Bis(2,6-dinitroaryl)platinum Complexes. 2.[1] Di- and Trinuclear Complexes Containing Pt−Hg Bonds

José Vicente,*,† Aurelia Arcas, and María Dolores Gálvez-López

Grupo de Química Organometálica,‡ Departamento de Química Inorgánica, Facultad de Química, Universidad de Murcia, Apartado 4021, E-30071 Murcia, Spain

Peter G. Jones*,§

Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany

Received April 27, 2004

$[Hg(O_2CR)_2]$ reacts with an equimolar amount of *cis*-$Me_4N[Pt(\kappa^2\text{-Ar})(\kappa^1\text{-Ar})Cl]$ (**1**) [κ^2-Ar = $C_6(NO_2)_2$-2,6-$(OMe)_3$-3,4,5-κ^2-*C,O*; κ^1-Ar = $C_6(NO_2)_2$-2,6-$(OMe)_3$-3,4,5-κ^1-*C*] or with *cis*-$[Pt(\kappa^2\text{-Ar})(\kappa^1\text{-Ar})(OH_2)]$ (**2**) in a 2:1 molar ratio to give $Me_4N[Hg(\mu\text{-OAc})_2\{Pt(\kappa^1\text{-Ar})_2Cl\}]$ (**5**) or, depending on R, $[Hg(\mu\text{-OAc})_2\{Pt(\kappa^2\text{-Ar})_2\}_2]$ (**6**) or $[Hg\{Pt(\kappa^2\text{-Ar})_2(O_2CR)\}_2]$ [R = Ar (**7**), C_6F_5 (**8**), CF_3 (**9**)]. Refluxing in toluene a mixture of $[HgAr_2]$ [Ar = $C_6(NO_2)_2$-2,6-$(OMe)_3$-3,4,5], $[Pt(dba)_2]$ (dba = dibenzylideneacetone), and (i) PPh_3 (1:1:2) or (ii) bpy in molar ratio 1:1.3:1.6 gave *cis*-$[Pt(\kappa^1\text{-Ar})\{Hg(\kappa^1\text{-Ar})\}L_2]$ [L = PPh_3 (**10**), L_2 = bpy (**11**)]. Complex **10** reacts with XyNC (Xy = $C_6H_3Me_2$-2,6) to give $[Pt(\kappa^1\text{-Ar})\{Hg(\kappa^1\text{-Ar})\}(CNXy)(PPh_3)]$ (**12**). The structures of complexes **7**, **9**·$CHCl_3$·CH_2Cl_2, and **10** have been solved by X-ray diffraction studies.

Introduction

We have reported in the previous article[1] the synthesis of $Q[Pt(\kappa^2\text{-Ar})(\kappa^1\text{-Ar})Cl]$ [κ^2-Ar = $C_6(NO_2)_2$-2,6-$(OMe)_3$-3,4,5-κ^2-*C,O*; κ^1-Ar = $C_6(NO_2)_2$-2,6-$(OMe)_3$-3,4,5-κ^1-*C*; Q = Ph_3PCH_2Ph, Me_4N (**1**)] by reacting $[HgAr_2]$ [Ar = $C_6(NO_2)_2$-2,6-$(OMe)_3$-3,4,5] with $Q_2[Pt_2Cl_6]$ (4:1) or $[Me_4N]_2[PtCl_4]$ (1:1). From **1** we have prepared neutral $[Pt(\kappa^2\text{-Ar})(\kappa^1\text{-Ar})(L)]$ (L = OH_2 (**2**), PhCN (**3**), tht (tetrahydrothiophene)] or anionic $[Pt(\kappa^1\text{-Ar})_2(acac\text{-}\kappa^2\text{-}O,O)]^-$ and $[Pt(\kappa^2\text{-Ar})(\kappa^1\text{-Ar})\{OC(O)CF_3\}]^-$ (**4**) complexes. Taking into account the proven ability of Hg to form Pt−Hg bonds, we have extended this work to study the reactivity of some of these aryl platinum(II) complexes toward carboxylate salts of mercury. Some mercury salts oxidatively add to platinum(II) complexes to give compounds containing Pt−Hg bonds,[2−13] while in other cases, Lewis acid−base Pt→Hg compounds are obtained.[4−6,8,14−16]

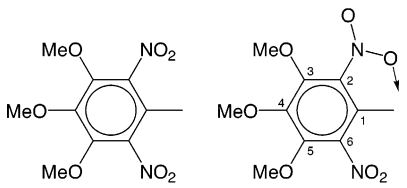
We have also focused our attention on oxidative addition reactions of organomercurials HgR_2 to zerovalent platinum complexes, providing an efficient route to σ-organoplatinum compounds. Such a process occurs by oxidative addition of HgR_2 and the rapid elimination of Hg, to give alkyl, aryl, or vinyl platinum derivatives.[17,18] The plausible intermediates containing a platinum−mercury bond were isolated only when R was a highly electron-withdrawing (e.g., CF_3, C_6F_5)[18−20] or (and) a sterically demanding group (e.g., R = 2,5-C_6H_3-

† E-mail: jvs@um.es.
‡ http://www.um.es/gqo/.
§ E-mail: p.jones@tu-bs.de.

