Reactivity of [M(C∧P)(S_2CNMe_2)] [M = Pt, Pd; C∧P = $CH_2-C_6H_4-P(o\text{-tolyl})_2$-κC,P] toward Mercury(II) Carboxylates. X-ray Molecular Structures of [Pt(C∧P)(S_2CNMe_2)(O_2CCF_3)Hg(O_2CCF_3)] and [Pd(S_2CNMe_2){μ-$P(o\text{-tolyl})_2-C_6H_4-CH_2-$}(μ-$O_2CCH_3$)Hg($O_2CCH_3$)]

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The reaction of the complex [Pt{$CH_2-C_6H_4-P(o\text{-tolyl})_2$-κC,P}($S_2CNMe_2$)] (**A**) with an equimolar amount of Hg(O_2CR)$_2$ (R = CH_3, CF_3) gives the binuclear compounds *OC-6-23* [Pt(C∧P)(S_2CNMe_2)(O_2CR)Hg(O_2CR)] [R = CH_3 (**1**), CF_3 (**2**)] containing a Pt−Hg covalent bond. These compounds result from the cis oxidative addition of the mercury(II) carboxylate to complex **A**. A concerted mechanism involving a platinum to mercury donor bond intermediate is proposed. The reaction of the complex [Pd{$CH_2-C_6H_4-P(o\text{-tolyl})_2$-κC,P}($S_2CNMe_2$)] (**B**) with Hg($O_2CR$)$_2$ (R = CH_3, CF_3) in a 1:1 molar ratio leads to the corresponding binuclear complexes [Pd(S_2CNMe_2){μ-$P(o\text{-tolyl})_2-C_6H_4-CH_2-$}(μ-$O_2CR$)Hg($O_2CR$)] [R = CH_3 (**3**), CF_3 (**4**)] with the bidentate C∧P ligand acting as an unusual bridging group. Compounds **3** and **4** come from a transmetalation process without the complete transference of the ligand from Pd to Hg.

Introduction

Metal−metal bonding in heteronuclear complexes containing d^8 and d^{10} metal ions has been known for some years.[1] In our group much work has been carried out 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.

There has been a progressive increase in the use of monoanionic chelating ligands in organometallic chemistry[4] since these ligands enhance the reactivity of the metal center, stabilize a variety of metal oxidation states, control the metal stereochemistry, and do not readily dissociate from the metal, as this would require the breaking of a σ-metal−carbon bond. Metal complexes based on such ligands are now becoming more and more important in homogeneous catalysis.[5]

We have previously described the synthesis of several complexes containing the monoanionic chelating ligand {$CH_2-C_6H_4-P(o\text{-tolyl})_2$-κC,P},[6] such as the neutral complexes [M{$CH_2-C_6H_4-P(o\text{-tolyl})_2$-κC,P}($S_2C-Z$)] [M = Pt, Pd; Z = NMe_2, OEt], and we have demonstrated their ability to form a donor−acceptor Pt−M′ bond [M′ = Hg, Ag, Au]. For M′ = Ag, Au, there are polynuclear compounds containing not only Pt→M′ interactions but also S−M′ bonds.[7] For M′ = Hg, [{Pt{$CH_2-C_6H_4-P(o\text{-tolyl})_2$-κC,P}($S_2C-Z$)HgX(μ-X)}$_2$] [Z = NMe_2, OEt; X = Br, I] compounds were formed by reaction of [Pt{$CH_2-C_6H_4-P(o\text{-tolyl})_2$-κC,P}($S_2C-Z$)] [Z = NMe_2, OEt] with HgX_2, in which the platinum fragments were connected to mercury through unsupported Pt→Hg donor−acceptor bonds.[6b] These facts indicate that in these kind of complexes the metal center (Pt) acts as a Lewis base toward suitable Lewis acids.

To extend the study of the reactivity of [M{$CH_2-C_6H_4-P(o\text{-tolyl})_2$-κC,P}($S_2CNMe_2$)] [M = Pt (**A**), Pd (**B**)] compounds toward other mercury(II) derivatives, we decided to examine the behavior of such compounds toward Hg(O_2CCH_3)$_2$ and Hg(O_2CCF_3)$_2$. As a result of this work, in this paper we report the synthesis, structural characterization, and NMR studies of new mixed Pt−Hg and Pd−Hg complexes.

(1) (a) Coffey, E.; Lewis, J.; Nyholm, R. S. *J. Chem. Soc.* **1964**, 1741. (b) Kuyper, J.; Vrieze, K. *J. Organomet. Chem.* **1976**, *107*, 129.

(2) (a) Usón, R.; Forniés, J. *J. Adv. Organomet. Chem.* **1988**, *28*, 219. (b) Usón, R.; Forniés, J. *Inorg. Chim. Acta* **1992**, *198−200*, 165.

(3) Usón, R.; Forniés, J.; Falvello, L. R.; Ara I.; Usón, I. *Inorg. Chim. Acta* **1993**, *212*, 105.

(4) (a) Maestri, M.; Sandrini, D.; von Zelewsky, A.; Deuschel-Cornioley, C. *Inorg. Chem.* **1991**, *30*, 2476. (b) Maestri, M.; Deuschel-Cornioley, C.; von Zelewsky, A. *Coord. Chem. Rev.* **1991**, *111*, 117. (c) Gruter, G.-J. M.; van Klink, G. P. M.; Akkerman, O. S.; Bickelhaupt, F. *Chem. Rev.* **1995**, *95*, 2405. (d) van der Boom, M. E.; Lion, S.-Y.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. *Organometallics* **1996**, *15*, 2562. (e) Rybtchinski, B.; Vigalok, A.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **1996**, *118*, 12406. (f) van der Boom, M. E.; Kraatz, H.-B.; Ben-David, Y.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1996**, 2167.

(5) (a) Herrmann, W. A.; Brossmer, C.; Öfele, K.; Reisinger, C. P.; Priermeier, T.; Beller, M.; Fischer, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1844. (b) Beller, M.; Fischer, H.; Herrmann, W. A.; Öfele, K.; Brossmer, C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1848. (c) Shaw, B. L.; Perera, S. D.; Staley, E. A. *J. Chem. Soc., Chem. Commun.* **1998**, 1361. (d) Ohff, M.; Ohff, A.; van der Boom, M. E.; Milstein, D. *J. Am. Chem. Soc.* **1997**, *119*, 11687.

(6) (a) Forniés, J.; Martín, A.; Navarro, R.; Sicilia, V.; Villarroya, P. *Organometallics* **1996**, *15*, 1826. (b) Falvello, L. R.; Forniés, J.; Martín, A.; Navarro, R.; Sicilia, V.; Villarroya, P. *Inorg. Chem.* **1997**, *36*, 6166.

(7) Forniés, J.; Martín, A.; Navarro, R.; Sicilia, V.; Villarroya, P.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1998**, 3721.

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Experimental Section

Elemental analyses were determined using a Perkin-Elmer 240-B microanalyzer. IR spectra were recorded on a Perkin-Elmer 599 spectrophotometer (Nujol mulls between polyethylene plates in the range 4000−200 cm^{-1}). NMR spectra were recorded on either a Varian XL-200 or a Varian Unity 300 NMR spectrometer using the standard references. [Pt{CH_2−C_6H_4−P(*o*-tolyl)$_2$-*κC,P*}(S_2CNMe_2)] (**A**)[6a] and [Pd{CH_2−C_6H_4−P(*o*-tolyl)$_2$-*κC,P*}(S_2CNMe_2)] (**B**)[6b] were prepared as described elsewhere.

