2]$,[12] with mercury salts.

**Conclusions.** The compounds reported here constitute the first sets of unambiguously characterized compounds containing M–H–Hg moieties. It is noteworthy that while the compounds described have low thermal stabilities, they are neither air- nor water-sensitive. Their ease of formation indicates that compounds of this type will be obtainable also with other transition metals given a suitable choice of parent hydride, i.e. one where electron-transfer processes occur only at high energies.

## Experimental Section

**NMR Measurements.** $^1H$ and $^{31}P$ spectra were recorded at 90 and 36.432 MHz by using a Bruker FT WH 90 spectrometer while the $^{195}Pt$ and $^{199}Hg$ spectra were recorded at 53.747 and 44.568 MHz by using a Bruker WM 250 instrument. $^1H$ chemical shifts are given relative to external $Me_4Si$ whereas $^{31}P$ chemical shifts are relative to external 85% $H_3PO_4$ and $^{195}Pt$ chemical shifts relative to external $Na_2PtCl_6$. Positive values denote shifts downfield of the reference.

**Chemicals.** The compound $Ph_2Hg$ was purchased from Fluka AG, Switzerland. Other starting materials $R_2Hg$ (R = *n*-dodecyl,[28] $PhCH_2$,[29] 4-$ClC_6H_4$[29]) were prepared by published procedures.

The compound $(2,4,6\text{-}Me_3C_6H_2)_2Hg$[30] was prepared by the Grignard method as described elsewhere,[31] while $(2,4,6\text{-}Cl_3C_6H_2)_2Hg$[32] was obtained by reacting the corresponding lithium derivative[33] with $HgCl_2$ as described elsewhere.[34]

The compounds RHgI (R = dodecyl,[28] $PhCH_2$,[35] 2,4,6-$Me_3C_6H_2$,[30] Ph,[35] 4-$ClC_6H_4$[36]) were prepared in situ as described for compounds 2–4 below. The compound 2,4,6-$Cl_3C_6H_2HgCl$[37] was obtained as described for the corresponding $C_6Cl_5$ compound.[38]

The complexes *trans*-$[PtH(C_6Cl_5)(PEt_3)_2]$[19] and $[IrH_3(triphos)]$[26] were prepared as described in the appropriate references.

**Synthesis of *trans*-$[PtH(C_6Cl_5)PMe_3)_2]$.** Compound $[Pt(PMe_3)_4]$[39] (0.882 g, 1.77 mmol) in 5 mL of THF was added to a well-stirred suspension of $C_6Cl_5Br$ (0.718 g, 2.19 mmol) in 8 mL of THF that had been cooled to −80 °C. An additional precipitate formed. The suspension was allowed to warm up to room temperature and then stirred for another 5 h. The solvent was decanted and the residual solid dried under vacuum. The intermediate $[Pt(C_6Cl_5)(PMe_3)_3]Br$ thus formed was extracted with 5 mL of MeOH to remove the excess of $C_6Cl_5Br$; the solution was evaporated to dryness and redissolved in $CH_2Cl_2$. Addition of $Et_2O$ to this solution gave the above intermediate (890 mg, 67%) as a white powder [$\delta(^{31}P_1)$ −24.6 (d) and $\delta$ $(^{31}P_2)$ −33.6 (t); $^1J(Pt,P_1)$ = 2395 Hz and $^1J(Pt,P_2)$ = 2098 Hz, $^2J(P_1,P_2)$ = 29.4 Hz (measured in MeOH)].