(1) Part 1. Vicente, J.; Arcas, A.; Gálvez-López, M. D.; Jones, P. G. *Organometallics* **2004**, *23*, 3521.
(2) Kuyper, J. *Inorg. Chem.* **1978**, *17*, 1458.
(3) Jawad, J. K.; Puddephatt, R. J. *Inorg. Chim. Acta* **1978**, *31*, L391. Canty, A. J.; van Koten, G. *Acc. Chem. Res.* **1995**, *28*, 406. van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K.; Spek, A. L. *Inorg. Chem.* **1982**, *21*, 2014.
(4) Janzen, M. C.; Jennings, M. C.; Puddephatt, R. J. *Inorg. Chem.* **2001**, *40*, 1728.
(5) Usón, R.; Forniés, J.; Falvello, L. R.; Ara, I.; Usón, I. *Inorg. Chim. Acta* **1993**, *212*, 105.
(6) Forniés, J.; Martín, A.; Sicilia, V.; Villarroya, P. *Organometallics* **2000**, *19*, 1107.
(7) van der Ploeg, A. F. M.; van Koten, G.; Vrieze, K.; Spek, A. L.; Duisenberg, A. J. M. *J. Chem. Soc., Chem. Commun.* **1980**, 469.
(8) van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K.; Spek, A. L. *Inorg. Chem.* **1982**, *21*, 2014.
(9) Braunstein, P.; O., R.; Seco, M.; Torra, I.; Solans, X.; Miravitlles, C. *Organometallics* **1986**, *5*, 1113. Batten, S. A.; Jeffery, J. C.; Jones, P. L.; Mullica, D. F.; Rudd, M. D.; Sappenfield, E. L.; Stone, F. G. A.; Wolf, A. *Inorg. Chem.* **1997**, *36*, 2570. Bochkarev, M. N.; Ermolaev, N. L.; Zakharov, L. N.; Saf'yanov, Y. N.; Razuvaev, G. A.; Struchkov, Y. T. *J. Organomet. Chem.* **1984**, *270*, 289. Tanase, T.; Yamamoto, Y.; Puddephatt, R. J. *Organometallics* **1996**, *15*, 1502. Cucciolito, M. E.; Giordano, F.; Ruffo, F.; De Felice, V. *J. Organomet. Chem.* **1995**, *503*, 251.
(10) Ghilardi, C. A.; Midollini, S.; Moneti, S.; Orlandini, A.; G.Scapacci, G.; Dakternieks, D. *J. Chem. Soc., Chem. Commun.* **1989**, 1686.
(11) Braunstein, P.; Knorr, M.; Strampfer, M.; Tiripicchio, A.; Ugozzoli, F. *Organometallics* **1994**, *13*, 3038. Rossell, O.; Seco, M.; Torra, I. *J. Organomet. Chem* **1984**, *270*, C63.
(12) Schuh, W.; Kopacka, H.; Wurst, K.; Peringer, P. *Eur. J. Inorg. Chem.* **2001**, 2399.
(13) Cucciolito, M. E.; Giordano, F.; Panunzi, A.; Ruffo, F.; Defelice, V. *J. Chem. Soc., Dalton Trans.* **1993**, 3421.
(14) van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K. *Organometallics* **1982**, *1*, 1066. Falvello, L. R.; Fornies, J.; Martin, A.; Navarro, R.; Sicilia, V.; Villarroya, P. *Inorg. Chem.* **1997**, *36*, 6166. Ara, I.; Falvello, L. R.; Fornies, J.; Sicilia, V.; Villarroya, P. *Organometallics* **2000**, *19*, 3091. Muller, J.; Zangrando, E.; Pahlke, N.; Freisinger, E.; Randaccio, L.; Lippert, B. *Chem. Eur. J.* **1998**, *4*, 397. Rauter, H.; Mutikainen, I.; Blomberg, M.; Lock, C. J. L.; Amoochoa, P.; Freisinger, E.; Randaccio, L.; Zangrando, E.; Chiarparin, E.; Lippert, B. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1296.
(15) Krumm, M.; Zangrando, E.; Randaccio, L.; Menzer, S.; Danzmann, A.; Holthenrich, D.; Lippert, B. *Inorg. Chem.* **1993**, *32*, 2183.
(16) Lüth, M. S.; Freisinger, E.; Glahé, F.; Lippert, B. *Inorg. Chem.* **1998**, *37*, 5044. Ara, I.; Fornies, J.; Sicilia, V.; Villarroya, P. *Dalton Trans.* **2000**, 4238.
(17) Sokolov, V. I.; Bashilov, V. V.; Anishchenko, L. M.; Reutov, O. A. *J. Organomet. Chem* **1974**, *71*, C41.
(18) Sokolov, V. I.; Reutov, O. A. *Coord. Chem. Rev.* **1978**, *27*, 89.
(19) Sokolov, V. I.; Bashilov, V. V.; Reutov, O. A. *J. Organomet. Chem* **1975**, *97*, 299.

10.1021/om049699y CCC: $27.50
Publication on Web 06/05/2004

Chart 1



κ^1-Ar κ^2-Ar

Cl_2; 2,3,4- and 2,4,6-$C_6H_2Cl_3$; 2,3,4,5-, 2,3,4,6-, and 2,3,5,6-C_6HCl_4 and C_6Cl_5).[11,21] As the starting Pt(0) complex was always [$Pt(PPh_3)_3$], the isolated Pt−Hg complexes were limited to those containing PPh_3 as the neutral ligand. It has been reported that the reaction of [$Pt(dba)_2$] (dba = dibenzylideneacetone) with organomercurials leads to decomposition.[19] We report here an alternative synthetic procedure that extends the range of complexes to those of the type [$ArL_2Pt-HgAr$], where L is PPh_3 and XyNC (Xy = $C_6H_3Me_2$-2,6) or L_2 is bpy.

Experimental Section

Unless otherwise stated, the reactions were carried out without precautions to exclude light or atmospheric oxygen or moisture. The IR (solid state, Nujol/polyethylene) and C, H, and N analyses, conductivity measurement in acetone, and melting point determinations were carried out as described elsewhere.[22] NMR spectra were recorded in Varian Unity 300, Bruker AC 200, Avance 300 or 400, or Bruker 600 spectrometers at room temperature unless otherwise stated. Chemical shifts were referred to TMS (^1H, ^{13}C), H_3PO_4 (^{31}P), Na_2PtCl_6 (^{195}Pt), or $CFCl_3$ (^{19}F). The syntheses of HgR_2, $Hg(O_2CAr)_2$,[23] [$Pt(PPh_3)_3$],[24] [$Pt(dba)_2$],[25] *cis*-Me_4N[$Pt(\kappa^2$-Ar)(κ^1-Ar)Cl] (**1**), and [$Pt(\kappa^2$-Ar)(κ^1-Ar)(L)] [L = OH_2 (**2**), PhCN (**3**)][1] were reported previously. The aryl group $C_6(NO_2)_2$-2,6-$(OMe)_3$-3,4,5 and the ligands $C_6(NO_2)_2$-2,6-$(OMe)_3$-3,4,5-κ^1-*C* and $C_6(NO_2)_2$-2,6-$(OMe)_3$-3,4,5-κ^2-*C*,*O* are represented by Ar, κ^1-Ar, and κ^2-Ar (see Chart 1).