[Pt{CH_2−C_6H_4−P(*o*-tolyl)$_2$-*κC,P*}(S_2CNMe_2)(O_2CCX_3)-Hg(O_2CCX_3)] [X = H (1), F (2)]. X = H (1). To a cooled solution of [Pt{CH_2−C_6H_4−P(*o*-tolyl)$_2$-*κC,P*}(S_2CNMe_2)] (**A**) (0.1950 g, 0.3151 mmol) in $CHCl_3$ (25 mL) at −20 °C was added Hg(O_2CCH_3)$_2$ (0.1004 g, 0.3151 mmol). The solution, which immediately acquired a bright yellow color, was stirred for 2 h at this temperature. It was then filtered through Celite and evaporated to dryness. Addition of diethyl ether to the residue at −20 °C afforded a yellow solid, **1** (0.2207 g, 74.7%) (Found: C, 36.17; H, 3.49; N, 1.51. $C_{28}H_{32}HgNO_4PPtS_2$ requires C, 35.88; H, 3.44; N, 1.49). IR (ν/cm^{-1}): 458m, 476m, 488m, 508w, 523m, 535m, 553m, 566m, 583m, 671m, 756s, 974m ν(C−S), 1538 ν(C−N) ($Me_2NCS_2^-$), 1566m, 1576m ($CH_3CO_2^-$). ^{1}H NMR ($CDCl_3$, 223 K) δ: 1.91 (s, CH_3 acetate), 1.97 (s, $CH_{3\ C\wedge P}$), 2.05 (s, $CH_{3\ C\wedge P}$), 2.11 (s, CH_3 acetate), 2.96 (s, CH_3 carbamate), 3.12 (s, CH_3 carbamate), 3.90 (ν_A, $^2J_{PtH}$ = 95.9 Hz, $^2J_{HH}$ = 14.3 Hz, CH_2), 4.34 (ν_B, $^2J_{PtH}$ = 73.3 Hz, $^2J_{HH}$ = 14.3 Hz, CH_2), 6.49 (dd, H6′, $^3J_{PH}$ = 13.2 Hz, $^3J_{H6'H\ 5'}$ = 7.6 Hz), 7.0−7.5 (m, 10H, C_6H_4), 8.22 (ddd, H6, $^3J_{PH}$ = 17.5 Hz, $^3J_{H6H5}$ = 7.7 Hz, $^4J_{H6H4}$ = 1.8 Hz). ^{13}C{^{1}H} δ: 10.03 (s, CH_2), 20.95 (d, $^3J_{PC}$ = 7.1 Hz, $Me_{C\wedge P}$), 23.16 (s, $Me_{acetate}$), 23.51 (d, $^3J_{PC}$ = 3.1 Hz, $Me_{C\wedge P}$), 24.31 (s, $Me_{acetate}$), 37.45 (s, $Me_{carbamate}$), 39.83 (s, $Me_{carbamate}$), 120−160 (m, C_6H_4) 176.80 (s, CO_2), 177.29 (s, CO_2), 205.58 (s, CS_2).

X = F (2). This complex was prepared in a similar way to **1** with [Pt{CH_2−C_6H_4−P(*o*-tolyl)$_2$-*κC,P*}(S_2CNMe_2)] (**A**) (0.2002 g, 0.3235 mmol) and Hg(O_2CCH_3)$_2$ (0.138 g, 0.3235 mmol). Yield: 0.2775 g, 82% (Found: C, 32.51; H, 2.55; N, 1.39. $C_{28}F_6H_{26}HgNO_4PPtS_2$ requires C, 32.17; H, 2.50; N, 1.34). IR (ν/cm^{-1}): 456m, 477m, 487m, 503w, 525m, 535m, 553m, 568m, 584m, 753m, 766m, 791s, 845s, 970m ν(C−S), 1556 ν(C−N) ($Me_2NCS_2^-$), 1151vs, 1192vs, 1667vs, 1684vs ($CF_3CO_2^-$). ^{1}H NMR ($CDCl_3$, 223 K) δ: 1.99 (s, $CH_{3\ C\wedge P}$), 2.01 (s, $CH_{3\ C\wedge P}$), 2.99 (s, $CH_{3\ carbamate}$), 3.19 (s, $CH_{3\ carbamate}$), 4.10 (ν_A, $^2J_{PtH}$ = 102.5 Hz, $^2J_{HH}$ = 14.2 Hz, CH_2), 4.44 (ν_B, $^2J_{PtH}$ = 78.0 Hz, $^2J_{HH}$ = 14.2 Hz, CH_2), 6.50 (dd, H6′, $^3J_{PH}$ = 13.4 Hz, $^3J_{H6'H\ 5'}$ = 7.6 Hz), 7.1−7.6 (m, 10H, C_6H_4), 8.06 (dd, H6, $^3J_{PH}$ = 17.9 Hz, $^3J_{H6H5}$ = 7.3 Hz). ^{19}F NMR δ: −73.38 (s), −74.16 (s). ^{13}C{^{1}H} δ: 12.65 (s, CH_2), 20.80 (s, $Me_{C\wedge P}$), 23.46 (s, $Me_{C\wedge P}$), 37.38 (s, $Me_{carbamate}$), 39.89 (s, $Me_{carbamate}$), 110−160 (m, C_6H_4, CF_3) 160.57 (q, $^2J_{CF}$ = 36.22 Hz, CO_2), 162.34 (q, $^2J_{CF}$ = 36.22 Hz, CO_2), 203.81 (s, CS_2).

[Pd(S_2CNMe_2){*μ*-P(*o*-tolyl)$_2$−C_6H_4−CH_2−}(*μ*-O_2CCX_3) Hg-(O_2CCX_3))] [X = H (3), F (4)]. X = H(3). To a solution of [Pd-{CH_2−C_6H_4−P(*o*-tolyl)$_2$-*κC,P*}(S_2CNMe_2)] (**B**) (0.1500 g, 0.283 mmol) in $CHCl_3$ (15 mL) was added Hg(O_2CCH_3)$_2$ (0.090 g, 0.283 mmol), and the solution immediately acquired a yellow-orange color. The mixture was stirred for 40 min until total solution of the Hg(O_2CCH_3)$_2$ and was then filtered through Celite. Evaporation of the solvent to dryness and addition of diethyl ether to the residue yielded **3** as a bright yellow solid (0.1890 g, 78.7%) (Found: C, 39.27; H, 3.92; N, 1.64. $C_{28}H_{32}$-$HgNO_4PPdS_2$ requires C, 39.63; H, 3.80; N, 1.65). IR (ν/cm^{-1}): 444m, 463m, 480s, 495m, 523m, 537m, 550w, 571m, 756s, sh, 969m ν(C−S), 1564 ν(C−N) ($Me_2NCS_2^-$), 1611m, 1626m ($CH_3CO_2^-$). ^{1}H NMR (CD_2Cl_2, 253 K) δ: 1.37 (s, $CH_{3\ acetate}$), 1.57 (s, $CH_{3\ C\wedge P}$), 1.90 (s, $CH_{3\ C\wedge P}$), 2.01 (s, $CH_{3\ acetate}$), 2.98 (d, $^2J_{HH}$ = 11.2 Hz, 1H, CH_2), 3.15 (s, $CH_{3\ carbamate}$), 3.22 (s, $CH_{3\ carbamate}$), 3.62 (d, $^2J_{HH}$ = 11.2 Hz, 1H, CH_2), 6.8−7.7 (m, 11H, C_6H_4), 9.06 (d, H6, $^3J_{PH}$ = 16.5 Hz). ^{13}C{^{1}H} δ: 22.32 (s, $Me_{C\wedge P,\ acetate}$), 23.53 (s, $Me_{C\wedge P}$), 23.77 (s, $Me_{acetate}$), 31.64 (d, $^3J_{PC}$ = 14.4 Hz, CH_2), 38.23 (s, $Me_{carbamate}$), 38.55 (s, $Me_{carbamate}$), 120−160 (m, C_6H_4) 175.66 (s, CO_2), 176.51 (s, CO_2), 205.16 (s, CS_2).