The above intermediate was dissolved in $EtOH/H_2O$ (10:1, ca. 10 mL), the solution cooled to 0 °C, 500 mg of $NaBH_4$ added, and the resulting suspension stirred for 5 h. The white precipitate was filtered off and recrystallized from acetone, giving 410 mg (58%) of pure product: decomp pt 210 °C; IR (KBr) $\nu$(PtH) 1995 (s) $cm^{-1}$; $^1H$ NMR ($CD_3COCD_3$, room temperature) $\delta$ −9.06 [t, with $^{195}Pt$ satellites, $^1J(PtH)$ = 780 Hz, $^2J(PH)$ = 20.3 Hz; $^{31}P$ NMR ($CD_3COCD_3$, room temperature) $\delta$ −21.8 (s, with $^{195}Pt$ satellites, $^1J(Pt,P)$ = 2653 Hz]. Anal. Calcd for $C_{12}H_{19}Cl_5P_2Pt$: C, 24.12; H, 3.20; Cl, 29.66. Found: C, 24.26; H, 3.21; Cl, 30.31.

The complexes $[L_2(C_6Cl_5)Pt(\mu\text{-}H)HgR](CF_3SO_3)$ were prepared only in solution, and a typical procedure, i.e., that for L = $PEt_3$ and R = Ph, is described below.

$CD_3COCD_3$ (ca. 0.5 mL) was added to solid $Ph_2Hg$ (7.8 mg, 2.2 × $10^{-2}$ mmol) and $HgI_2$ (10 mg, 2.2 × $10^{-2}$ mmol) and the mixture stirred until the red color of $HgI_2$ disappeared (ca. 30 min). Solid $AgCF_3SO_3$ (11.3 mg, 4.4 × $10^{-2}$ mmol) was then added, and the precipitate was removed by filtration, the resulting colorless solution being placed directly into an NMR tube. This solution was cooled off to −80 °C, and a colorless solution of *trans*-$[PtH(C_6Cl_5)(PEt_3)_2]$ (30.0 mg, 4.4 × $10^{-2}$ mmol) in ca. 0.5 mL of $CD_3COCD_3$ was slowly added. No color change was observed. After complete mixing of the solutions was ensured, the NMR tube was inserted in a spectrometer procooled to −90 °C and the spectra were immediately recorded. These solutions should be kept below −50 °C as above this temperature even the more stable compounds, i.e., **2d** and **2e**, begin to decompose.

Also the complexes $[(triphos)(H_{3-x})Ir(\mu\text{-}H)_xHgR](CF_3SO_3)$ were prepared only in solution by using the following general procedure.

A solution of the $RHg^+$ cation (3.05 × $10^{-2}$ mmol) in ca. 0.5 mL of $CD_2Cl_2$, prepared as described above, was added to a solution of $[IrH_3(triphos)]$ (25.0 mg, 3.05 × $10^{-2}$ mmol) in ca. 0.5 mL of $CD_2Cl_2$ that had been precooled to −80 °C. The spectra of the resulting colorless solutions were recorded at −90 °C. (For the preparation of 2,4,6-$Cl_3C_6H_2Hg^+$ the corresponding chloride was used.)

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**Registry No.** 1 (L = $PEt_3$), 83527-86-0; 1 (L = $PMe_3$), 107441-01-0; **2a**, 107441-02-1; **2b**, 107441-03-2; **2c**, 107441-04-3; **2d**, 107441-05-4; **2e**, 107441-06-5; **3b**, 107441-07-6; **3c**, 107441-08-7; **3d**, 107441-09-8; **4a**, 107441-10-1; **4b**, 107441-11-2; **4c**, 107441-12-3; **4d**, 107441-13-4; **4e**, 107441-14-5; **4f**, 107441-15-6; $Pt(PMe_3)_4$, 33937-27-8; $Pt(C_6Cl_5)(PMe_3)_3]Br$, 107452-99-3; $(C_{12}H_{25})_2Hg$, 10217-68-2; $IrH_3(triphos)$, 104453-08-9; 2,4,6-$Cl_3C_6H_2HgCl$, 84015-06-5; $C_6Cl_5Br$, 13074-96-9; $HgI_2$, 37320-91-5; $AgCF_3SO_3$, 2923-28-6; $Ph_2Hg$, 587-85-9; $(PhCH_2)_2Hg$, 780-24-5; $(4\text{-}ClC_6H_4)_2Hg$, 2146-79-4; $(2,4,6\text{-}Me_3C_6H_2)_2Hg$, 26562-17-4.

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