Synthesis of Me_4N[Hg(μ-OAc)$_2${Pt(κ^1-Ar)$_2$Cl}] (5). To a solution of **1** (96 mg, 0.12 mmol) in CH_2Cl_2 (4 mL) was added $Hg(OAc)_2$ (37 mg, 0.12 mmol), and the mixture was stirred for 1 h. The solution was concentrated (1 mL), addition of Et_2O (10 mL) gave a suspension, which was filtered, and the solid was air-dried to give **5** as a pale salmon-pink solid. Yield: 114 mg, 86%. Mp: 127−129 °C. Λ_M (acetone, 5.2×10^{-4} M): 152 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(Pt−Cl) 302. ^1H NMR (300 MHz, $CDCl_3$): δ 3.89 (s, 6 H, OMe), 3.88 (s, 12 H, OMe), 3.35 (s, 12 H, Me_4N), 1.91 (s, 6 H, OAc). $^{13}C\{^1H\}$ NMR (50.30 MHz, $CDCl_3$): δ 178.67 (CO_2), 149.95 (br, Ar), 146.63 (br, Ar), 143.97 (Ar), 62.31 (OMe), 61.27 (OMe), 56.38 (Me Me_4N), 22.37 (Me OAc). $^{13}C\{^1H\}$ NMR (50.30 MHz, $CDCl_3$, −50 °C): δ 178.76 (CO_2), 178.46 (CO_2), 150.51 (Ar) 149.74 (Ar), 148.88 (Ar), 148.27 (Ar), 146.99 (Ar), 146.21 (Ar), 145.06 (Ar), 143.73 (Ar), 143.43 (Ar), 62.50 (OMe), 62.19 (OMe), 61.20 (OMe), 55.85 (Me Me_4N), 22.91 (Me OAc), 21.18 (Me OAc). $^{195}Pt\{^1H\}$ NMR (86.18 MHz, $CDCl_3$): δ −1917 (s, $^1J_{PtHg}$ = 23600 Hz). Anal. Calcd for $C_{26}H_{36}ClHgN_5O_{18}Pt$: C, 27.45; H, 3.19; N, 6.16. Found: C, 27.17; H, 3.00; N, 6.06.

Synthesis of [Hg(μ-OAc)$_2${Pt(κ^2-Ar)$_2$}$_2$] (6). Method a. To a stirred solution of **2** (from 0.11 mmol of **1**) in CH_2Cl_2 (5 mL) was added $Hg(OAc)_2$ (17 mg, 0.06 mmol). The resulting mixture, which changed from red to orange after 1 h, was filtered, and the filtrate was concentrated (2 mL). Addition of *n*-hexane (10 mL) gave a suspension that was filtered, and the solid was air-dried to give **6** as a yellow-orange solid. Yield: 88 mg, 93%.

Method b. To a stirred solution of **3** (58 mg, 0.07 mmol) in CH_2Cl_2 (4 mL) was added $Hg(OAc)_2$ (21 mg, 0.066 mmol). The resulting mixture, which changed from red to orange after 1 h, was filtered through Celite, and the filtrate was concentrated (2 mL). Addition of *n*-hexane (15 mL) gave a suspension, which was filtered, and the solid was recrystalized from CH_2Cl_2/*n*-hexane to give **6**. Yield: 37 mg, 30%. Mp: 181°C (dec). ^1H NMR (300 MHz, $CDCl_3$): δ 4.11 (s, 6 H, OMe), 3.99 (s, 12 H, OMe), 3.97 (s, 6 H, OMe), 3.87 (s, 6 H, OMe), 3.86 (s, 6 H, OMe),1.94 (s, 6 H, AcO). ^1H NMR (300 MHz, $CDCl_3$, −60 °C): δ 4.14 (s, 6 H, OMe), 4.09 (s, 6 H, OMe), 4.02 (s, 6 H, OMe), 3.97 (s, 6 H, OMe), 3.86 (s, 12 H, OMe), 2.00 (s, 6 H, AcO). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 177.13 (CO_2), 155.61 (Ar), 154.24 (Ar), 148.57 (Ar), 145.28 (Ar), 145.23 (Ar), 138.42 (Ar), 110.07 (Ar), 62.25 (OMe), 62.10 (OMe), 61.53 (OMe), 61.48 (OMe), 61.34 (OMe), 61.30 (OMe), 21.76 (Me). $^{13}C\{^1H\}$ NMR (100.81 MHz, $CDCl_3$, −50 °C): δ 176.82 (CO_2), 155.94 (Ar), 154.20 (Ar), 151.95 (Ar), 150.11 (Ar), 147.74 (Ar), 146.30 (Ar), 144.76 (Ar), 144.36 (Ar), 141.69 (Ar), 137.22 (Ar), 109.72 (Ar), 109.02 (Ar), 62.41 (OMe), 62.38 (OMe), 62.22 (OMe), 61.53 (OMe), 61.35 (OMe), 22.06 (Me). $^{195}Pt\{^1H\}$ NMR (86.18 MHz, $CDCl_3$): δ −1549 (s). Anal. Calcd for $C_{40}H_{42}HgN_8O_{32}Pt_2$: C, 27.65; H, 2.44; N, 6.45. Found: C, 27.40; H, 2.48; N, 6.27.