X = F (4). This complex was prepared in a similar way to **3** with [Pd{CH_2−C_6H_4−P(*o*-tolyl)$_2$-*κC,P*}(S_2CNMe_2)] (**B**) (0.1537 g, 0.290 mmol) and Hg(O_2CCF_3)$_2$ (0.1237 g, 0.290 mmol). Yield: 0.1334 g, 59.72% (Found: C, 35.44; H, 2.80; N, 1.53. $C_{28}F_6H_{26}HgNO_4PPdS_2$ requires C, 35.16; H, 2.74; N, 1.46). IR (ν/cm^{-1}): 442m, 461m, 480s, 501m, 523m, 536m, 551w, 573m, 751s, 760s, 787s, 818s, 968m ν(C−S), 1567vs ν(C−N) ($Me_2NCS_2^-$), 1143vs, 1168vs, 1189vs, 1676vs, 1709vs ($CF_3CO_2^-$). ^{1}H NMR (CD_2Cl_2, 188 K) δ: 1.47 (s, $CH_{3\ C\wedge P}$), 1.89 (s, $CH_{3\ C\wedge P}$), 3.05 (d, $^2J_{HH}$ = 11.0 Hz, 1H, CH_2), 3.12 (s, 6H, $CH_{3\ carbamate}$), 3.77 (d, $^2J_{HH}$ = 11.0 Hz, 1H, CH_2), 6.7−7.7 (m, 11H, C_6H_4), 8.87 (dd, H6, $^3J_{PH}$ = 16.9 Hz, $^3J_{H6H5}$ = 6.1 Hz). ^{19}F NMR δ: −73.10 (s), −73.57 (s).

X-ray Crystal Structure Determinations of [Pt{CH_2−C_6H_4−P(*o*-tolyl)$_2$-*κC,P*}(S_2CNMe_2)(O_2CCF_3)Hg(O_2C-CF_3)]·0.5Me_2CO (2) and [Pd(S_2CNMe_2){*μ*-P(*o*-tolyl)$_2$−C_6H_4−CH_2−}(*μ*-O_2CMe)Hg(O_2CMe)]·H_2O (3). Suitable crystals of **2**·0.5Me_2CO were obtained by slow diffusion of *n*-pentane in Me_2CO/CH_2Cl_2 solutions of complex **2** at 5 °C. Suitable crystals of **3**·H_2O were obtained by slow diffusion of *n*-hexane in CH_2-Cl_2 solutions of complex **3** 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 quartz fibers and mounted on diffractometers. Unit cell constants were determined from 60 accurately centered reflections with 25.9° < 2θ < 35.4° for **2**·0.5Me_2CO and 60 reflections in the range 24° < 2θ < 26° for **3**·H_2O. Data were collected using ω/θ scans for **2**·0.5Me_2CO and ω scans for **3**·H_2O. Three check reflections were measured at regular intervals, and no loss of intensity was observed in either case. The positions of the heavy atoms were determined from the Patterson maps. The remaining atoms were located in successive difference Fourier syntheses. H atoms were added at calculated positions (C−H = 0.96 Å) with isotropic displacement parameters assigned as 1.2 times the equivalent isotropic *U*'s of the corresponding C atoms. For **2**·0.5Me_2CO, there are two molecules of the platinum complex in the asymmetric part of the unit cell. Three of the four CF_3 groups of the trifluoroacetate ligands are badly disordered. This disorder has been modeled assigning two sets of positions for the fluorine atoms of each CF_3 group (0.5/0.5 occupancy). The thermal parameter of the opposite fluorine atoms have been constrained to be the same. The C−F distances have been restrained for all the CF_3 groups. The thermal parameters of the atoms of the acetone solvent molecule have been constrained to be the same. The interatomic distances in the solvent molecule have been restrained. For **2**·0.5Me_2CO a final difference electron density maps showed one peak above 1 e $Å^{-3}$ (1.37; largest diff hole −1.45) lying 1.16 Å from the mercury atom. For **3**·H_2O a final difference electron density map showed no peaks above 1 e $Å^{-3}$ (max 0.69; largest diff hole −0.81). All calculations were carried out using the program SHELXL-93.[8]

Results

Reactivity of [M{CH_2−C_6H_4−P(*o*-tolyl)$_2$-*κC,P*}-(S_2CNMe_2)] [M = Pt (A), Pd (B)] with Mercury(II) Carboxylates. Synthesis of Complexes 1−4. Complexes [M(C∧P)(S_2CNMe_2)] [M = Pt (**A**), Pd (**B**)] react in chloroform with an equimolar amount of mercury(II) carboxylates, Hg(O_2CR)$_2$ (R = CH_3, CF_3), to afford complexes **1**−**4**, as indicated in Scheme 1. All complexes are obtained in good yield and are stable for a long time in the solid state. However, in $CHCl_3$ solution, only

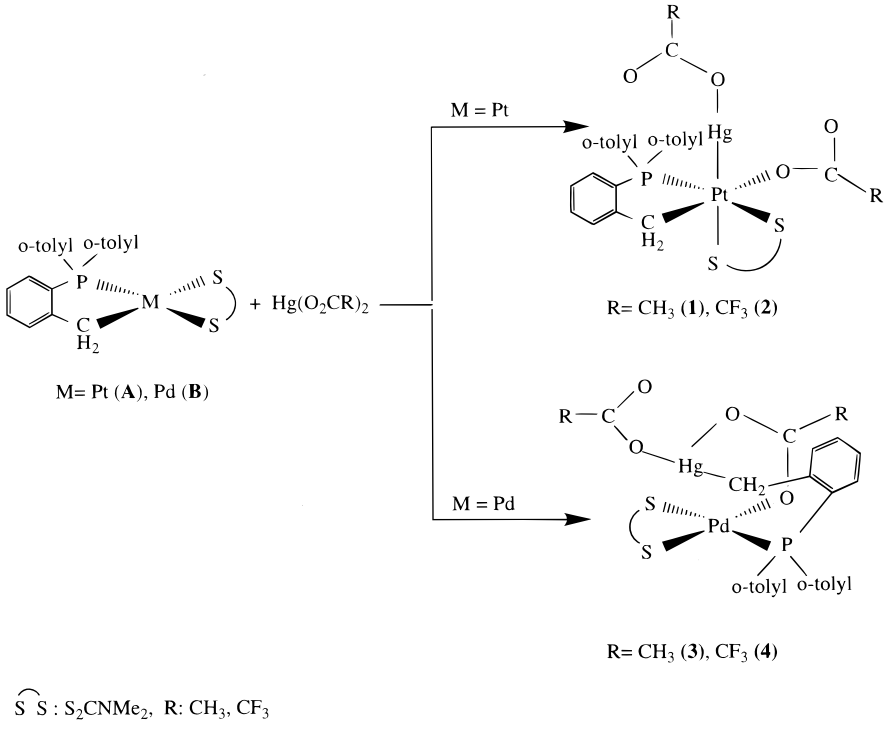
(8) Sheldrick, G. M. *SHELXL-93*, a program for crystal structure determination; University of Göttingen: Germany, 1993.

