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Reactivity of [M(C∧P)(acac-O,O′)] [M = Pt, Pd; C∧P = CH_2-C_6H_4-P(*o*-tolyl)$_2$-κC,P; acac = 2,4-pentanedionato] toward HgX_2 (X = Br, I, CH_3COO, CF_3COO). New Polynuclear Complexes Containing Pt−Hg Bonds. Molecular Structures of [{Pt(C∧P)(acac-O,O′)-HgBr(μ-Br)}$_2$(μ-$HgBr_2$)], an Unprecedented Square-Planar Bromomercurate Complex, and [{Pt(C∧P)(μ-O_2CCH_3)$_2$Hg(μ^3-acac^{2-}-κC^3,O)Hg(O_2CCH_3-κO)}·$CHCl_3$]$_2$, the First Complex Containing Asymmetric Dimercurated Acetylacetone

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The complexes [M(C∧P)(acac-O,O′)] [M = Pt (**1**) Pd (**1′**); C∧P = CH_2-C_6H_4-P(*o*-tolyl)$_2$-κC,P; acac = 2,4-pentanedionato] were prepared by the reaction of [M(C∧P)(μ-Cl)]$_2$ [M = Pt, Pd] with Tl(acac) and fully characterized. The reactions of [Pt(C∧P)(acac-O,O′)] (**1**) with equimolar amounts of HgX_2 (X = I, Br) give the polynuclear complexes [Pt(C∧P)(acac-O,O′)HgI(μ-I)]$_2$ (**2**) and [{Pt(C∧P)(acac-O,O′)HgBr(μ-Br)}$_2$(μ-$HgBr_2$)] (**3**) containing unsupported Pt-to-Hg donor bonds. In the pentanuclear complex **3**, the central mercury atom shows an unexpected square-planar environment, unprecedented for halomercurates(II). The complex [Pt(C∧P)-(acac-O,O′)] (**1**) also reacts with Hg(O_2CR)$_2$ (R = CH_3, CF_3), but in 1:2 molar ratio, to afford the neutral hexanuclear complexes [Pt(C∧P)(μ-O_2CR)$_2$Hg(μ^3-acac^{2-}-κC^3,O)Hg(O_2CR-κO)]$_2$ [R = CH_3 (**4**), CF_3 (**5**)]. An X-ray study of **4** revealed that these compounds contain very short platinum-to-mercury donor bonds supported by two carboxylate groups, along with an unusual dimercurated acetylacetone moiety. The reactions of [Pd(C∧P)(acac-O,O′)] (**1′**) with HgX_2 (X = Br, I, CH_3COO, CF_3COO) proceed mainly (X = Br, CH_3COO, CF_3COO) with substitution of the acac-O,O′ ligand by X from the coordination environment of the palladium center to give the binuclear derivatives [Pd(C∧P)(μ-X)]$_2$ (X = Br, CH_3COO, CF_3COO), hindering the obtention of palladium−mercury compounds by this route.

Introduction

Metal−metal bonding in heteronuclear complexes containing d^8 and d^{10} metal ions has been known for some years.[1] A rich chemistry has been developed in our group on the synthesis of heteronuclear Pt → Ag[2] and Pt → Hg[3] compounds using mono- or binuclear anionic pentahalophenyl complexes of Pt(II) as Lewis bases.

More recently we have described the synthesis of neutral M(II) complexes, [M(C∧P)(S_2C−Z)] [M = Pt, Pd; C∧P = CH_2-C_6H_4-P(*o*-tolyl)$_2$-κC,P; Z = NMe_2, OEt],[4] and have also observed, when M = Pt, their ability to form heteronuclear compounds containing Pt−Hg bonds when they react with Hg(II) salts (HgX_2, X = Br, I, CH_3COO, CF_3COO). These reactions proceed differently depending on the nature of X. In some cases (X = Br, I) adducts containing unsupported Pt^{II} → Hg donor−acceptor bonds are formed; in other cases, the oxidative addition of HgX_2 (X = CH_3COO, CF_3COO) to Pt(II) takes place, affording compounds containing covalent Pt−Hg bonds.[5] None of these reactions is accompanied by Pt−C bond

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cleavage. However, the reactions of the analogous palladium complexes with HgX_2 (X = Br, CH_3COO, CF_3COO) proceed with transmetalation, giving rise to binuclear compounds with the C∧P acting as an unprecedented bridging ligand between the palladium and mercury atoms. Such transmetalation reactions were thought to proceed through electrophilic attack of the mercury salt on the Pd−C(sp^3) bond rather than on the palladium center.[5]

β-Diketonate complexes usually contain the β-diketonate bonded via the two oxygen atoms forming a six-membered planar ring.[6] It has been shown that the central carbon atom on the β-diketonate ring has nucleophilic character and undergoes metal−carbon bond formation under appropriate conditions.[7]

Taking into account the proven ability of the Hg to form Pt−Hg and C−Hg bonds,[4,5] we extended our work to the synthesis of new neutral complexes of Pd(II) and Pt(II) containing the same C∧P group and acetylacetonate as auxiliary ligand. These complexes contain different nucleophilic centers (Pt or Pd, O, C) capable of reacting with mercury salts acting as electrophilic reagents. The synthesis of [M(C∧P)(acac)] (M = Pt, Pd) and a study of their reactivity toward HgX_2 (X = Br, I, CH_3COO, CF_3COO) form the subject of this work. As a result, we report here the synthesis and the structural characterization of new mixed Pt−Hg heteropolynuclear complexes.

Experimental Section

General Procedures. Elemental analyses were performed on a Perkin-Elmer 240-B microanalyzer. IR spectra were recorded on a Perkin-Elmer 599 spectrophotometer (Nujol mulls between polyethylene plates in the range 200−4000 cm^{-1}). NMR spectra were recorded on either a Varian XL-200 or a Varian Unity 300 NMR spectrometer using the standard references. [Pd{CH_2-C_6H_4-P(*o*-tolyl)$_2$-κC,P}(acac-O,O′)] was prepared as described elsewhere.[8]

[Pt{CH_2-C_6H_4-P(*o*-tolyl)$_2$-κC,P}(acac-O,O′)] (1). To a suspension of [{Pt{CH_2-C_6H_4-P(*o*-tolyl)$_2$-κC,P}(μ-Cl)}$_2$] (1.0075 g, 0.944 mmol) in $CHCl_3$ (30 mL) was added Tl(acac) (0.5726 g, 1.887 mmol), and the mixture was refluxed for 3 h. The TlCl formed was removed by filtration. After evaporation of the solution to dryness and addition of *n*-pentane (20 mL) to the residue, a white solid was isolated, **1** (0.992 g, 88%). Anal. Calcd for $C_{26}H_{27}O_2PPt$: C, 52.26; H, 4.55. Found: C, 52.29; H, 4.41. IR: 1591 (vs), 1569 (vs), 1520 (vs), 1271 (s), 790 (s), 774 (vs), 760 (vs), 744 (vs), 605 (s), 591 (s), 566 (s), 532 (s), 522 (m), 510 (m), 488 (s), 481 (s), 462 (s), 445 (m). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): 11.10 (s, J_{Pt-P} = 4734.1 Hz). ^1H: 7.5−6.7 (m, C_6H_4, C∧P), 5.34 (s, C^3-H, acac), 3.65 (ν_A), 3.47 (ν_B) ($^2J_{H-H}$ = 13.79 Hz, CH_2, C∧P), 2.82 (s, CH_3, C∧P), 2.43 (s, CH_3, C∧P), 1.92 (s CH_3, acac), 1.75 (s CH_3, acac). $^{13}C\{^1H\}$ NMR: 185.43 (s, CO, acac), 183.61 (s, CO, acac), 101.15 (s, $^3J_{Pt-C}$ = 54.8 Hz, C^3, acac), 28.24 (s, CH_3, acac), 27.62 (d, $^4J_{P-C}$ = 6.4 Hz, CH_3, acac), 22.84 (s, CH_3, C∧P), 22.31 (s, CH_3, C∧P), 10.86 (s, J_{Pt-C} = 763.4 Hz, CH_2, C∧P).