Synthesis of [Hg{Pt(κ^2-Ar)$_2$(O_2CAr)}$_2$] (7). To a solution of **2** (from 0.07 mmol of **1**) in CH_2Cl_2 (5 mL) was added [$Hg(O_2CAr)_2$] (28 mg, 0.035 mmol). The resulting mixture was stirred for 15 min and then filtered. The filtrate was concentrated (2 mL), addition of *n*-hexane (10 mL) gave a suspension, which was filtered, and the solid was air-dried to give **7** as a yellow-orange solid. Yield: 64 mg, 83%. Mp: 179−181 °C. IR (cm^{-1}): $\nu_{asym}(CO_2)$ 1636. ^1H NMR (400 MHz, $CDCl_3$): δ 4.08 (s, 6 H, OMe), 4.00 (s, 6 H, OMe), 3.94 (s, 6 H, OMe), 3.93 (s, 6 H, OMe), 3.92 (s, 18 H, OMe), 3.88 (s, 6 H, OMe), 3.85 (s, 6 H, OMe). $^{13}C\{^1H\}$ NMR (100.81 MHz, $CDCl_3$, −50 °C): δ 162.19 (CO_2), 155.83 (C_q), 153.72 (C_q), 150.91 (C_q), 147.92 (C_q), 147.43 (C_q), 146.65 (C_q), 145.37 (C_q), 144.48 (C_q), 140.50 (C_q), 140.17 (C_q), 137.44 (C_q), 117.79 (C_q), 109.70 (C_q), 107.41 (C_q), 62.68 (OMe), 62.52 (OMe), 62.28 (OMe), 62.23 (OMe), 61.75 (OMe), 61.47 (OMe), 61.34 (OMe). $^{195}Pt\{^1H\}$ NMR (86.18 MHz, $CDCl_3$): δ −1529 (s, $^1J_{PtHg}$ = 26750 Hz). Anal. Calcd for $C_{56}H_{54}N_{12}O_{46}HgPt_2$: C, 30.27; H, 2.45; N, 7.56. Found: C, 30.07; H, 2.22; N, 7.48. Single crystals of **7**·CH_2Cl_2 were obtained by slow diffusion of *n*-hexane into a CH_2Cl_2 solution of **7**.

Synthesis of [Hg{Pt(κ^2-Ar)$_2$($O_2CC_6F_5$)}$_2$] (8). To a solution of **2** (from 0.09 mmol of **1**) in CH_2Cl_2 (5 mL) was added [$Hg(O_2CC_6F_5)_2$] (28 mg, 0.045 mmol). The resulting mixture was stirred for 10 min and then filtered through dry Celite. The filtrate was concentrated (1 mL), and addition of Et_2O (10 mL) gave a suspension, which was filtered. The filtrate was concentrated to dryness, and the solid was recrystallized from CH_2Cl_2/*n*-hexane (1/10 mL) to give **8** as a yelow solid. Yield: 71 mg, 78%. Mp: 187−190 °C. IR (cm^{-1}): ν (CO_2) 1650 and 1622. ^1H NMR (400 MHz, $CDCl_3$): δ 4.06 (s, 6 H, OMe), 4.03 (s, 6 H, OMe), 4.01 (s, 6 H, OMe), 3.95 (s, 6 H, OMe), 3.88 (s, 6 H, OMe), 3.84 (s, 6 H, OMe). $^{19}F\{^1H\}$ NMR (188 MHz, $CDCl_3$): δ −139.04 (dd, 4F, *o*-F, $^3J_{FF}$ = 22 Hz, $^5J_{FF}$ = 8 Hz), −154.53 (t, 2F, *p*-F, $^3J_{FF}$ = 22 Hz), −162.645 (dt, 4F, *m*-F, $^3J_{FF}$ = 22 Hz, $^5J_{FF}$ = 8 Hz). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 163.12 (CO_2), 155.87 (Ar), 154.41 (Ar), 153.09 (Ar), 150.86 (Ar), 148.20 (Ar), 147.19 (Ar), 145.64 (Ar), 145.16 (Ar), 145.00 (m, C_q C_6F_5), 143.28 (m, C_q C_6F_5), 141.73 (Ar), 140.53 (m, C_q

(20) Sokolov, V. I.; Bashilov, V. V.; Reutov, O. A. *J. Organomet. Chem* **1976**, *111*, C13.
(21) Rossell, O.; Sales, J.; Seco, M. *J. Organomet. Chem* **1982**, *236*, 415.
(22) Vicente, J.; Chicote, M. T.; Huertas, S.; Bautista, D.; Jones, P. G.; Fischer, A. K. *Inorg. Chem*. **2001**, *40*, 2051.
(23) Vicente, J.; Arcas, A.; Blasco, M. A.; Lozano, J.; Ramírez de Arellano, M. C. *Organometallics* **1998**, *17*, 5374.
(24) Ugo, R.; Cariati, F.; La Monica, G. *Inorg. Synth*. **1968**, *XI*, 106.
(25) Cherwinski, W. J.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1974**, 1405.

C_6F_5), 138.06 (m, C_q C_6F_5), 137.78 (Ar), 136.39 (m, C_q C_6F_5), 111.88 (m, C_q C_6F_5), 109.90 (Ar), 107.15 (Ar), 62.37 (OMe), 62.32 (OMe), 61.96 (OMe), 61.64 (OMe), 61.35 (OMe). $^{13}C\{^1H\}$ NMR (100.81 MHz, $CDCl_3$, −50 °C): δ 162.97 (CO_2), 156.37 (Ar), 154.61 (Ar), 152.79 (Ar), 151.09 (Ar), 147.05 (Ar), 146.29 (Ar), 145.30 (Ar), 144.86 (m, C_q C_6F_5), 143.33 (Ar), 142.34 (m, C_q C_6F_5), 141.39 (Ar), 139.68 (m, C_q C_6F_5), 138.06 (m, C_q C_6F_5), 135.90 (Ar), 135.56 (m, C_q C_6F_5), 111.43 (m, C_q C_6F_5), 109.76 (Ar), 107.36 (Ar), 62.56 (OMe), 62.51 (OMe), 62.36 (OMe), 61.58 (OMe), 61.33 (OMe). $^{195}Pt\{^1H\}$ NMR (86.18 MHz, $CDCl_3$): δ −1497 (s, $^1J_{PtHg}$ = 28026 Hz). Anal. Calcd for $C_{50}H_{36}F_{10}HgN_8O_{32}Pt_2$: C, 29.42; H, 1.78; N, 5.49. Found: C, 29.37; H, 1.80; N, 5.46