Table 1. Crystal Data and Structure Refinement Parameters for 2·0.5Me_2CO and 3·H_2O

	2·0.5Me_2CO	3·H_2O
empirical formula	$C_{30}H_{31}F_6HgNO_{4.5}PPtS_2$	$C_{28}H_{34}HgNO_5PPdS_2$
fw	2164.66	866.64
unit cell dimens		
a (Å)	14.191(12)	8.012(1)
b (Å)	14.937(12)	35.069(5)
c (Å)	19.488(15)	11.355(1)
α (deg)	111.53(5)	90
β (deg)	102.65(4)	101.31(1)
γ (deg)	101.93(4)	90
volume (Å^3), *Z*	3556.9(13), 4	3128.5(7), 4
wavelength (Å)	0.71073	0.71073
temperature (K)	173(2)	200(2)
radiation	graphite-monochromated Mo Kα	
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2(1)/n$
abs coeff (mm^{-1})	8.470	5.697
transmission factors	0.951, 0.742	0.809, 0.566
abs corr	*ψ* scans	*ψ* scans
diffractometer	Siemens STOE/AED2	Siemens STOE/AED2
2*θ* range for data collect. (deg)	4−50 (−*h*, ±*k*, ±*l*)	4−50 (+*h*, +*k*, ±*l*)
no. of reflns collected	13 065	6162
no. of ind reflns	12 475 (*R*(int) = 0.0314)	4875 (*R*(int) = 0.0388)
refinement method	full-matrix least-squares on F^2	
goodness-of-fit on F^2	1.073	1.102
final *R* indices ($I > 2\sigma(I)$)[a]	*R*1 = 0.0427, *wR*2 = 0.0838	*R*1 = 0.0297, *wR*2 = 0.0580
R indices (all data)	*R*1 = 0.0756, *wR*2 = 0.1189	*R*1 = 0.0484, *wR*2 = 0.0870

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

Scheme 1



complex **1** is unstable at room temperature and has to be handled at a low temperature (−20 °C) to avoid its decomposition.

Elemental analyses revealed the same stoichiometry for all compounds. However NMR data and the X-ray studies on complexes **2** and **3** indicated important structural differences between the platinum (**1** and **2**) and the palladium (**3** and **4**) derivatives.

Structural Characterization of Complexes 1 and 2. Compounds **1** and **2** have been formulated on the basis of their elemental analyses and NMR data together with the X-ray molecular structure of compound **2**. The ^{31}P $\{^1H\}$ NMR spectra of **1** and **2** show the presence of only one species in each case. They also show a noticeable decrease in the value of J_{Pt-P} in accordance with an increase in the oxidation state of the metal center. Evidence for a Pt−Hg bond comes from the observation of $^{199}Hg-P$ coupling (Table 2). These facts suggest that complexes **1** and **2** are the result of the oxidative addition of $Hg(O_2CR)_2$ (R = CH_3, CF_3) to complex **A**. Oxidative addition reactions of electrophiles RX to square-planar d^8 organometallic complexes often

Table 2. $^{31}P\{^1H\}$ NMR Data for Complexes 1−4[a]

complex	δP (ppm)	J_{Pt-P} (Hz)	J_{Hg-P} (Hz)
[Pt(C∧P)(S_2CNMe_2)] (**A**)	24.70 (s)	3969.4	
[Pd(C∧P)(S_2CNMe_2)] (**B**)	35.58 (s)		
1	26.98 (s)	2744.0	398.1
2	27.77 (s)	2645.74	445.20
3	21.02 (s)		
4	18.31 (s)		

[a] C∧P: $CH_2-C_6H_4-P(o\text{-tolyl})_2$. (s): singlet. [b] $CDCl_3$, 223 K. [c] CD_2Cl_2, 188 K.

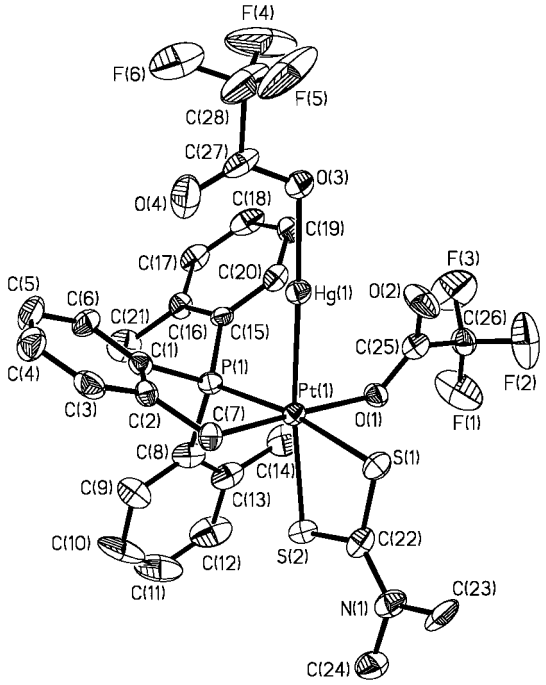


Figure 1. Molecular structure of [Pt(C∧P)(S_2CNMe_2)(O_2CCF_3)Hg(O_2CCF_3)] (**2**).

result in the formation of octahedral complexes. In **A**, two bidentate ligands are present, and consequently for the octahedral products, [Pt{$CH_2-C_6H_4-P(o\text{-tolyl})_2$-$\kappa C,P$}($S_2CNMe_2$)($O_2CCX_3$)Hg($O_2CCX_3$)], nine pairs of enantiomers are possible. The possible structure of one enantiomer for each pair is given as Supporting Information. The stereochemical descriptors recommended by IUPAC denote each enantiomer. Since the analysis of all available spectroscopic data does not allow us to distinguish among all the possible diastereomers, the molecular structure of **2** has been determined by X-ray diffraction methods. The stereogeometry of **2** is presented in Figure 1 together with the atomic labeling scheme used. Selected bond distances and angles are shown in Table 3. As can be seen, complex **2** is a binuclear platinum−mercury derivative in which the Pt−Hg distance of 2.5535(7) Å is an appropriate value for a single Pt−Hg bond. Platinum reveals a distorted octahedral coordination, with the angle between the perpendicular to the equatorial plane defined by Pt(1), O(1), S(1), C(7), P(1) and the Hg(1)−S(2) axis being 7.2°.[9] Distortion may be mainly due to the small bite angle of both chelating ligands bonded to platinum [S_2CNMe_2, 73.63(9)°; C∧P, 82.1(3)°]. Mercury has a linear environment formed by an oxygen atom of one monodentate

(9) Nardelli, M. *Comput. Chem.* **1983**, *7*, 95.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 2

Pt(1)−C(7)	2.081(9)	Pt(1)−O(1)	2.175(6)
Pt(1)−P(1)	2.285(3)	Pt(1)−Hg(1)	2.5535(7)
Pt(1)−S(1)	2.387(3)	Pt(1)−S(2)	2.411(3)
Hg(1)−O(3)	2.137(7)	N(1)−C(22)	1.317(12)
Hg(1)−Pt(1)−O(1)	94.4(2)	Hg(1)−Pt(1)−P(1)	92.34(7)
Hg(1)−Pt(1)−C(7)	87.3(3)	Hg(1)−Pt(1)−S(1)	94.36(7)
Hg(1)−Pt(1)−S(2)	167.78(7)	C(7)−Pt(1)−P(1)	82.1(3)
P(1)−Pt(1)−O(1)	98.1(2)	O(1)−Pt(1)−S(1)	87.7(2)
S(1)−Pt(1)−C(7)	91.9(3)	S(1)−Pt(1)−S(2)	73.63(9)
S(2)−Pt(1)−O(1)	87.5(2)	S(2)−Pt(1)−P(1)	99.34(10)
S(2)−Pt(1)−C(7)	90.7(3)	Pt(1)−Hg(1)−O(3)	177.4(2)

CF_3COO group [O(3)] and the Pt atom [Pt(1)−Hg(1)−O(3) = 177.4(2)°].