[Pt{CH_2-C_6H_4-P(*o*-tolyl)$_2$-κC,P}(acac-O,O′)HgI(μ-I)]$_2$ (2). To a colorless solution of compound **1** (0.252 g, 0.422 mmol) in Et_2O/CH_2Cl_2 (80/7 mL) was added HgI_2 (0.191 g, 0.422 mmol), and the mixture was stirred for 1 h. The resulting yellow solution was evaporated to dryness, and Et_2O (25 mL) was added to the residue to afford a yellow solid, **2** (0.326 g, 74%). Anal. Calcd for $C_{52}H_{54}Hg_2I_4O_4P_2Pt_2$: C, 29.68; H, 2.59. Found: C, 29.32; H, 2.35. IR: 1565 (vs), 1527 (vs), 1275 (s), 787 (m), 754 (s), 745 (m), 611 (m), 590 (m), 567 (m), 531 (m), 523 (m), 506 (m), 488 (m), 479 (w), 458 (m). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): 10.10 (s, J_{Pt-P} = 4527.3 Hz).^1H NMR: 7.6−6.7 (m, C_6H_4, C∧P), 5.42 (s, C^3-H, acac), 3.84 (ν_A), 3.76 (ν_B) ($^2J_{H-H}$ = 13.12 Hz, CH_2, C∧P), 2.78 (s, CH_3, C∧P), 2.43 (s, CH_3, C∧P), 1.94 (s CH_3, acac), 1.80 (s CH_3, acac). $^{13}C\{^1H\}$: 186.04 (s, CO, acac), 183.63 (s, CO, acac), 101.74 (s, $^3J_{Pt-C}$ = 54.6 Hz, C^3, acac), 28.36 (s, CH_3, acac), 27.71 (d, $^4J_{P-C}$ = 6.9 Hz, CH_3, acac), 23.31 (s, CH_3, C∧P), 22.32 (s, CH_3, C∧P), 14.22 (s, J_{Pt-C} = 747.3 Hz, CH_2, C∧P).

[{Pt{CH_2-C_6H_4-P(*o*-tolyl)$_2$-κC,P}(acac-O,O′)HgBr(μ-Br)}$_2$-(μ-$HgBr_2$)] (3). Compound **3** was prepared in the same way as compound **2**. **1** (0.2202 g, 0.369 mmol) in Et_2O/CH_2Cl_2 (60/7 mL), $HgBr_2$ (0.1328 g, 0.369 mmol), 15 min. Yield = 0.2160 g, 51.4%. Anal. Calcd for $C_{52}H_{54}Hg_3Br_6O_4P_2Pt_2$: C, 27.44; H, 2.39. Found: C, 27.28; H, 2.28. IR: 1568 (vs), 1515 (s), 1265 (m), 785 (s), 760 (m), 748 (m), 691 (m), 609 (m), 591 (m), 564 (m), 530 (s), 519 (m), 508 (m), 491 (m), 475 (m), 460 (m). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): 9.43 (s, J_{Pt-P} = 4244.8 Hz). ^1H NMR: 7.6−6.8 (m, C_6H_4, C∧P), 5.49 (s, C^3-H, acac), 4.06 (s, $^2J_{Pt-H}$ = 116.1 Hz, 1H, CH_2, C∧P), 4.06 (s, $^2J_{Pt-H}$ = 77.4 Hz, 1H, CH_2, C∧P), 2.76 (s, CH_3, C∧P), 2.44 (s, CH_3, C∧P), 1.97 (s, CH_3, acac), 1.86 (s, CH_3, acac). $^{13}C\{^1H\}$: 187.27 (s, CO, acac), 184.01 (s, CO, acac), 102.59 (s, $^3J_{Pt-C}$ = 55.7 Hz, C^3, acac), 28.41 (s, CH_3, acac), 27.87 (d, $^4J_{P-C}$ = 6.6 Hz, CH_3, acac), 24.29 (d, $^3J_{P-C}$ = 8.3 Hz, CH_3, C∧P), 22.75 (d, $^3J_{P-C}$ = 5.1 Hz, CH_3, C∧P), 17.14 (s, CH_2, C∧P).

[Pt{CH_2-C_6H_4-P(*o*-tolyl)$_2$-κC,P}(μ-O_2CCH_3)$_2$Hg(μ^3-acac^{2-}-κC^3,O)Hg(O_2CCH_3-κO)]$_2$ (4). To a suspension of [Pt{CH_2-C_6H_4-P(*o*-tolyl)$_2$-κC,P}(acac-O,O′)] (**1**) (0.1865 g, 0.312 mmol) in CH_3OH (20 mL) at 0 °C was added Hg(O_2CCH_3)$_2$ (0.1988 g, 0.624 mmol). The mixture was stirred for 10 min, and the filtered solution was evaporated to dryness. The residue was treated with 20 mL of $CHCl_3$, and the suspended solid was removed by filtration. The solution was then evaporated to dryness, and *n*-pentane (30 mL) was added to the residue. A yellow solid remained and was filtered off, **4** (0.0856 g, 23.3%). Anal. Calcd for $C_{64}H_{70}Hg_4O_{16}P_2Pt_2$: C, 32.71; H, 3.00. Found: C, 33.12; H, 2.92. IR: 1652 (w), 1582 (m), 751 (s), 675 (m), 616 (w), 605 (w), 591 (s), 565 (s), 531 (s), 508 (w), 488 (m), 478 (s), 461 (m). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): 11.78 (s, J_{Pt-P} = 3779.9 Hz, $^2J_{Hg-P}$ = 111.8 Hz).^1H NMR: 7.7−6.8 (m, C_6H_4, C∧P), 4.14 (ν_A), 4.05 (ν_B) ($^2J_{H-H}$ = 16.8 Hz, CH_2, C∧P), 3.05 (s, CH_3, C∧P), 2.02 (s, CH_3, C∧P, bridging acetate), 1.98 (s, CH_3, bridging acetate), 1.95 (s, CH_3, acac), 1.90 (s CH_3, terminal acetate). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 293 K): 204.37 (s, CO, acac), 202.92 (s, CO, acac), 179.14 (s, COO, bridging acetate) 178.43 (s, COO, bridging acetate), 176.74 (s, COO, terminal acetate), 30.12 (s, CH_3, acac), 26.64 (d, $^3J_{P-C}$ = 9.1 Hz, CH_3, C∧P), 24.28 (s, CH_3, bridging acetate), 23.75 (d, $^4J_{P-C}$ = 6.2 Hz, CH_3, bridging acetate), 22.61 (s, CH_3, C∧P), 21.94 (s CH_3, terminal acetate), 15.88 (s, J_{Pt-C} = 647.1 Hz, CH_2, C∧P).