Synthesis of [Hg{Pt(κ^2-Ar)$_2$(O$_2$CCF$_3$)}$_2$] (9). To a solution of **2** (from 0.08 mmol of **1**) in CH_2Cl_2 (5 mL) was added [Hg(O_2CCF_3)$_2$] (40 mg, 0.09 mmol). The resulting mixture was stirred for 1 h and then filtered through dry Celite. The filtrate was concentrated (1 mL), addition of *n*-hexane (10 mL) gave a suspension, which was filtered, and the solid was air-dried to give **9** as an orange solid. Yield: 62 mg, 75%. Mp: 183−187 °C. IR (cm^{-1}): $\nu_{asym}(CO_2)$ 1674. ^1H NMR (200 MHz, $CDCl_3$, 30 °C): δ 4.11 (s, 6 H, OMe, the most abundant, isomer 1), 4.10 (s, 3 H, OMe isomer 2), 4.08 (s, 6 H, OMe isomer 1), 4.07 (s, 9 H, OMe isomer 2), 4.01 (s, 6 H, OMe, isomer 1), 3.96 (s, 6 H, OMe isomer 1), 3.92 (s, 3 H, OMe isomer 2), 3.90 (s, 6 H, OMe isomer 1), 3.89 (s, 3 H, OMe isomer 2), 3.86 (s, 6 H, OMe isomer 1). ^1H NMR (200 MHz, $CDCl_3$, −33 °C): δ 4.13 (s, OMe), 4.10 (s, OMe), 4.07 (s, OMe), 4.01 (s, OMe), 3.92 (s, OMe), 3.88 (s, OMe), 3.86 (s, OMe). $^{19}F\{^1H\}$ NMR (188.30 MHz, $CDCl_3$, 30 °C): δ −72.81 (s, isomer 2), −72.89 (s, isomer 1). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 161.89 (q, CO, isomer 1, $^2J_{CF}$ = 38 Hz), 161.28 (q, CO isomer 2, $^2J_{CF}$ = 37.6 Hz), 156.30 (Ar, isomer 1), 155.95 (Ar, isomer 2), 154.53 (Ar, isomer 1), 153.56 (Ar, isomer 2), 153.18 (Ar, isomer 1), 151.66 (Ar, isomer 2), 151.04 (Ar, isomer 1), 148.10 (Ar, isomer 1), 147.61 (Ar, isomer 2), 147.00 (Ar, isomer 2), 146.72 (Ar, isomer 1), 145.92 (Ar, isomer 2), 145.74 (Ar, isomer 1), 145.45 (Ar, isomer 1), 144.97 (Ar, isomer 2), 141.62 (Ar, isomer 1), 141.53 (Ar, isomer 2), 137.42 (Ar, isomer 1), 137.28 (Ar, isomer 2), 115.60 (q, CF_3 isomer 1, $^1J_{CF}$ = 289 Hz), 109.01 (Ar, isomer 1), 108.53 (Ar, isomer 2), 106.47 (Ar, isomer 2), 104.75 (Ar, isomer 1), 62.74 (OMe), 62.45 (OMe), 62.41 (OMe), 62.25 (OMe), 62.10 (OMe), 61.68 (OMe), 61.66 (OMe), 61.55 (OMe), 61.43 (OMe). $^{13}C\{^1H\}$ NMR (100.81 MHz, $CDCl_3$, − 50 °C): δ 161.56 (q, CO isomer 1, $^2J_{CF}$ = 38 Hz), 161.03 (q, CO isomer 2, $^2J_{CF}$ = 37.6 Hz), 156.74 (Ar, isomer 1), 156.23 (Ar, isomer 2), 154.69 (Ar, isomer 1), 154.23 (Ar, isomer 2), 153.66 (Ar, isomer 2), 153.06 (Ar, isomer 1), 151.96 (Ar, isomer 2), 151.49 (Ar, isomer 1), 147.16 (Ar, isomer 1), 146.42 (Ar, isomer 2), 146.30 (Ar, isomer 2), 145.78 (Ar, isomer 1), 145.67 (Ar, isomer 2), 145.47 (Ar, isomer 1), 143.97 (Ar, isomer 1), 143.50 (Ar, isomer 2), 141.16 (Ar, isomer 1), 140.91 (Ar, isomer 2), 135.91 (Ar, isomer 1), 135.73 (Ar, isomer 2), 115.32 (q, CF_3 isomer 1, $^1J_{CF}$ = 289 Hz), 115.16 (q, CF_3 isomer 2, $^1J_{CF}$ = 290 Hz), 109.09 (Ar, isomer 1), 108.81 (Ar, isomer 2), 105.95 (Ar, isomer 2), 104.64 (Ar, isomer 1), 62.84 (OMe), 62.71 (OMe), 62.61 (OMe), 62.57 (OMe), 62.51 (OMe), 62.39 (OMe), 61.60 (OMe), 61.42 (OMe). $^{195}Pt\{^1H\}$ NMR (128.81 MHz, $CDCl_3$): δ −1470 (s, isomer 1, $^1J_{PtHg}$ = 28040 Hz), −1471 (s, isomer 2). Anal. Calcd for $C_{40}H_{36}F_6HgN_8O_{32}Pt_2$: C, 26.03; H, 1.97; N, 6.07. Found: C, 25.81; H, 2.00; N, 5.96. Single crystals of **9**·$CHCl_3$·CH_2Cl_2 were obtained by slow diffusion of *n*-hexane into a $CDCl_3$ solution of **9**.

Synthesis of *cis*-[Pt(κ^1-Ar){Hg(κ^1-Ar)}(PPh$_3$)$_2$] (10). Method a. A suspension of [$HgAr_2$] (255 mg, 0.36 mmol) and [$Pt(PPh_3)_3$] (346 mg, 0.35 mmol) was refluxed under nitrogen for 1 h in dry and deoxygenated toluene (6 mL). Addition of *n*-hexane gave a suspension, which was filtered, and the solid was recrystallized from CH_2Cl_2/*n*-hexane to give **10** as a yellow solid. Yield: 457 mg, 90%.