The Pt−Hg bond length [2.5535(7) Å] is slightly shorter than the sum of the radii for Pt and Hg (2.632 Å) calculated from *trans*-[$PtCl_3\{(E)$-NH=C(OMe)Me$\}_2$]$_2$ [Pt−Pt = 2.758(3) Å][10] and Hg_2Cl_2 [Hg−Hg = 2.507 Å],[11] which have a single unsupported metal−metal bond. Similar Pt−Hg distances have been reported in other compounds exhibiting Pt−Hg covalent bonds: [(2-$Me_2NCH_2-C_6H_4)_2$(μ-$MeCO_2$)PtHg(O_2CMe)] [2.513(1) Å];[12] [$(PPh_3)_2$R−Pt−Hg−R] [2.637(1) Å];[13] [PhCH[HgPt-$(PPh_3)_2$Br]$COOC_{10}H_{19}$] [2.499 Å];[14] [$N(CH_2CH_2PPh_2)_3$-Pt(HgMe)]BPh_4 [2.531 (1) Å];[15] [PtCl(HgMe)(dmphen)(*Z*-$MeO_2-CCH=CHCO_2Me$)] [2.558 (1) Å].[16] In contrast the Pt−Hg distance is clearly different from those observed in mixed Pt−Hg compounds in which the metal interaction has been described as a $Pt^{II}\rightarrow Hg^{II}$ donor bond: [{2,6-$(Me_2NCH_2)_2-C_6H_3$}Pt(μ-{*p*-tol″NC(H)N(^{i}Pr)}Hg-BrCl] [2.8331(7) Å],[17] *trans*-[$(CH_3NH_2)_2$Pt(1,5-diMeC^-)$_2$-Hg]$(NO_3)_2\cdot 0.5H_2O$ [2.765(1) Å],[18] *trans*-[$(CH_3NH_2)_2$Pt(1-MeC^-)$_2$HgCl(NO_3)] [2.835(1) Å],[18] *trans*-[$(CH_3NH_2)_2$Pt(1-MeC^-)$_2$Hg]$(NO_3)_2$ [2.785(1) Å],[18] and [{Pt{$CH_2-C_6H_4-P(o\text{-tolyl})_2$-$\kappa C,P$}($S_2C-Z$)HgX($\mu$-X)}$_2$] [Z = NMe_2, OEt; X = Br, I].[6b]

It is noteworthy that although complex **2** has been obtained in a similar way to that described by van Koten et al., [(2-$Me_2N-CH_2-C_6H_4)_2$(μ-$MeCO_2$)PtHg(O_2CMe)],[12] in our complex the Pt−Hg bond is not supported by an acetato group. Despite this difference both Pt−Hg distances are quite similar. Both acetate groups are coordinated to Pt and Hg in a monodentate fashion. The Pt−O(1) [2.175(6) Å] distance is slightly longer than those observed in other platinum derivatives with monodentate acetate groups, [Pt$(O_2CCF_3)_2$(dppm)] [2.080-(4), 2.074(4) Å][19] and [$PtCl_2(O_2CCH_3)_2(C_6H_{13}N)(NH_3)$]

(10) Bandoli, G.; Caputo, P. A.; Intini, F. P.; Sivo, M. F.; Natile, G. *J. Am. Chem. Soc.* **1997**, *119*, 10370.
(11) Dorn, E. *J. Chem. Soc., Chem. Commun.* **1971**, 466.
(12) (a) van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K.; Spek, A. L.; Duisenberg, A. J. M. *J. Chem. Soc., Chem. Commun.* **1980**, 469. (b) van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K.; Spek, A. L. *Inorg. Chem.* **1982**, *21*, 2014.
(13) Rossell, O.; Seco, M.; Torra, I.; Solans, X.; Font-Altaba, M. *J. Organomet. Chem.* **1984**, *270*, C63.
(14) Suleimanov, G. Z.; Bashilov, V. V.; Musaev, A. A.; Sokolov, V. I.; Reutov, O. A. *J. Organomet. Chem.* **1980**, *202*, C61.
(15) Ghilardi, C. A.; Midollini, S.; Moneti, S.; Orlandini, A.; Scapacci, G.; Dakternieks, D. *J. Chem. Soc., Chem. Commun.* **1989**, 1686.
(16) Cucciolito, E.; Giordano, F.; Panunzi, A.; Rufo, F.; de Felice, V. *J. Chem. Soc., Dalton Trans.* **1993**, 3421.
(17) van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K.; Spek, A. L.; Duisenberg, A. J. M. *Organometallics* **1982**, *1*, 1066.
(18) Krumm, M.; Zangrando, E.; Randaccio, L.; Menzer, S.; Danzmann, A.; Holthenrich, D.; Lippert, B. *Inorg. Chem.* **1993**, *32*, 2183.
(19) Tan, A. L.; Low, P. M. N.; Zhou, Z.-Y.; Zheng, W.; Wu, B. M.; Mak, T. C. W.; Hor, T. S. A. *J. Chem. Soc., Dalton Trans.* **1996**, 2207.

[2.06(2) Å],[20] probably due to the trans influence of the *σ*-bonded carbon atom [C(7)]. The Hg−O(3) bond length [2.137(7) Å] is similar to that observed in [(2-Me$_2$N−CH$_2$−C$_6$H$_4$)$_2$(*μ*-MeCO$_2$)PtHg(O$_2$CMe)] [Hg−O = 2.10(1) Å] for the monodentate acetate group.[12] Pt−P, Pt−C, and Pt−S bond distances are similar to those found in other complexes containing this kind of ligand.[6,7] The S$_2$CNMe$_2$ group is perfectly planar, and the C(22)−N(1) bond length [1.317(12) Å] indicates a marked degree of C−N double bond,[21] as is usual for dithiocarbamate ligands.[22] In accordance with what is usually observed, the five-membered metallacycle is not planar but rather is bent through the P(1)−C(7) vector in such a way that the angle between the equatorial plane [Pt(1), O(1), S(1), C(7), P(1)] and the best plane calculated for P(1), C(1), C(2), C(7) is 24.4°.[9]

The two unmetalated *o*-tolyl groups are planar and are oriented forming angles of 99.3° [C(8)−C(14)] and 11.5° [C(15)−C(21)] with their corresponding Pt−P−C$_{ipso}$ planes.

As for [(2-Me$_2$N−CH$_2$−C$_6$H$_4$)$_2$(*μ*-MeCO$_2$)PtHg(O$_2$C-Me)],[12] the solid-state structure of **2** shows coordination geometries for Pt and Hg that are comparable with those of Pt(IV) and Hg(II) when Pt and Hg are considered as ligands for each other.

The spectroscopic NMR data obtained in solution for **1** and **2** allow us to assign the same structure for them and confirm that the structure observed for **2** in the solid state is maintained in solution. The ^{31}P NMR spectra of **1** and **2** show only a singlet flanked by satellites due to ^{195}Pt−P and ^{199}Hg−P couplings. The values of the ^{195}Pt−P coupling constants, about 1250 Hz less than in the starting complex **A**, are in agreement with a higher oxidation state of the platinum center.[23] These values, close to 2700 Hz, are similar to those observed in the Pt(IV) complexes [Pt{CH$_2$−C$_6$H$_4$−P(*o*-tolyl)$_2$-*κC,P*}(S$_2$-CNMe$_2$)X$_2$] (X = Cl, Br, I).[6a] The values of the ^{199}Hg−P coupling constant (**1**, 398.1 Hz; **2**, 445.2 Hz) are as expected for a Pt−Hg bond cis to the phosphorus atom in these complexes.[24] These spectroscopic features point out that the oxidative addition of Hg(O$_2$CR)$_2$ (R = CH$_3$ (**1**), CF$_3$(**2**)] to compound **A** is stereoselective, affording only the isomer *OC-6-23* (Scheme 1) in each case.