[Pt{CH_2-C_6H_4-P(*o*-tolyl)$_2$-κC,P}(μ-O_2CCF_3)$_2$Hg(μ^3-acac^{2-}-κC^3,O)Hg(O_2CCF_3-κO)]$_2$ (5). Complex **5** was prepared in manner similar to that for complex **4**. **1** (0.1857 g, 0.317 mmol), Hg(O_2CCF_3)$_2$ (0.2705 g, 0.634 mmol), T = −5 °C. Yield = 0.3116 g, 75%. Anal. Calcd for $C_{64}H_{52}F_{18}Hg_4O_{16}P_2Pt_2$: C, 28.75; H, 1.96. Found: C, 28.51; H, 1.76. IR: 1788 (m), 1658 (vs), 1190 (vs), 854 (vs), 788 (s), 756 (s), 671 (w), 614 (m), 590 (s), 565 (s), 526 (s), 505 (w), 488 (w), 476 (m), 458 (m). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): 14.76 (s, J_{Pt-P} = 3619.6 Hz). ^1H NMR: 7.7−7.0 (m, C_6H_4, C∧P), 4.42 (s, $^2J_{Pt-H}$ = 160.2 Hz, 1H, CH_2, C∧P), 4.42 (s, $^2J_{Pt-H}$ = 126.6 Hz, 1H, CH_2, C∧P), 3.10 (s, CH_3, C∧P), 2.05 (s, CH_3, acac), 2.01 (s, CH_3, C∧P). $^{19}F\{^1H\}$ NMR: −73.63 (s, CF_3), −73.50 (s, CF_3), −72.99 (s, CF_3). $^{13}C\{^1H\}$ NMR: 30.15 (s, CH_3, acac), 27.00 (s, CH_3, C∧P), 22.64 (s, CH_3, C∧P), 14.23 (s, CH_2, C∧P).

X-ray Crystal Structure Determinations. Suitable crystals of **3** were obtained by slow diffusion of *n*-hexane into CH_2Cl_2 solutions of complex **3** at 5 °C. Suitable crystals of **4**·$CHCl_3$ were obtained by slow diffusion of *n*-hexane into $CHCl_3$ solutions of complex **4** at 5 °C.

Crystal data and other details of the structure analyses are presented in Table 1. Crystals were fixed on top of glass or

Table 1. Crystal Data and Structure Refinement Parameters for 3 and 4·CHCl₃

	3	**4**·CHCl$_3$
empirical formula	($C_{26}H_{27}Br_3Hg_{1.5}O_2PPt$) × 2	($C_{33}H_{36}Cl_3Hg_2O_8PPt$) × 2
fw	1138.15 × 2	1294.21 × 2
unit cell dimens		
a (Å)	21.787(4)	10.488(1)
b (Å)	8.178(2)	13.158(2)
c (Å)	32.205(6)	15.821(2)
α (deg)	90	77.15(1)
β (deg)	97.23(3)	75.74(1)
γ (deg)	90	68.39(1)
volume (Å^3), *Z*	5692(2), 4	1946.2(4), 1
wavelength (Å)	0.71073	0.71073
temperature (K)	153(2)	200(2)
radiation	graphite-monochromated Mo Kα	
cryst syst	monoclinic	triclinic
space group	*I*2/*a*	$P\bar{1}$
abs coeff (mm^{-1})	17.271	11.747
transmsn factors	0.979, 0.332	1.000, 0.548
abs corr	Ψ scans	Ψ scans
cryst size (mm)	0.25 × 0.15 × 0.15	0.32 × 0.18 × 0.08
diffractometer	Enraf-Nonius CAD4	Siemens STOE/AED2
2*θ* range for data collect. (deg)	4−50 ($\pm h, +k, \pm l$)	4−50 ($-h, \pm k, \pm l$)
no. of reflns collected	10 072	7159
no. of ind reflns	5029 (*R*(int) = 0.0814)	6678 (*R*(int) = 0.0332)
refinement method	full-matrix least-squares on F^2	
goodness-of-fit on F^{2a}	1.021	1.040
final *R* indices ($I > 2\sigma(I)$)^b	R1 = 0.0494, wR2 = 0.1157	R1 = 0.0425, wR2 = 0.0907
R indices (all data)	R1 = 0.1058, wR2 = 0.1388	R1 = 0.0681, wR2 = 0.1011

[a] Goodness-of-fit = $[\sum w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$. $w = [\sigma^2 (F_o) + (g_1P)^2 + g_2P]^{-1}$; $P = [\max (F_o^2; 0) + 2F_c^2]/3$. [b] $R1 = (|F_o| - |F_c|)/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_c^2)^2]^{1/2}$.

quartz fibers and mounted on the diffractometers. Unit cell constants were determined from 25 accurately centered reflections with 22° < 2θ < 31.7° for **3** and 70 reflections in the range 24° < 2θ < 26 ° for **4**·CHCl$_3$. Data were collected using *ω* scans for **3** and using *ω*/2*θ* scans for **4**·CHCl$_3$. Three check reflections were measured at regular intervals, and no loss of intensity was observed for **4**·CHCl$_3$, but a decay of 32% over the period of data collection was observed for **3**. The structures were solved by an automated Patterson interpretation routine and developed in the usual series of least-squares refinements and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement parameters. H atoms were added at calculated positions (C−H = 0.96 Å) and refined with isotropic displacement parameters equal to 1.2 or 1.5 times the equivalent isotropic *U*'s of the corresponding C atoms. The residual peaks of significant height (>1 e/Å^3) that were observed in the final difference Fourier map in both complexes were ghosts of the heavy atoms. In the case of **4**·CHCl$_3$ there are also some peaks in the solvent area, indicating some disorder. The refinements were carried out using the program SHELXL-93.[9]

Results and Discussion

A. Synthesis and Characterization of [Pt{CH$_2$-C$_6$H$_4$-P(*o*-tolyl)$_2$-*κ*C,P}(acac-O,O′)] (1). The reaction of [{Pt{CH$_2$-C$_6$H$_4$-P(*o*-tolyl)$_2$-*κ*C,P}(*μ*-Cl)}$_2$] with Tl(acac) in 1:2 molar ratio in refluxing chloroform proceeds with precipitation of TlCl and formation of [Pt{CH$_2$-C$_6$H$_4$-P(*o*-tolyl)$_2$-*κ*C,P}(acac-O,O′)] (**1**), which is obtained from the solution as a white, air-stable solid in a good yield (eq 1).

$$[\{Pt\{CH_2\text{-}C_6H_4\text{-}P(o\text{-tolyl})_2\text{-}\kappa C,P\}(\mu\text{-Cl})\}_2] + 2Tl(acac) \rightarrow 2TlCl(s) + 2[Pt\{CH_2\text{-}C_6H_4\text{-}P(o\text{-tolyl})_2\text{-}\kappa C,P\}(acac\text{-}O,O')]\ (\mathbf{1}) \quad (1)$$

Compound **1** has been formulated as a square-planar mononuclear compound (Scheme 1) on the basis of its elemental analysis and spectroscopic data (IR and NMR) (see Experimental Section).

The ν(C═O) stretching vibrations for **1** appear at 1591 and 1569 cm^{-1}, at significantly lower energies than those found for the free ligand (1720 cm^{-1}), and are indicative of *β*-diketonate chelation to the metal center.[10−13] The inequivalence of the two halves of the acac ligand, expected for chelate coordination, is evident from the ^{1}H and ^{13}C NMR spectra of **1**. Thus, the ^{1}H NMR spectrum of **1** in CDCl$_3$ at room temperature shows three resonances due to the acac ligand: a singlet at 5.34 ppm due to the C^{3}H and two singlets due to the methyl groups. The ^{13}C{^{1}H} NMR spectrum of **1** shows five resonances due to the acac ligand: one at 101.15 ppm corresponding to the C^3 atom, which appears as a singlet flanked by the ^{195}Pt satellites ($^3J_{Pt-C}$ = 54.8 Hz), two carbonyl resonances close to 184 ppm, and two methyl resonances close to 28 ppm. One of the methyl signals appears as a doublet due to coupling with the *trans* ^{31}P nucleus. These NMR data confirm the structure proposed for compound **1**.[7a,14]

In addition, the C∧P chelate ligand in **1** gives the expected signals in the ^{31}P, ^{1}H, and ^{13}C NMR spectra (see Experimental Section). A HETCOR experiment was performed on complex **1** in order to correctly assign the ^{1}H methyl resonances (Supporting Information).