Method b. PPh_3 (114 mg, 0.43 mmol) was added under nitrogen to a solution of [$Pt(dba)_2$] (102 mg, 0.15 mmol) in dry and deoxygenated toluene (10 mL). After 5 min stirring, [$HgAr_2$] (82 mg, 0.11 mmol) and toluene (5 mL) were added, and the mixture was stirred for 6 h. The suspension was concentrated to dryness, and the residue was treated with CH_2Cl_2 (10 mL) and filtrated though Celite. The filtrate was concentrated (1 mL), and Et_2O (15 mL) was added to give a suspension, which was filtered and the solid air-dried to give **10** as a yellow solid. Yield: 97 mg, 61%. Mp: 135−137 °C. Λ_M (acetone, 5×10^{-4} M): 0.4 Ω^{-1} cm^2 mol^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.06−7.38 (m, 30 H, PPh_3), 3.84 (s, 3 H, OMe), 3.83 (s, 6 H, OMe), 3.825 (s, 6 H, OMe), 3.75 (s, 3 H, OMe). $^{31}P\{^1H\}$ NMR (81.01 MHz, $CDCl_3$): δ 30.63 (d, $P_{trans\ to\ Hg}$, $^2J_{PP}$ = 16 Hz, $^1J_{PPt}$ = 2529 Hz, $^2J_{PHg}$ = 3325 Hz), 19.68 (d, $P_{cis\ to\ Hg}$, $^2J_{PP}$ = 16 Hz, $^1J_{PPt}$ = 2647 Hz, $^2J_{PHg}$ = 291 Hz). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$): δ 172.22 (dd, Ar_{Hg}, $^3J_{PC}$ = 3.7 Hz, $^3J_{PC}$ = 61 Hz), 150.18 (d, C_q, J_{PC} = 3.2 Hz, J_{PtC} = 18 Hz), 147.99 (dd, C_q, J_{PC} = 2.6 Hz, J_{PC} = 6 Hz, J_{PtC} = 51 Hz), 145.93 (C_q), 144.74 (d, C_q, J_{PC} = 1.6 Hz), 142.42 (d, C_q, J_{PC} = 2.6 Hz), 140.54 (dd, *i*-C Ar_{Pt}, $^2J_{PC}$ = 9 Hz, $^2J_{PC}$ = 99 Hz), 135.76 (dd, *i*-C PPh_3, $^3J_{PC}$ = 3.7 Hz, $^1J_{PC}$ = 52 Hz, $^2J_{PtC}$ = 29 Hz), 134.14 (d, *o*-C PPh_3, $^2J_{PC}$ = 12 Hz, $^3J_{PtC}$ = 24 Hz), 129.93 (s, *p*-C PPh_3), 128.04 (d, *m*-C PPh_3, $^3J_{PC}$ = 11 Hz,), 62.00 (*m*-OMe), 61.79 (*m*-OMe), 61.36 (*p*-OMe), 61.02 (*p*-OMe). $^{195}Pt\{^1H\}$ NMR (86.18 MHz, $CDCl_3$): δ −4636 (dd, $^1J_{PtP}$ = 2530 Hz, $^1J_{PtP}$ = 2647 Hz, $^1J_{PtHg}$ = 14945 Hz). Anal. Calcd for $C_{54}H_{48}HgN_4O_{14}P_2Pt$: C, 45.21; H, 3.37; N, 3.90. Found: C, 45.43; H, 3.34; N, 3.81. Single crystals of **10** were obtained by slow diffusion of *n*-hexane into a solution of **10** in $CDCl_3$/ether.

Synthesis of *cis*-[Pt(κ^1-Ar){Hg(κ^1-Ar)}(bpy)] (11). A mixture of [$Pt(dba)_2$] (102 mg, 0.15 mmol) and bpy (30 mg, 0.19 mmol) in dry and deoxygenated toluene (15 mL) was stirred under nitrogen. After 10 min, [$HgAr_2$] (87 mg, 0.12 mmol) was added and the mixture was stirred for 24 h. The solvent was evaporated to dryness, and the residue was treated with CH_2Cl_2 to give a suspension, which was filtered off though Celite. The filtrate was concentrated (1 mL), addition of Et_2O (15 mL) gave a suspension, which was filtered, and the solid was air-dried to give **11** as a yellow solid. Yield: 82 mg, 64%. Mp: 170−174 °C. ^1H NMR (200 MHz, $CDCl_3$): δ 9.68 (m, 1 H, bpy), 8.44−8.46 (m, 1 H, bpy), 7.98−8.12 (m, 4 H, bpy), 7.46−7.52 (m, 2 H, bpy), 4.06 (s, 6 H, OMe), 4.02 (s, 6 H, OMe), 4.00 (s, 3 H, OMe), 3.89 (s, 3 H, OMe). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$): δ 168.78 (Ar_{Hg}), 159.47 (CH bpy), 155.79 (C_q), 155.19 (C_q), 150.97 (C_q), 149.80 (C_q), 148.70 (CH bpy), 146.34 (C_q), 145.98 (C_q), 144.96 (C_q), 141.76 (C_q), 138.18 (CH bpy), 128.06 (CH bpy), 127.66 (CH bpy), 122.98 (CH bpy), 122.08 (CH bpy), 117.03 (C_q), 62.30 (OMe), 62.23 (OMe), 61.26 (OMe), 61.02 (OMe). $^{195}Pt\{^1H\}$ NMR (86.18 MHz, $CDCl_3$): δ −3333 (s, $^1J_{PtHg}$ = 25828 Hz). Anal. Calcd for $C_{28}H_{26}HgN_6O_{14}Pt$: C, 31.54; H, 2.46; N, 7.88. Found: C, 31.74; H, 2.35; N, 7.79.