The ^{1}H and ^{13}C NMR data can also be interpreted in terms of this geometry. The ^{1}H NMR spectra of complexes **1** and **2** in CDCl$_3$ at 223 K display a common pattern due to the metalacycle "Pt{CH$_2$−C$_6$H$_4$−P(*o*-tolyl)$_2$-*κC,P*}" (see Experimental Section): (a) two singlets at ca. 2 ppm due to the methyl of the inequivalent *o*-tolyl groups; (b) a multiplet close to 4 ppm due to the methylene group which appears as an AB system with a $^2J_{H-H}$ close to 14 Hz; both hydrogen atoms also appear coupled to ^{195}Pt (*I* = 1/2, 33%), indicating the existence of a Pt−C bond in the complex;[25] (c) several signals between 6.5 and 8.5 ppm corresponding to the aromatic hydrogen atom. Two signals appear separately at about 6.5 and 8.0 ppm, which can be unambiguously assigned to the ortho-hydrogen [H6] of each inequivalent *o*-tolyl group. The values of the P−H6 and H6−H5 coupling constants were calculated in all cases, the $^3J_{P-H}$ being similar to those observed in other complexes with arylphosphine ligands.[26] These spectra also show two singlets at about 3 ppm for the S$_2$CNMe$_2$ ligand, in agreement with its chelate coordination mode.[27] The two inequivalent CX$_3$COO$^-$ groups give two singlets in the ^{1}H or ^{19}F NMR spectra of **1** (X = H) and **2** (X = F), respectively. The correct assignments of the signals due to methyl groups in the ^{1}H NMR spectrum of **1** could be carried out with the help of a HETCOR experiment[28] and are submitted as Supporting Information.

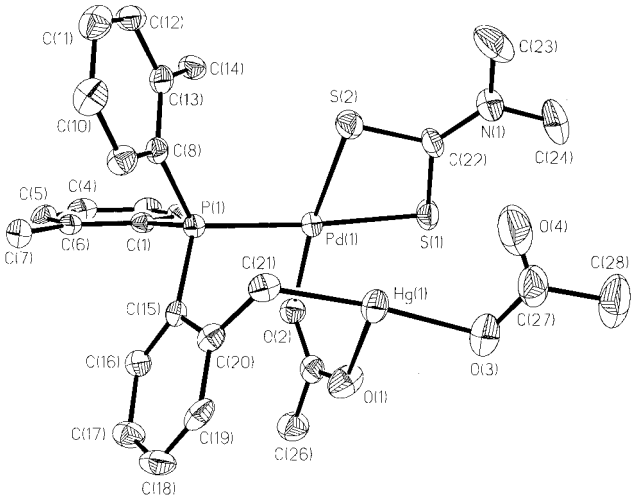


Figure 2. Molecular structure of [Pd(S$_2$CNMe$_2$){*μ*-P(*o*-tolyl)$_2$−C$_6$H$_4$−CH$_2$−}(*μ*-O$_2$CCH$_3$)Hg(O$_2$CCH$_3$)] (**3**).

The ^{13}C NMR spectra of **1** and **2** in CDCl$_3$ at 223 K display the expected signals for the ligands present in such complexes and show the inequivalence of the two carboxylate groups, in agreement with the structure observed in the solid state for complex **2**, but they are not worthy of further comment (see Experimental Section)

Structural Characterization of Complexes 3 and 4. The molecular structure of **3** is represented in Figure 2 together with the atomic labeling scheme. Bond distances and angles are indicated in Table 4.

As can be seen, complex **3** is a Pd/Hg binuclear derivative in which both metal centers are bridged by two bidentate ligands (CH$_3$COO$^-$, P(*o*-tolyl)$_2$−C$_6$H$_4$−CH$_2$-*κC,P*). The intermetallic distance is 3.1726(12) Å.

The palladium center is located in a distorted square-planar environment. The angles between adjacent atoms in the coordination sphere of palladium lie in the range 75.66(7)−99.96(7)°, the smallest angle corresponding to the dimethyldithiocarbamate ligand.

(20) Neidle, S.; Snook, C.; Murrer, B. A.; Bernard, C. F. J. *Acta Crystallogr. Sect. C* **1995**, *51*, 822.
(21) Pauling, L. *The Nature of the Chemical Bond*, 2nd ed.; Cornell University Press: Ithaca, NY, 1960.
(22) Chan, L. T.; Chen, H.-W.; Fackler, J. P.; Masters, A. F.; Pan, W.-H. *Inorg. Chem.* **1982**, *21*, 4291.
(23) Parish, R. V. *NMR, NQR, EPR and Mössbauer Spectroscopy in Inorganic Chemistry*; Ellis Horwood Ltd: New York, 1990.
(24) (a) Tanase, T.; Yamamoto, Y.; Puddephatt, R. J. *Organometallics* **1996**, *15*, 1502. (b) van Vliet, P. I.; Kuyper, J.; Vrieze, K. *J. Organomet. Chem.* **1976**, *122*, 99.
(25) Kuyper, J. *Inorg. Chem.* **1978**, *17*, 1458.
(26) (a) Okeya, S.; Miyamoto, T.; Ooi, S.; Nakamura, Y.; Kawaguchi, S. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 395. (b) Ooi, S.; Matsushita, T.; Nishimoto, K.; Nakamura, Y.; Kawaguchi, S.; Okeya, S. *Inorg. Chim. Acta* **1983**, *76*, L55. (c) Widenhoefer, R. A.; Zhong, H. A.; Buchwald, S. L. *Organometallics* **1996**, *15*, 2745.
(27) (a) Fackler, J. P., Jr.; Lim, I. J. B.; Andrews, J. *Inorg. Chem.* **1977**, *16*, 450. (b) Narayan, S.; Jain, V. K.; Chaudhury, S. *J. Organomet. Chem.* **1997**, *530*, 101.
(28) (a) Croosmur, W. R.; Carlson, R. M. K. *Two-Dimensional NMR Spectroscopy*, 2nd ed.; VCH: New York, 1994. (b) Sanders, J. K. M.; Hunter, B. K. *Modern NMR Spectroscopy*, 2nd ed.; University Press: Oxford, 1993.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 3

Pd(1)−S(1)	2.364(2)	Pd(1)−S(2)	2.307(2)
Pd(1)−P(1)	2.322(2)	Pd(1)−O(2)	2.081(4)
Hg(1)−C(21)	2.103(6)	Hg(1)−O(1)	2.639(4)
Hg(1)−O(3)	2.120(5)	N(1)−C(22)	1.314(8)
S(1)−Pd(1)−S(2)	75.66(6)	S(1)−Pd(1)−O(2)	97.64(11)
O(2)−Pd(1)−P(1)	86.78(11)	P(1)−Pd(1)−S(2)	99.96(6)
O(3)−Hg(1)−C(21)	170.9(2)	O(3)−Hg(1)−O(1)	82.3(2)
O(1)−Hg(1)−C(21)	101.1(2)	Hg(1)−C(21)−C(20)	110.0(4)

The $Me_2NCS_2^-$ ligand is planar and nearly coplanar with the palladium coordination plane (interplanar angle 5.16°).[9] Bond distances and angles in the ligand indicate a pronounced degree of C−N double bounding,[21] as usual for dithiocarbamate ligands.[22]

The Pd−S, Pd−P, and Pd−O bond distances are in the range of distances found in other palladium derivatives containing this type of ligand.[5a,6b,29]