The analogous palladium compound (**1′**) was prepared similarly to **1. 1′** has been described previously in the literature.[8]

B. Reactivity of [Pt{CH$_2$-C$_6$H$_4$-P(*o*-tolyl)$_2$-*κ*C,P}(acac-O,O′)] (1) toward HgX$_2$ (X = I, Br). The

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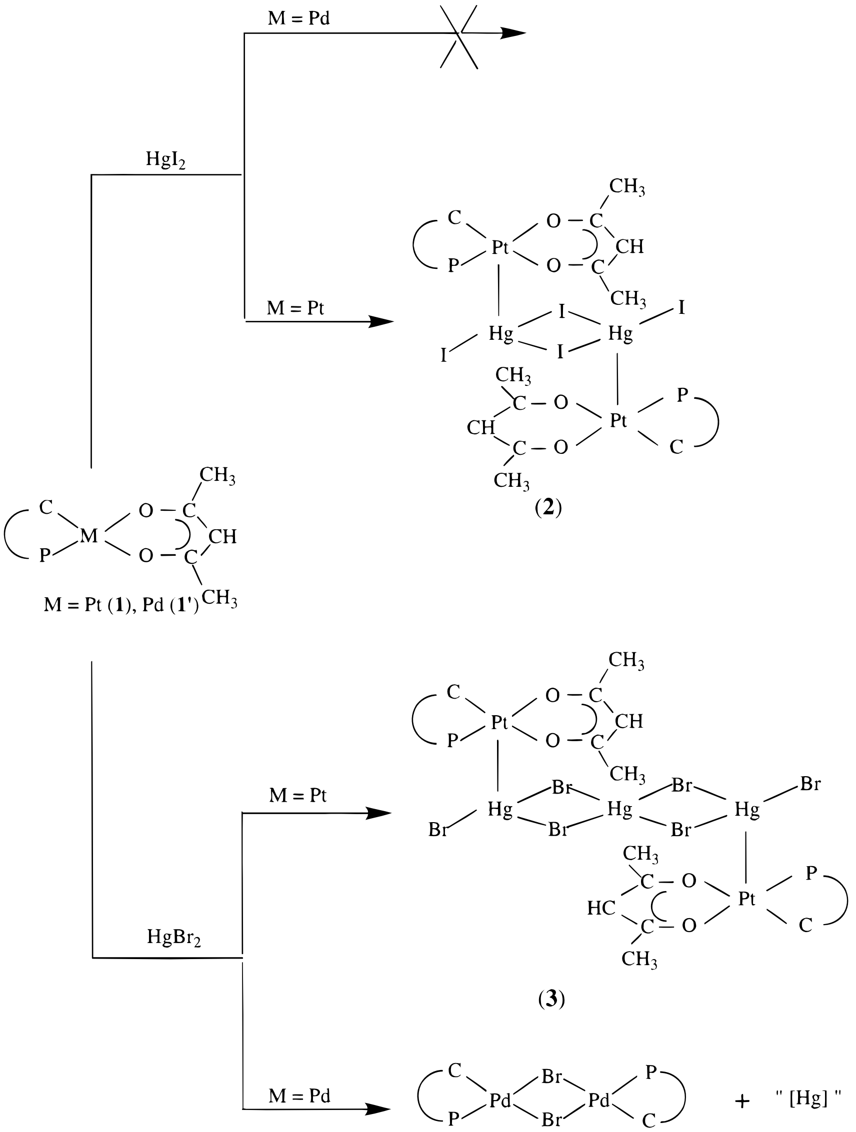
Scheme 1



reactions of [Pt{CH$_2$-C$_6$H$_4$-P(*o*-tolyl)$_2$-*κ*C,P}(acac-O,O′)] (**1**) with HgI$_2$ and HgBr$_2$ in 1:1 molar ratio afford the polynuclear complexes [Pt{CH$_2$-C$_6$H$_4$-P(o-tolyl)$_2$-*κ*C,P}-(acac-O,O′)HgI(*μ*-I)]$_2$ (**2**) and [Pt{CH$_2$-C$_6$H$_4$-P(*o*-tolyl)$_2$-*κ*C,P}(acac-O,O′)HgBr(*μ*-Br)}$_2$(*μ*-HgBr$_2$)] (**3**) in high yields as air-stable solids (Scheme 1).

Compounds **2** and **3** show similar IR and NMR spectra, but the elemental analyses of **3** are indicative of a higher amount of HgBr$_2$ in the complex (see Experimental Section). The X-ray crystal study of **3** confirms the proposed stoichiometry. This means that although the reaction between **1** and HgBr$_2$ is carried out in 1:1 molar ratio, the reactants combine with each other in a 2:3 molar ratio (eq 2). However, the remaining quantity of **1** is removed completely from the mixture because of its high solubility in diethyl ether, used as precipitating agent for **3**.

$$3[\mathrm{Pt}\{\mathrm{CH_2\text{-}C_6H_4\text{-}P}(o\text{-tolyl})_2\text{-}\kappa\mathrm{C,P}\}(\mathrm{acac\text{-}O,O'})]\ (\mathbf{1}) + 3\mathrm{HgBr_2} \rightarrow [\{\mathrm{Pt}\{\mathrm{CH_2\text{-}C_6H_4\text{-}P}(o\text{-tolyl})_2\text{-}\kappa\mathrm{C,P}\}(\mathrm{acac\text{-}O,O'})\mathrm{HgBr}(\mu\text{-Br})\}_2(\mu\text{-HgBr_2})]\ (\mathbf{3}) + [\mathrm{Pt}\{\mathrm{CH_2\text{-}C_6H_4\text{-}P}(o\text{-tolyl})_2\text{-}\kappa\mathrm{C,P}\}(\mathrm{acac\text{-}O,O'})]\ (\mathbf{1}) \quad (2)$$

In contrast, the reactions between the palladium derivative [Pd{CH$_2$-C$_6$H$_4$-P(*o*-tolyl)$_2$-*κ*C,P}(acac-O,O′)] (**1′**) and HgX$_2$ (X = I, Br) proceed very differently, as can be seen in Scheme 1. Whereas HgI$_2$ does not react with **1′**, HgBr$_2$ does; but the reaction takes place with substitution of the acac$^-$ ligand by Br$^-$ from the coordination environment of the palladium center and the formation of the binuclear derivative [{Pd{CH$_2$-C$_6$H$_4$-P(o-tolyl)$_2$-*κ*C,P}(*μ*-Br)}$_2$]. As a result, no mixed palladium−mercury derivatives could be prepared from **1′** and HgX$_2$ (X = I, Br).

Compounds **2** and **3** have been characterized by elemental analysis and spectroscopic methods (IR and NMR). In addition, the solid-state structure of **3** has been unambiguously established by X-ray diffraction analysis.

X-ray Crystal Structure of 3. A drawing of the molecule is shown in Figure 1. Selected bond distances and angles are given in Table 2. As can be seen, the pentanuclear complex **3** can be regarded as being formed by two “Pt{CH$_2$-C$_6$H$_4$-P(*o*-tolyl)$_2$-*κ*C,P}(acac-O,O′)HgBr$_2$” fragments bridged by an “HgBr$_2$” unit and related to each other by a center of symmetry.