Synthesis of [Pt(κ^1-Ar){Hg(κ^1-Ar)}(CNXy)(PPh$_3$)] (12). To a solution of **10** (64 mg, 0.045 mmol) in CH_2Cl_2 (4 mL) was added XyNC (5.9 mg, 0.045 mmol), and a yellow solution was obtained. After 15 h the solvent was evaporated almost to dryness, addition of Et_2O (10 mL) gave a suspension, which was filtered, and the solid was air-dried to give **12** as a pale yellow solid. Yield: 38 mg, 65%. Mp: 196−198 °C. IR (cm^{-1}): ν(N≡C) 2144. ^1H NMR (200 MHz, $CDCl_3$): δ 7.55−7.45 (m, 6 H, PPh_3), 7.34−7.31 (m, 9 H, PPh_3), 7.15−7.07 (m, 1 H, *p*-H XyNC), 6.96−6.92 (m, 2 H, *m*-H XyNC), 3.98 (s, 6 H, OMe), 3.86 (s, 3 H, OMe), 3.84 (s, 3 H, OMe), 3.83 (s, 6 H, OMe), 1.94 (s, 6 H, Me). $^{31}P\{^1H\}$ NMR (81.01 MHz, $CDCl_3$): δ 25.70 (s, $^1J_{PPt}$ = 2373 Hz, $^2J_{PHg}$ = 3195 Hz). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$): δ 175.33 (d, *i*-C Ar_{Hg}, $^3J_{PC}$ = 60 Hz), 151.24 (d, Ar, J_{PC} = 3.6 Hz), 147.94 (d, Ar, J_{PC} = 2.5 Hz, J_{PtC} = 50 Hz), 146.44 (Ar), 146.37 (Ar), 144.51 (Ar), 142.53 (d, Ar, J_{PC} = 2.6 Hz), 136.61 (d, Ar, J_{PC} = 9.4 Hz), 135.18 (*o*-C Xy), 134.36 (d, *o*-CH PPh_3, $^2J_{PC}$ = 12 Hz, $^3J_{PtC}$ = 16 Hz), 130.93 (d, *i*-C PPh_3, $^1J_{PC}$ = 47 Hz, $^2J_{PtC}$ = 25 Hz), 130.39 (*p*-C PPh_3), 128.69 (*p*-CH Xy), 128.11 (d, *m*-C PPh_3, $^3J_{PC}$ = 11 Hz), 127.73 (*m*-C Xy), 127.43 (*i*-C Xy), 62.19 (*m*-OMe), 61.93 (*m*-OMe), 61.43 (p-OMe),

Table 1. Crystallographic Data for Compounds 7, 9, and 10

	7·3CH_2Cl_2	**9**·$CHCl_3$·CH_2Cl_2	**10**
formula	$C_{59}H_{60}Cl_6HgN_{12}O_{46}Pt_2$	$C_{42}H_{40}Cl_5F_6HgN_8O_{32}Pt_2$	$C_{54}H_{48}HgN_4O_{14}P_2Pt$
M_r	2476.66	2050.93	1434.58
habit	orange tablet	orange parallelepiped	yellow parallelepiped
cryst. size (mm)	0.18 × 0.15 × 0.08	0.10 × 0.10 × 0.06	0.15 × 0.14 × 0.12
cryst syst	monoclinic	monoclinic	monoclinic
space group	*Cc*	$P2_1/n$	$P2_1/c$
cell constants:			
a (Å)	22.5114(18)	14.3092(14)	13.3346(11)
b (Å)	21.7827(16)	17.0902(16)	21.8052(18)
c (Å)	17.4364(14)	14.4137(14)	18.3639(14)
α (deg)	90	90	90
β (deg)	104.396(4)	117.032(4)	95.089(4)
γ (deg)	90	90	90
V (Å^3)	8281.6(11)	3139.7(5)	5318.5(7)
Z	4	2	4
D_x (Mg m^{-3})	1.986	2.169	1.792
μ (mm^{-1})	5.52	7.21	5.64
F(000)	4816	1957	2800
T (°C)	−140	−140	−140
$2\theta_{max}$	60	56.6	60
no. of reflns measd	65 865	52 360	81 413
no. of indep reflns	23 755	7789	15 560
transmns	0.36−0.65	0.61−0.72	0.45−0.57
R_{int}	0.043	0.067	0.053
no. of params	1136	463	691
no. of restraints	1047	48	158
$wR(F^2$, all reflns)	0.070	0.046	0.046
$R(F, >4\sigma(F))$	0.032	0.028	0.021
S	0.96	0.89	0.97
max. Δ*ρ* (e Å^{-3})	3.2	1.4	1.5

61.19 (*p*-OMe), 18.48 (Me Xy). $^{195}Pt\{^1H\}$ NMR (86.18 MHz, $CDCl_3$): δ −4432 (d, $^1J_{PPt}$ = 2373 Hz, $^1J_{PtHg}$ = 15004 Hz). Anal. Calcd for $C_{45}H_{42}HgN_5O_{14}PPt$: C, 41.46; H, 3.25; N, 5.37. Found: C, 41.56; H, 3.23; N, 5.27.

X-ray Structure Determinations. Numerical details are presented in Table 1. Data collection and reduction: Crystals were mounted in inert oil on glass fibers and transferred to the cold gas stream of the diffractometer (Bruker SMART 1000 CCD). Measurements were performed with monochromated Mo Kα radiation. Absorption corrections were performed on the basis of face-indexing (**7** and **10**) or multiscans (program SADABS; **9**). Structure refinement: The structures were refined anisotropically against F^2 (program SHELXL-97, G. M. Sheldrick, University of Göttingen). Solvent molecules were well-ordered except as indicated below. Hydrogen atoms were included as rigid methyl groups or with a riding model. Systems of restraints to local ring symmetry and light atom displacement factor components were employed to improve refinement stability. Special features of refinement: Structure **7** was refined as an enantiomeric twin with a twinning parameter of 0.274(4); the methoxy carbon C59 is disordered over two positions in the ratio 1:1. The solvent site in **9** was interpreted as superimposed chloroform and dichloromethane in the ratio 1:1, but this should be interpreted with caution; the composition and derived parameters are based on protium rather than deuterium for the deuterochloroform component, because any error would be minimal compared to the uncertainty in the exact nature of the solvent site.