As in the complex [PdBr(S_2COEt){μ-P(*o*-tolyl)$_2$−C_6H_4−CH_2−}HgBr],[6b] the Pd−P length [2.321(2) Å] is longer than that observed in complexes in which this C∧P group acts as a chelate ligand: [Pd{CH_2−C_6H_4−P(*o*-tolyl)$_2$-$\kappa C,P$}(μ-I)]$_2$[30] and [Pd{CH_2−C_6H_4−P(*o*-tolyl)$_2$-$\kappa C,P$}(μ-O_2CMe)]$_2$.[5a]

The Hg atom is bonded to the oxygen of one monodentate acetate group with a Hg−O(3) distance of 2.120(5) Å to the oxygen of the bridging acetate group with a longer Hg−O(1) bond of 2.638(4) Å and to the C(21) of the bridging P(*o*-tolyl)$_2$−C_6H_4−CH_2− group with a Hg−C(21) bond of 2.103(6) Å, showing a T-shaped coordination environment. The different bond lengths between Hg−O (terminal acetate) and Hg−O (bridging acetate) have been previously observed in [(2-Me_2N−CH_2−C_6H_4)$_2$(μ-$MeCO_2$)PtHg(O_2CMe)].[12] The Hg−C(21) bond distance is similar to that observed in the analogue derivative [PdBr(S_2COEt){μ-P(*o*-tolyl)$_2$−C_6H_4−CH_2−}HgBr][6b] and in other organomercury compounds.[3,13−16,31] The bridging acetate group is asymmetrically bonded [Pd−O(2) = 2.081(4) Å, Hg−O(1) = 2.638(4) Å]. The fragment Hg(1), O(1), C(25), O(2), Pd(1) is not completely planar, O(1) and O(2) being displaced out of the best plane by 0.1595 and 0.1136 Å, respectively. The best plane defined for this fragment is almost perpendicular to the coordination plane of the Pd atom [Pd(1), S(1), S(2), P(1), O(2)] with an interplanar angle of 97.12°.[9]

The mercury atom is located close to the perpendicular of the coordination plane of the palladium center, the angle between this perpendicular and the Pd−Hg vector being 9.97°.[9] However, despite this small angle, the long Pd−Hg separation [3.1726(12) Å] suggests that no bond is formed between both metal centers.[18]

The two *o*-tolyl groups of the "P(*o*-tolyl)$_2$−C_6H_4−CH_2−" bridging ligand are perfectly planar. In one of them, [C(8)−C(14)], the *o*-methyl group is oriented toward the metal atom (*exo*), with the *o*-tolyl ring rotated 63.91° off the Pd−P−*ipso*-C plane. In the other one, [C(1)−C(7], the *o*-methyl group is directed away from the metal atom (*endo*) with the *o*-tolyl ring rotated only 4.51° off the Pd−P−*ipso*-C plane.

The low-temperature $^{31}P\{^1H\}$ and ^1H NMR spectra of **3** and **4** are very similar, allowing us to assign the same structure to both complexes (Scheme 1). A HETCOR[28] experiment was performed on complex **3** in order to correctly assign the ^1H methyl resonances (Supporting Information).

In these complexes (**3** and **4**) the change in the coordination mode of the P(*o*-tolyl)$_2$−C_6H_4−CH_2− ligand using the starting complex, **B**, causes some differences in the corresponding ^{31}P and ^1H NMR signals: (a) the ^{31}P NMR signals of **3** and **4** are shifted to a higher field in about 15 ppm [14.56 ppm (**3**), 17.27 ppm (**4**)]; (b) the ^1H signals, due to the methyl (*o*-tolyl) groups are also shifted to a higher field in about 1 ppm; and (c) the ^1H signal corresponding to the H-6 proton of the *endo* ring appears at ca. 9.0 ppm. This H-6 proton experiences a downfield shift due to the paramagnetic anisotropy of the palladium atom. A similar chemical shift and J_{PH} values were observed for the H-6 proton of the *endo*-P(*o*-tolyl)$_3$ ring in the ^1H NMR spectra of [Pd{P(*o*-tol)$_3$}(hfac)$_2$] (hfac = 1,1,1,5,5,5,-hexafluoro-2,4-pentanedionate)[26a,b] and [Pd{P(*o*-tol)$_3$}(*p*-C_6H_4Me)(NH(Me)Bn)]Br.[26c] The $Me_2NCS_2^-$ ligand and the two inequivalent carboxylate groups give the expected signals in the ^1H or ^{19}F NMR spectra (see Experimental Section).

Reactivity of [Pt{CH_2−C_6H_4−P(*o*-tolyl)$_2$-$\kappa C,P$}(S_2CNMe$_2$)(O_2CCF$_3$)Hg(O_2CCF$_3$)] (2) with HBr. The reaction of [Pt{CH_2−C_6H_4−P(*o*-tolyl)$_2$-$\kappa C,P$}(S_2CNMe$_2$)(O_2CCF$_3$)Hg(O_2CCF$_3$)] (**2**) with a methanol solution of HBr in chloroform in 1:2 molar ratio at −40 °C give rise to complex **C** (Scheme 2a). Complex **C** had been prepared previously by reaction of complex **A** with an equimolar amount of $HgBr_2$ in dichloromethane (Scheme 2b).[6b] This result seems to indicate that several processes take place in this reaction: the displacement of HO_2CCF_3 by HBr (Scheme 2c) followed by the reductive elimination of $HgBr_2$ and formation of complex **C** in which the two different metal fragments are joined through a donor platinum to mercury metal bond (Scheme 2d).

Discussion

As it has been shown, the reactions of [Pt{CH_2−C_6H_4−P(*o*-tolyl)$_2$-$\kappa C,P$}(S_2CNMe$_2$)] (**A**) with Hg(O_2CR)$_2$ (R = CH_3, CF_3) afford the stable platinum−mercury complexes [M{CH_2−C_6H_4−P(*o*-tolyl)$_2$-$\kappa C,P$}(S_2CNMe$_2$)(O_2CR)Hg(O_2CR)] [R = CH_3 (**1**), CF_3 (**2**)] as a result of the cis addition of Hg(O_2CR)$_2$ to complex **A**. These reactions proceed without Pt−C bond cleavage, although such a process is promoted by phosphine ligands.[32] Other stable platinum−mercury complexes containing a covalent Pt−Hg single bond have been prepared by reaction of square-planar Pt(II) substrates and HgX_2 salts as [$PtMe_2X(HgX)(N{-}N)$] [N−N = bpy, X = O_2CCH_3, O_2CCF_3; N−N = Ph_2Me_2phen, X = Cl, Br, I, O_2CCH_3, O_2CCF_3], resulting from cis addition of HgX_2 to the platinum complexes[25] and [(2-Me_2N−CH_2−C_6H_4)$_2$(μ-