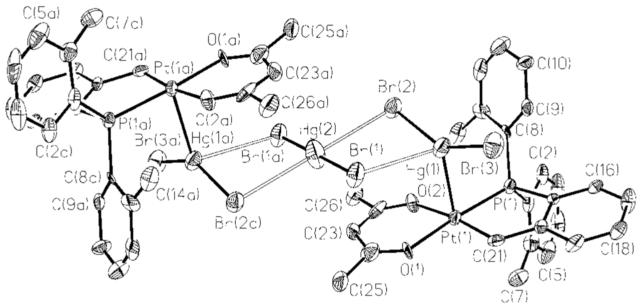


Figure 1. Molecular structure of [{Pt(C∧P)(acac-O,O′)-HgBr(μ-Br)}$_2$(μ-HgBr$_2$)] (**3**). Hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [{Pt(C∧P)(acac-O,O′)HgBr(μ-Br)}$_2$(μ-HgBr$_2$)] (3)

Pt(1)−P(1)	2.222(4)	Pt(1)−C(21)	2.044(13)
Pt(1)−O(2)	2.090(9)	Pt(1)−O(1)	2.066(9)
Pt(1)−Hg(1)	2.808(1)	Hg(1)−Br(1)	3.096(2)
Hg(1)−Br(2)	2.491(2)	Hg(1)−Br(3)	2.458(2)
Hg(2)−Br(1)	2.475(2)	Hg(2)−Br(2)	3.006(2)
Hg(1)⋯Hg(2)	3.991(1)		
O(1)−Pt(1)−O(2)	89.1(4)	O(2)−Pt−C(21)	173.2(5)
C(21)−Pt(1)−P(1)	84.9(4)	P(1)−Pt(1)−O(1)	171.1(3)
O(1)−Pt(1)−Hg(1)	89.3(3)	O(2)−Pt(1)−Hg(1)	99.1(3)
C(21)−Pt(1)−Hg(1)	85.9(4)	P(1)−Pt(1)−Hg(1)	88.74(11)
Pt(1)−Hg(1)−Br(3)	111.87(5)	Pt(1)−Hg(1)−Br(2)	99.53(5)
Pt(1)−Hg(1)−Br(1)	100.69(5)	Br(1)−Hg(1)−Br(2)	84.52(5)
Br(1)−Hg(1)−Br(3)	99.00(6)	Br(2)−Hg(1)−Br(3)	146.96(7)
Br(1)−Hg(2)−Br(2)	86.77(5)	Br(1)−Hg(2)−Br(2a)[a]	93.23(6)
C(22)−C(23)−C(24)	124.2(14)		

[a] Atoms with "a" appended to their names are at $-x$, $-y + 1$, $-z + 1$.

Each Pt{CH$_2$-C$_6$H$_4$-P(o-tolyl)$_2$-κC,P}(acac-O,O′)HgBr$_2$ unit contains one unsupported Pt → Hg bond. The five-coordinated Pt atom is located at the center of the base of a square pyramid with the Hg atom in the apical position. The angle between the Pt−Hg vector and the perpendicular to the Pt basal plane [Pt(1), O(1), O(2), P(1), C(21)] is 7.6(2)°.[15] Bond distances and angles in the metallacycle Pt{CH$_2$-C$_6$H$_4$-P(*o*-tolyl)$_2$-κC,P} are similar to those observed in other Pt(II) complexes containing the same group.[4] The Pt−O bond lengths [Pt(1)−O(1) = 2.067(10) Å, Pt(1)−O(2) = 2.090(9) Å] are similar to those found in (NBu$_4$)[{Pt(C$_6$F$_5$)$_2$(acac)}$_2$Ag][7a] and [Pt$_2$Ag$_2$(C$_6$F$_5$)$_4$(acac)$_2$(CH$_2$Cl$_2$)$_2$],[16] in which each Pt atom is involved in a platinum-to-silver dative bond.

The acac ligand [O(1), O(2), C(22), C(23), C(24), C(25), C(26)] and the metallacycle [Pt(1), P(1), C(15), C(16), C(21)] are basically planar and almost coplanar with the basal plane [Pt(1), O(1), O(2), P(1), C(21)], the interplanar angles being 1.8(2)° and 2.8(2)°, respectively.[15]

The Pt−Hg distance [2.8078(11) Å] and the geometry around the Pt center are similar to those observed in [{2,6-(Me$_2$NCH$_2$)$_2$-C$_6$H$_3$}Pt(μ-{(p-tol)NC(H)N(^{i}Pr)}-HgBrCl] [2.8331(7) Å],[17] *trans*-[(CH$_3$NH$_2$)$_2$Pt(1,5-diMeC$^-$)$_2$-Hg](NO$_3$)·0.5 H$_2$O [2.765(1) Å],[18] *trans*-[(CH$_3$NH$_2$)$_2$Pt(1-MeC$^-$)$_2$HgCl(NO$_3$)] [2.835(1) Å],[18] *trans*-[(CH$_3$NH$_2$)$_2$Pt(1-MeC$^-$)$_2$Hg](NO$_3$)$_2$ [2.785(1) Å],[18] and [Pt{CH$_2$-C$_6$H$_4$-P(*o*-tolyl)$_2$-κC,P}(S$_2$CNMe$_2$)HgI(μ-I)]$_2$,[4b] for which the Pt−Hg interaction has been described as a Pt → Hg donor bond with both metal centers in a formal oxidation state of II. In contrast, the Pt−Hg distance is clearly different from those observed in mixed Pt−Hg compounds displaying a covalent bond (Pt−Hg ca. 2.5 Å).[19] It is noteworthy that, as was observed in [Pt{CH$_2$-C$_6$H$_4$-P(*o*-tolyl)$_2$-κC,P}(S$_2$CNMe$_2$)HgI(μ-I)]$_2$,[4b] which contains the same metallacycle Pt{CH$_2$-C$_6$H$_4$-P(*o*-tolyl)$_2$-κC,P}, in complex **3** the Pt−Hg bond is not supported by any bridging ligand, despite the presence of two O atoms capable of bonding to the Hg atom.

The Hg atom of each unit {Pt{CH$_2$-C$_6$H$_4$-P(*o*-tolyl)$_2$-κC,P}(acac-O,O′)HgBr$_2$ has a distorted tetrahedral environment formed by one Pt, two bridging, and one terminal Br atoms. The Hg(1)−Br$_t$ distance [Hg(1)−Br(3) = 2.458(2) Å] is at the lower limit of the range of terminal Br−Hg distances reported in the literature (2.47−2.65 Å).[20] The Hg(1)−Br$_{br}$ distances are very different from each other; while one of them [Hg(1)−Br(1) = 3.096(2) Å] is at the high end of the range of Br−Hg bridging distances (>2.7 Å), the other one [Hg(1)−Br(2) = 2.491(2) Å] is the shortest Hg−Br$_{br}$ distance reported to date.[20] Unsymmetrical Hg$_2$(μ-Br)$_2$ bridges are commonly observed in other halogenomercuriates.[20,21]

The mercury atom of the HgBr$_2$ unit, Hg(2), is located at the inversion center of the molecule. Hg(2) is linearly coordinated by two covalent Hg−Br bonds [Hg(2)−Br(1) = Hg(2)−Br(1a) = 2.475(2) Å] and two weak Hg⋯Br bonds [Hg(2)−Br(2) = Hg(2)−Br(2a) = 3.006(2) Å] giving rise to a rhombic-planar geometry. This coordination environment involves bond angles around Hg(2) between *cis* bromide atoms very close to 90°. The most common coordination in bromo- and iodomercurates is tetrahedral, but other types of coordination are also observed, such as trigonal, trigonal bipyramidal, or octahedral and are mostly described as heavily distorted.[20,21] The adduct [{(C$_4$H$_9$)$_3$As}$_2$Hg$_2$Br$_4$·HgBr$_2$][21g] has the same stoicheometry as **3**, but the additional Hg atom (from the HgBr$_2$ unit) shows an octahedral envi-

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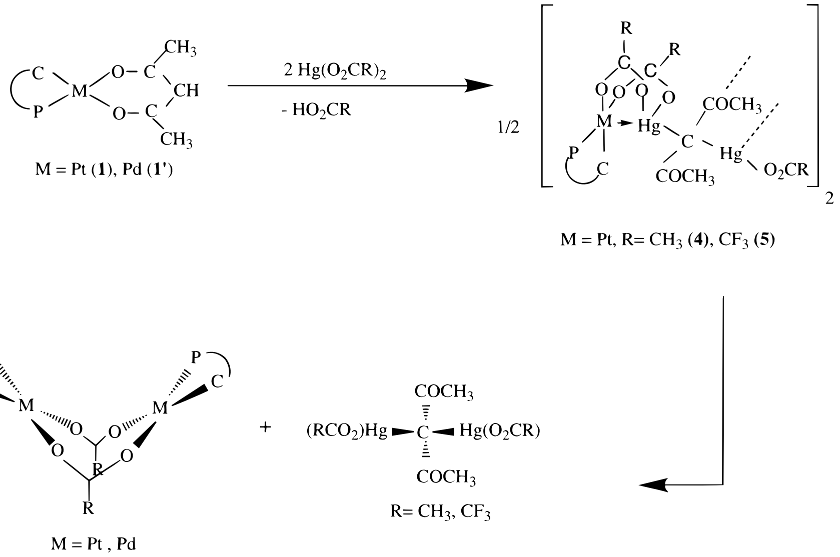
Scheme 2



ronment formed by two covalent Hg−Br bonds and additional weak bonds to four bromide atoms from two neighboring [{$(C_4H_9)_3As$}HgBr (μ-Br)]$_2$ fragments. Thus, as far as we know, complex **3** is the first example of bromomercurate(II) containing a mercury atom in a distorted square-planar coordination environment, and it also exhibits the shortest Hg−Br$_{br}$ bond lengths reported to date.

Spectroscopic Behavior of 2 and 3. The IR spectra of **2** and **3** show in each case one absorption due to the ν_{st}(CO) of the acac ligand at lower frequency than the corresponding bond in the starting material, complex **1**. This fact indicates that bonding betweeen the Pt and Hg fragments is not through the C^3 of the acac ligand but through the metal atoms,[6,7a,16] as it has been unambiguously established from the X-ray study on complex **3**.

The NMR spectra of **2** and **3** in solution show the signals due only to one Pt{CH_2-C_6H_4-P(*o*-tolyl)$_2$-κC,P}(acac-O,O′)$HgBr_2$ unit, in agreement with the molecular symmetry observed in the crystal for **3**. The ^{31}P{^{1}H} NMR spectra of both complexes show only one singlet flanked by the ^{195}Pt satellites. The frequencies of these signals are similar, and the ^{195}Pt−P coupling constants are smaller than those observed in the starting complex **1** (see Experimental Section). As was the case in the complexes [Pt{CH_2-C_6H_4-P(*o*-tolyl)$_2$-κC,P}(S_2CZ)HgX(μ-X)]$_2$ (Z = NMe_2, OEt; X = Br, I),[4b] these facts suggest that the Pt and Hg fragments are connected through a Pt-to-Hg donor bond.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **2** and **3** in $CDCl_3$ at room temperature (20 °C) also confirm the equivalence of the two halves of the molecules and the interaction of the two metal fragments [Pt{CH_2-C_6H_4-P(*o*-tolyl)$_2$-κC,P}(acac-O,O′), HgX_2] through the metal atoms, since no important shifts of the C^3 and carbonyl resonances are observed when compared to the starting complex **1** (see Experimental Section).[7a,14,22]

The similarities of the spectroscopic data of **2** and **3** imply that in complex **2**, as in complex **3**, the interaction between the neutral platinum and mercury fragments takes place through a Pt−Hg bond. This observation, along with the elemental analysis of **2** leads us to propose for it the molecular structure represented in Scheme 1, which is analogous to the structure of the complexes [Pt{CH_2-C_6H_4-P(*o*-tolyl)$_2$-κC,P}(S_2CZ)HgX(μ-X)]$_2$ (Z = NMe_2, OEt; X = Br, I), reported previously.[4b]

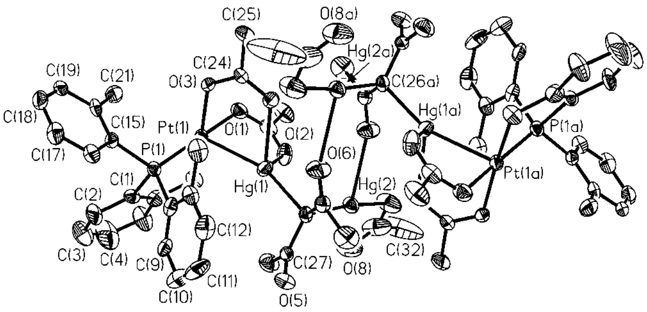


Figure 2. Molecular structure of [Pt(C∧P)(μ-O_2CCH_3)$_2$-Hg(μ^3-acac^{2-}-κC^3,O)Hg(O_2CCH_3-κO)]$_2$ (**4**). Hydrogen atoms have been omitted for clarity.

C. Reactivity of [M{CH_2-C_6H_4-P(*o*-tolyl)$_2$-κC,P}(acac-O,O′)] [M = Pt (1), Pd (1′)] toward Hg(O_2CR)$_2$ (R = CH_3, CF_3). The reactions of [M{CH_2-C_6H_4-P(*o*-tolyl)$_2$-κC,P}(acac-O,O′)] [M = Pt (**1**), Pd (**1′**)] with Hg(O_2CR)$_2$ (R = CH_3, CF_3) proceed with the displacement of the acac$^-$ ligand from the coordination sphere of the metal (M) by the carboxylate groups. Because of the different stabilities of the species initially formed, the resulting derivatives are different when M is Pt or Pd.

The reactions of [Pt{CH_2-C_6H_4-P(*o*-tolyl)$_2$-κC,P}(acac-O,O′)] (**1**) with Hg(O_2CR)$_2$ (R = CH_3, CF_3) in 1:2 molar ratio in methanol at low temperature result in the formation of the neutral hexanuclear complexes [Pt-{CH_2-C_6H_4-P(*o*-tolyl)$_2$-κC,P}(μ-O_2CR)$_2$Hg(μ^3-acac^{2-}-κC^3,O)Hg(O_2CR-κO)]$_2$ [R = CH_3 (**4**), CF_3 (**5**)], as is represented in Scheme 2. The molecular structure of **4** (X-ray diffraction, Figure 2) will be discussed in detail later. During the course of the reaction, complexes **4** and **5** decompose to give [Pt{CH_2-C_6H_4-P(*o*-tolyl)$_2$-κC,P}(μ-O_2CR)]$_2$ (R = CH_3, CF_3) and [{Hg(O_2CR-κO)}$_2$(μ^2-acac^{2-}-

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for [{Pt(C∧P)(μ-O_2CCH_3)$_2$Hg(μ^3-acac^{2-}-κC^3,O)Hg(O_2CCH_3-κO)}·$CHCl_3$]$_2$ (4)

Pt(1)−C(7)	2.046(12)	Pt(1)−P(1)	2.229(3)
Pt(1)−O(1)	2.071(7)	Pt(1)−O(3)	2.149(7)
Pt(1)−Hg(1)	2.6498(9)	Hg(1)−O(2)	2.533(8)
Hg(1)−O(4)	2.426(8)	Hg(1)−C(26)	2.157(11)
Hg(2)−C(26)	2.110(10)	Hg(2)−O(6a)[a]	2.654(9)
Hg(2)−O(7)	2.104(9)		

O(3)−Pt(1)−Hg(1)	89.9(2)	O(1)−Pt(1)−Hg(1)	87.1(2)
Hg(1)−Pt(1)−C(7)	94.8(4)	P(1)−Pt(1)−Hg(1)	97.79(8)
C(7)−Pt(1)−P(1)	83.9(3)	P(1)−Pt(1)−O(3)	100.4(2)
O(3)−Pt(1)−O(1)	86.4(3)	O(1)−Pt(1)−C(7)	88.8(4)
Pt(1)−Hg(1)−O(4)	78.2(2)	Pt(1)−Hg(1)−O(2)	76.3(2)
Pt(1)−Hg(1)−C(26)	159.2(3)	O(2)−Hg(1)−O(4)	95.4(3)
O(2)−Hg(1)−C(26)	106.4(3)	O(4)−Hg(1)−C(26)	121.3(4)
Hg(1)−C(26)−Hg(2)	98.5(4)	C(27)−C(26)−C(29)	119.6(9)
C(29)−C(26)−Hg(2)	108.9(7)	C(29)−C(26)−Hg(1)	108.9(8)
C(27)−C(26)−Hg(1)	109.4(7)	C(27)−C(26)−Hg(2)	109.3(7)
C(26)−Hg(2)−O(7)	171.3(4)	O(7)−Hg(2)−O(6a)	82.0(3)
C(26)−Hg(2)−O(6a)	105.7(4)		

[a] Atoms with "a" appended to their names are at $-x$, $-y + 1$, $-z + 1$.