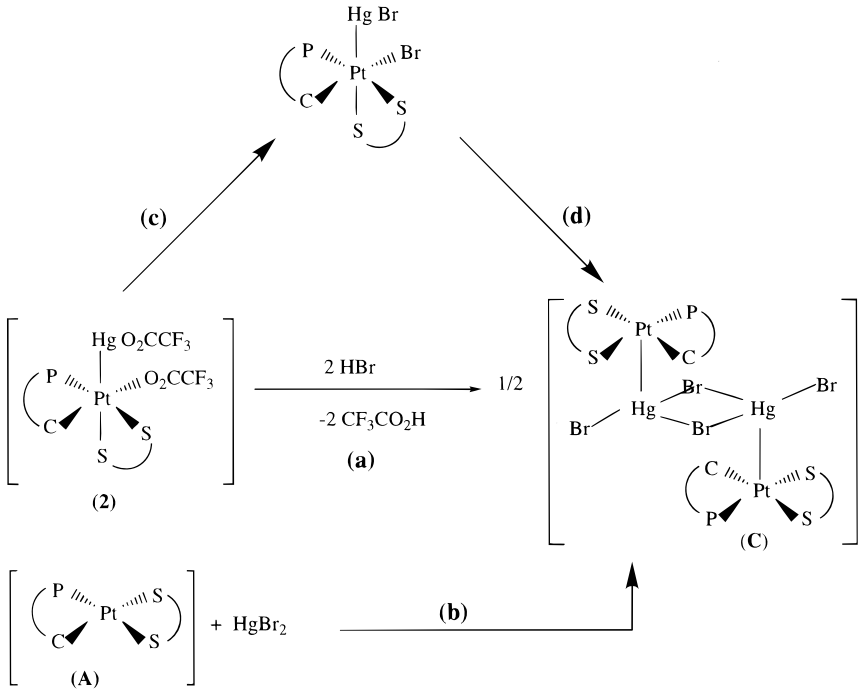
(29) Orpen, G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

(30) Rheingold, A. L.; Fultz, W. C. *Organometallics* **1984**, *3*, 1414.

(31) (a) Casas, J. S.; Castellano, E. E.; García-Tasende, M. S.; Sánchez, A.; Sordo, J.; Vázquez-López, E. M.; Zukerman-Schpector, J. *J. Chem. Soc., Dalton Trans.* **1996**, 1973. (b) Höpp, M.; ErxLeben, A.; Rombeck, I.; Lippert, B. *Inorg. Chem.* **1996**, *35*, 397. (c) Carlson, T. F.; Fackler, J. P., Jr.; Staples, R. J.; Winpenny, R. E. P. *Inorg. Chem.* **1995**, *34*, 426.

(32) Puddephatt, R. J.; Thompson, P. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1219.

Scheme 2



RCO$_2$)PtHg(O$_2$CR)] or [(2-Me$_2$N−C$_6$H$_4$−CH$_2$)$_2$(*μ*-RCO$_2$)-PtHg(O$_2$CR)] (R = Me, ^{i}Pr).[12] The latter compounds have been isolated by van Koten et al. and have been considered as "trapped" intermediates in the concerted cis addition of a mercury−acetate bond to the Pt(II) substrate in which the first step involves a Lewis acid−base type interaction through the filled d_{z^2} orbital of a platinum atom and an empty orbital of a mercury atom. Since the reaction of **A** with Hg(O$_2$CCF$_3$)$_2$ in the presence of $CH_3CO_2^-$ renders exclusively compound **2**, the formation of **1** and **2** seems probable to proceed through a concerted mechanism such as that proposed by van Koten better than through a polar S_N2-type.

The reactions of [Pd{CH$_2$−C$_6$H$_4$−P(*o*-tolyl)$_2$-*κC,P*}(S$_2$-CNMe$_2$)] (**B**) with Hg(O$_2$CR)$_2$ (R = CH$_3$, CF$_3$) give rise to the formation of complexes [Pd(S$_2$CNMe$_2$){*μ*-P(*o*-tolyl)$_2$−C$_6$H$_4$−CH$_2$−}(*μ*-O$_2$CR) Hg(O$_2$CR))] [R = CH$_3$ (**3**), CF$_3$ (**4**)] as a result of a transmetalation process. The same reactivity was observed for complex **B** when it was reacted with HgBr$_2$.[6b]

Cleavage of the platinum− or palladium−C bond by electrophiles such as HgX$_2$ (X = Cl, O$_2$CR) has been observed previously.[33] These reactions result in alkyl or aryl transfer from the substrate to mercury and the formation of organomercurials (eq 1).

$$\text{“R−M”} + HgX_2 \rightarrow \text{“X−M”} + RHgX \qquad (1)$$

It is noteworthy that the internal P-coordination of the chelating C∧P ligand "CH$_2$−C$_6$H$_4$−P(*o*-tolyl)$_2$-*κC,P*" did not prevent such a reaction, although in these cases the C∧P ligand is not completely transferred, leading to the formation of mixed Pd−Hg complexes with said ligand acting as a bridge between the two metal centers. In other cases, for example in the reaction of *cis*-[Pd(2-Me$_2$NCH$_2$−C$_6$H$_4$)$_2$] with Hg(O$_2$CCH$_3$)$_2$,[34] which renders [Pd(2-Me$_2$NCH$_2$−C$_6$H$_4$)(*μ*-MeCO$_2$)]$_2$ as the final product, a transmetalation process together with the complete transference of one C∧N chelating ligand occurs and proceeds very quickly, so that there is no evidence of the formation of a palladium−mercury intermediate. Two mechanisms for the electrophilic cleavage of an *σ* M−C bond have been proposed.[33] The first one involves the oxidative addition of the electrophile (HgX$_2$) to the metal center and the reductive elimination of "RHgX". The second one occurs through the electrophilic attack of the mercury salts on the *σ* M−C bond. Because of the low reactivity of our palladium(II) complex, **B**, toward oxidative addition reactions, the formation of complexes **3** and **4** must probably occur through the electrophilic attack of the Hg(II) salt on the Pd−C bond.

Conclusion

The reaction of the complexes [Pt{CH$_2$−C$_6$H$_4$−P(*o*-tolyl)$_2$-*κC,P*}(S$_2$CNMe$_2$)] (**A**) and [Pd{CH$_2$−C$_6$H$_4$−P(*o*-tolyl)$_2$-*κC,P*}(S$_2$CNMe$_2$)] (**B**) with an equimolar amount of Hg(O$_2$CR)$_2$ (R = CH$_3$, CF$_3$) occurs in very different ways. While **A** oxidatively adds Hg(O$_2$CR)$_2$ to give the octahedral compounds *OC-6-23* [Pt(C∧P)(S$_2$CNMe$_2$)(O$_2$-CR)Hg(O$_2$CR)] [R = CH$_3$ (**1**), CF$_3$ (**2**)], which contain a Pt−Hg covalent bond, the palladium compound **B** reacts with Hg(O$_2$CR)$_2$ with cleavage of the *σ* Pd−C bond. In these transmetalation processes the C∧P ligand is not completely transferred, remaining as a bridge between the two metals centers. The oxidative addition of the mercury(II) carboxylate to complex **A** is stereoselective, and a concerted mechanism seems likely to be operative. For the transmetalation process the electrophilic attack

(33) (a) Jawad, J. K.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1977**, 892. (b) Jawad, J. K.; Puddephatt, R. J. *Inorg. Chim. Acta* **1978**, *31*, L391.

(34) van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K. *J. Organomet. Chem.* **1981**, *222*, 155.

of the Hg(II) salt on the σ Pd−C bond seems plausible. It would thus seem that the electrophilic attack of the Hg(II) salt takes place on the metal center when M = Pt but on the σ Pd−C bond when M = Pd, in accordance with the higher nucleophilicity of platinum with respect to palladium. Similar results were observed previously in the reactions of **A** and **B** with $HgBr_2$, although in these cases the $HgBr_2$ was not added to complex **A**, but a 1:1 adduct $[Pt(C\wedge P)(S_2CNMe_2)HgBr(\mu\text{-}Br)]_2$ was formed in which the platinum fragment was connected to the mercury through a weaker platinum to mercury donor−acceptor bond.

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Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for complexes **2** and **3**. For complexes **1** and **3** $^1H-^{13}C$ HETCOR NMR spectra. For **1** and **2** a drawing showing the possible diastereoisomers. This material is available free of charge via the Internet at http://pubs.acs.org.

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