κC^3)][23] (R = CH_3, CF_3) (Scheme 2), which could be separated from the reaction mixture because of their very low solubility in methanol and chloroform, respectively. When the reactions between **1** and Hg(O_2CR)$_2$ (R = CH_3, CF_3) were carried out in 1:1 molar ratio, complexes **4** and **5** were formed as well, but they were obtained with the starting complex, **1**, as impurity. The new complexes, **4** and **5**, have been characterized by elemental analysis and spectroscopic methods (IR and NMR). The solid-state structure of **4** has been established by X-ray diffraction analysis.

The reactions of the palladium derivative, **1′**, with Hg(O_2CR)$_2$ (R = CH_3, CF_3) in methanol at low temperature render [Pd{CH_2-C_6H_4-P(*o*-tolyl)$_2$-κC,P}(μ-O_2CR)]$_2$ (R = CH_3, CF_3)[24] and [{Hg(O_2CR-κO)}$_2$(μ^2-acac^{2-}-κC^3)][23] (R = CH_3, CF_3) (Scheme 2) when the reactions are carried out in 1:2 or in 1:1 molar ratio. These compounds are analogous to those obtained as byproducts in the syntheses of the Pt derivatives **4** and **5**. Because of that, we think that intermediate species (**A**, **B**) similar to **4** and **5** are initially formed, but that the poor ability of palladium(II) to form Pd → Hg bonds makes the intermediates very unstable and they decompose quickly to give the final products in high yield.

X-ray Crystal Structure of 4. A drawing of the molecule is shown in Figure 2. Selected bond distances and angles are given in Table 3. As can be seen, complex **4** is a hexanuclear species of platinum and mercury formed by two trinuclear units Pt{CH_2-C_6H_4-P(*o*-tolyl)$_2$-κC,P}(μ-O_2CR)$_2$Hg(μ^3-acac^{2-}-κC^3,O)Hg(O_2CR-κO) related to each other by a center of symmetry and connected by one oxygen atom of the acac^{2-} bridging ligand.

In each unit the five-coordinated Pt atom is located at the center of the base of a distorted square pyramid with the Hg atom in the apical position. The angle between the Pt−Hg vector and the perpendicular to the Pt basal plane [Pt(1), O(1), O(3), P(1), C(7)] is only 7.2(1)°.[15] The base of the pyramid is not rigorously planar, with the atoms C(7) and O(1) away from the best least-squares plane by 0.124 and 0.147 Å, respectively. Angles around the platinum between *cis* ligands deviate from the expected value (90°), especially the angle P(1)−Pt(1)−O(3), with a value of 100.4(2)°. The Pt−P,[4] Pt−C,[4] and Pt−O[19a,b,25] bond lengths are similar to those found in other complexes containing the same kinds of ligands. The Pt−O bond lengths [Pt(1)−O(1) = 2.071(7) Å, Pt(1)−O(3) = 2.149(7) Å] show the higher *trans* influence of C with respect to P.[25,26]

The geometry around the Pt atom is similar to that observed in other complexes for which the Pt−Hg interaction has been described as a Lewis acid−base type.[4,17,18] However, the Pt(1)−Hg(1) bond length [2.6498(9) Å] is clearly shorter than those observed in this kind of complex, but similar to that observed in the complex [(PPh_3)$_2$R−Pt−Hg−R] [Pt−Hg = 2.637(1) Å],[19c] in which the Pt^{I} and Hg^{I} centers are covalently bonded. These facts indicate that the Pt−Hg interaction is most likely a very strong Pt-to-Hg dative bond with both metals in a formal oxidation state of 2. Two acetate groups bridge Pt(1) and Hg(1), but they seem not to be responsible for the short Pt−Hg distance in light of the numerous binuclear complexes of transition elements with double carboxylate bridges and with nonbonded intermetallic separations (ca. 3 Å).[27,28] These two bridging acetate groups are asymmetrically bonded, with the Pt−O bond distances [Pt(1)−O(1) = 2.071(7) Å, Pt(1)−O(3) = 2.149(7) Å] clearly shorter than Hg(1)−O [Hg(1)−O(2) = 2.533(8) Å, Hg(1)−O(4) = 2.426(8) Å]. The two fragments Pt(1)(μ-O_2CCH_3)Hg(1) show distortions from planarity.[15] The best least-squares planes calculated for these fragments are perpendicular to each other [interplanar angle, 93.5(1)°], and they are also nearly perpendicular to the basal plane, with the angle between Pt(1), O(1), C(22), O(2), Hg(1), and the basal plane being 92.9(2)° and the angle between Pt(1), O(3), C(24), O(4), Hg(1), and the basal plane being 83.2(1)°.

The four-coordination environment around Hg(1) is completed by the C^3 atom of a dianionic acac group [C(26)]. The Hg(1)−C(26) distance [2.157(11) Å] is similar to those observed in other complexes containing Hg−C σ bonds.[3,4b,19c−f,29] Hg(1) has a very distorted tetrahedral environment, with the bond angles around Hg(1) ranging from 76.3(2)° to 159.2(3)°. The angles Pt(1)−Hg(1)−O(2) [76.3(2)°] and Pt(1)−Hg(1)−O(4) [78.2(2)°] are rather acute, but both are similar to that found in the complex [(2-Me_2NCH_2-C_6H_4)$_2$($MeCO_2$)PtHg(O_2CMe)] [80.4(2)°].[19a,b] A noteworthy feature of complex **4** is the presence of the dianionic acac^{2-} ligand, which bridges two mercury atoms [Hg(1), Hg(2)] through its central carbon [C(26)]. As far as we know, only one compound, [{HgCl}$_2$(μ^2-acac^{2-}-κC^3)],[29] showing this unusual coordination mode for the acac^{2-} ligand has been

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reported to date. Atom C(26) is bonded to four atoms [Hg(1), Hg(2), C(27), C(29)], displaying a tetrahedral environment. The Hg(1)−C(26)−Hg(2) angle [98.5(4)°] shows the largest deviation from the ideal tetrahedral value. The distance C(26)−Hg(2) [2.110(19) Å] is very similar to C(26)−Hg(1) [2.157(11) Å] and to that observed in other complexes containing Hg−C σ bonds.[3,4b,19c−f,29]

The atom Hg(2) is bonded to C(26) of the acac^{2-} ligand, to O(7) of a monodentate acetate ligand, and to O(6a) from the acac^{2-} ligand of the second Pt{CH$_2$−C$_6$H$_4$−P(*o*-tolyl)$_2$-κC,P}(μ-O$_2$CR)$_2$Hg(μ^3-acac^{2-}-κC^3,O)Hg(O$_2$CR-κO) unit. Hg(2) shows a T-shaped coordination environment with two short distances to C(26) [2.110(10) Å] and O(7) [2.104(9) Å] and a longer one to O(6a) [2.654(9) Å]. The angles around Hg(2) are similar to those observed in other mercury complexes showing the same coordination environment.[19a,b,30] The distance Hg(2)−O(7) is similar to those observed in other complexes containing mercury bonded to a monodentate acetate group, such as [(2-Me$_2$NCH$_2$-C$_6$H$_4$)$_2$-(MeCO$_2$)PtHg(O$_2$CMe)] [Hg−O = 2.10(1) Å],[19a,b] C$_6$H$_5$-Hg(O$_2$CMe) [Hg−O = 2.11(4) Å],[31] and [Pd(S$_2$CNMe$_2$)-{μ-P(*o*-tolyl)$_2$-C$_6$H$_4$-CH$_2$}(μ-O$_2$CCH$_3$)Hg(O$_2$CCH$_3$)] [Hg−O = 2.120(5) Å].[5] The Hg(2)−O(6a) bond distance [2.654(9) Å] is very long although within the range of distances observed for Hg−O bonds (2.07−2.666 Å).[32]

Spectroscopic Behavior of 4 and 5. The NMR spectra of **4** and **5** in solution show only the signals due to one trinuclear unit Pt{CH$_2$-C$_6$H$_4$-P(*o*-tolyl)$_2$-κC,P}(μ-O$_2$CR)$_2$Hg(μ-acac^{2-}-κC^3)Hg(O$_2$CR-κO).

The ^{31}P{^{1}H} NMR spectra of both complexes show only one singlet flanked by the ^{195}Pt satellites. For complex **4** the singlet is also flanked by two satellites due to the coupling ^{199}Hg−P (I = 1/2, 16.8%), which means that the platinum−mercury bond is present in solution. The value of $^2J_{\mathrm{Hg-P}}$ (111.8 Hz) is in agreement with the *cis* disposition of the two groups relative to the platinum atom.[33] The ^{1}H NMR spectra of both complexes and the ^{19}F{^{1}H} NMR spectrum of **5** show the signals corresponding to one C∧P group, to the acac^{2-} ligand, and to three inequivalent carboxylate groups (see Experimental Section). In complex **4**, seven methyl groups are present. The assignments of these signals to the positions found in the spectrum were done with the help of HETCOR and NOE experiments (Supporting Information). It should be noted that the two diasterotopic COCH$_3$ groups of the acac^{2-} ligand are isochronous. The coincidence in the frequency of the methyl hydrogen atoms indicates that all of them have very similar chemical environments. Because of that, it is reasonable to conclude that in solution the equivalence of the two trinuclear fragments is more probably due to the breaking of the interaction Hg···O(acac^{2-}) than to the symmetry of the hexanuclear molecules. The other ^{1}H and ^{19}F NMR data are those expected on the basis of the solid-state structure of **4** as well as for the trinuclear fragments probably present in solution and merit no further comment.

The ^{13}C NMR signals of the acac derivatives provide very useful structural information. The ^{13}C{^{1}H} NMR spectrum of complex **4** shows, at room temperature, an important downfield shift of the carbonyl resonances when compared to complexes **1**, **2**, or **3**. These shifts can be understood as the result of a high keto character of the acac ligand in this complex, in agreement with its solid-state structure.[7a] Unfortunately, the signal due to the C^3 atom cannot be observed in the spectrum. The scarce solubility of **5** and the presence of F atoms in the complex hindered the observation of relevant ^{13}C NMR signals corresponding to the acac^{2-} and CF$_3$COO$^-$ groups.

Conclusion

In this report we describe the reactivity between [M(C∧P)(acac-O,O′)] [M = Pt (**1**), Pd (**1′**); C∧P = CH$_2$-C$_6$H$_4$-P(*o*-tolyl)$_2$-κC,P; acac = 2,4-pentanedionato] and HgX$_2$ (X = I, Br, CH$_3$COO, CF$_3$COO). The results show once again the different behavior between platinum and palladium and also between the mercury salts probed.

When M = Pt, the electrophilic attack of the Hg(II) salt HgX$_2$ (X = I, Br) takes place at the metal center instead of at C^3 of the acac ligand, affording the compounds [Pt(C∧P)(acac-O,O′)HgI(μ-I)]$_2$ (**2**) and [{Pt(C∧P)-(acac-O,O′)HgBr(μ-Br)}$_2$(μ-HgBr$_2$)] (**3**). The binding between the metal fragments, as established in the crystal structure of **3**, is through a direct Pt-to-Hg donor bond not supported by any bridging ligand. In compound **3** both Pt centers show a square-pyramidal coordination geometry with the Hg atom in the apical position. The Hg atoms bonded to Pt show distorted tetrahedral environments, common in Hg(II) derivatives with the stoichiometry [HgXL(μ-X)]$_2$. Also, **3** contains a third Hg atom which is bonded to four Br atoms in an unexpected square-planar geometry, unprecedented for halomercurates(II).

In light of the recently observed reactions between [Ni(tmtaa)] and HgBr$_2$ to give [Ni(tmtaa)HgBr]$_2$-[Hg$_2$Br$_6$][H$_2$tmtaa = 5,14-dihydro-6,8,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine), in which the Hg atom is bonded to the central carbon of the six-membered β-diiminate chelate rings,[34] and considering the less nucleophilic character of Pd with respect to Pt, in the reactions between [Pd(C∧P)(acac-O,O′)] (**1′**) and HgX$_2$ (X = I, Br) we expected to obtain mixed Pd/Hg compounds with the metal fragments connected through the nucleophilic central carbon of the β-diketonate ring. However, the compounds [Pd(C∧P)(μ-X)]$_2$ (X = Br, I) were obtained, which result from the substitution of acac$^-$ by X$^-$ from the coordination environment of the Pd center.

The complex [Pt(C∧P)(acac-O,O′)] (**1**) also reacts with Hg(O$_2$CR)$_2$ (R = CH$_3$, CF$_3$) but in 1:2 molar ratio to give the neutral hexanuclear complexes [Pt(C∧P)(μ-O$_2$CR)$_2$Hg-(μ^3-acac^{2-}-κC^3,O)Hg(O$_2$CR-κO)]$_2$ [R = CH$_3$ (**4**), CF$_3$ (**5**)]. The structures of **4** and **5** imply that displacement of the acac ligand from **1** by the carboxylate groups of one Hg(O$_2$CR)$_2$ unit followed by deprotonation of its central

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carbon by another $Hg(O_2CR)_2$ unit occurs during complex formation. It is worthwhile to note that in compound **4** the Pt−Hg bond distance [2.6498(9) Å] is extremely short considering that the metal−metal bond is better described as a Pt → Hg donor bond with both metals in a formal oxidation state of II. Although the ability of Hg(II) salts to activate C−H bonds from carbonyl compounds is well known,[35] compound **4** is only the second example, characterized by X-ray diffraction, of a μ^2-acac^{2-}-κC^3 ligand, and the first with this ligand asymmetrically dimercurated.

The reactions of [Pd(C∧P)(acac-O,O′)] (**1′**) with $Hg(O_2CR)_2$ (R= CH_3, CF_3) seem to proceed similarly. However, the poor ability of palladium(II) to form Pd → Hg donor bonds, which is reflected in the absence of Pd → Hg complexes,[5,36,46] leads to rapid decomposition of the first products formed, presumably analogous to those isolated for Pt, giving $[Pd(C{\wedge}P)(\mu\text{-}O_2CR)]_2$ (R = CH_3, CF_3) as the final products in high yield.

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Supporting Information Available: Tables of atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for complexes **3** and **4**; for complexes **1** and **4** $^1H-^{13}C$ HETCOR NMR spectra; for complex **4** a NOE spectrum. This material is available free of charge via Internet at. http://pubs.acs.org.

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