Results and Discussion

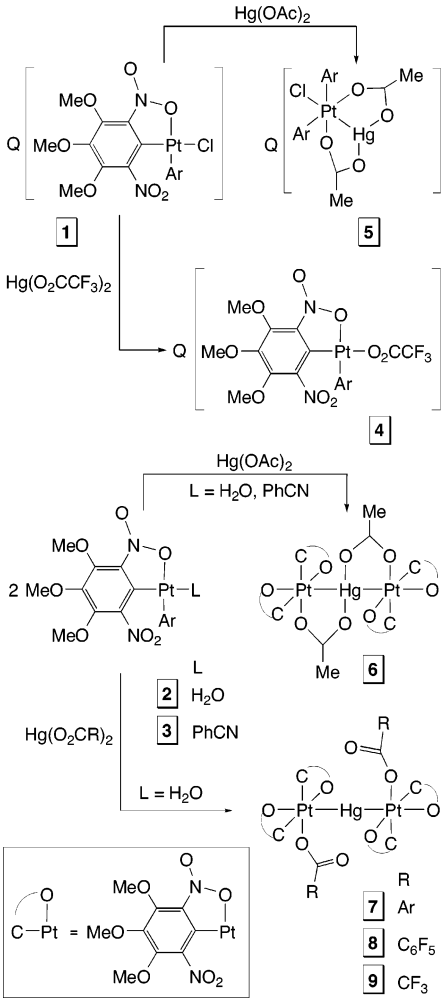
To prepare the heteronuclear Pt−Hg compound, we have used some platinum complexes we reported in the previous article:[1] $Me_4N[Pt(\kappa^2\text{-Ar})(\kappa^1\text{-Ar})Cl]$ (**1**) and $[Pt(\kappa^2\text{-Ar})(\kappa^1\text{-Ar})(L)]$ [L = OH_2 (**2**), PhCN (**3**)].

Reactions of Complexes 1−3 with Mercury(II) Carboxylates. For the synthesis of Pt→Hg complexes in which the Pt center acts as a donor atom, anionic platinum complexes are suitable precursors. With this purpose, we chose the anionic complex **1** and reacted it with $[Hg(O_2CR)_2]$ (R = Me, CF_3) with different results. Thus, while the reaction of **1** with $[Hg(OAc)_2]$ (1:1) gave the complex $Me_4N[Hg(\mu\text{-OAc})_2\{Pt(\kappa^1\text{-Ar})_2Cl\}]$ (**5**) (Scheme 1), that with $Hg(O_2CCF_3)_2$ (1:1) proceeded with substitution of chloride by carboxylate to give **4** (Scheme 1).[1] Complex **1** also reacts with $[Hg(O_2CC_6F_5)_2]$, but complex mixtures of unidentified products were obtained.

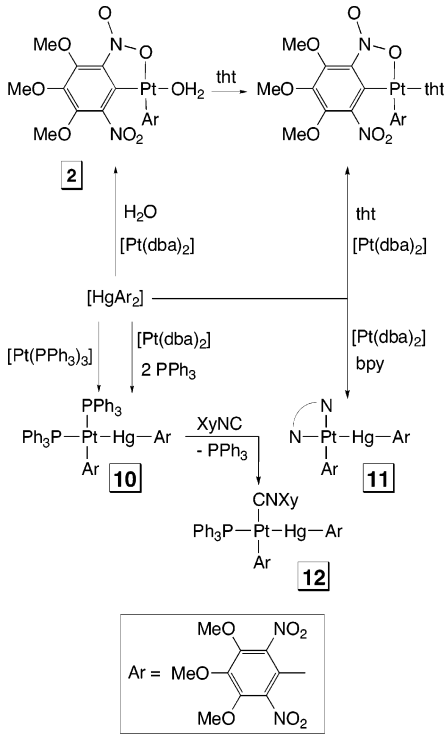
When a mixture of **2** and $[Hg(OAc)_2]$ (2:1) in CH_2Cl_2 was stirred at room temperature for 1 h, an oxidative addition occurred leading to $[Hg(\mu\text{-OAc})_2\{Pt(\kappa^2\text{-Ar})_2\}_2]$ (**6**) in good yield (88%) (Scheme 1). Complex **6** can also be obtained by reacting **3** and $Hg(OAc)_2$ (2:1) in CH_2Cl_2, but recrystallization is necessary to give a moderate yield (30%) of pure complex **6**. Although **6** is air stable, its CH_2Cl_2 solutions are only moderately stable at room temperature. Thus if the reaction time is greater than 1 h, the isolated complex is not analytically pure. Acetone solutions of complex **6** immediately transform into a complex mixture of products. The reactions of **2** with $Hg(O_2CR)_2$ in 2:1 (R = Ar, C_6F_5) or 1:1 (CF_3) molar ratio at room temperature proceed with formation of $[Hg\{Pt(\kappa^2\text{-Ar})_2(O_2CR)\}_2]$ [R = Ar (**7**), C_6F_5 (**8**), CF_3 (**9**)], which are obtained from their solutions as air-stable solids. The reaction of **2** with $Hg(O_2CCF_3)_2$ in 2:1 molar ratio proceeds with formation of a complex mixture of nonidentified products. Single crystals of **7**·CH_2Cl_2 or **9**·CH_2Cl_2·$CHCl_3$ were obtained by slow diffusion of *n*-hexane into a solution of **7** in CH_2Cl_2 or **9** in $CDCl_3$/CH_2Cl_2, respectively. However, slow crystallization of **7** from CH_2Cl_2/Et_2O leads to a complex mixture of nonidentified products.

Reactions of [$HgAr_2$] with Platinum(0) Complexes. The synthesis of Pt−Hg complexes has also been carried out by oxidative addition of organomercu-

Scheme 1



Scheme 2



rials to Pt(0) complexes.[11,18−21] In some cases, the resulting Pt−Hg complexes decompose to give organoplatinum complexes.[17,18] We have found both behaviors. Thus, when a mixture of $[HgAr_2]$, $[Pt(dba)_2]$, and tht in a 1:1:8 molar ratio was stirred at room temperature in toluene for 20 h, a redox transmetalation reaction occurred to give $[Pt(\kappa^2\text{-Ar})(\kappa^1\text{-Ar})(tht)]$, i.e., the same complex that we prepared by reacting **2** with tht (Scheme 2).[1] Similarly, refluxing for 1 h a toluene solution of $[HgAr_2]$ and $[Pt(dba)_2]$ in 1:1 molar ratio gave a solution containing **2**. However, the same reaction, in the presence of PPh_3, in 1:1:2 molar ratio, took place to give in moderate yield (61%) the Pt−Hg derivative *cis*-$[Pt(\kappa^1\text{-Ar})\{Hg(\kappa^1\text{-Ar})\}(PPh_3)_2]$ (**10**) as an air-stable solid (Scheme 2). Complex **10** has also been obtained in good yield (90%) by reacting $[HgAr_2]$ with $[Pt(PPh_3)_3]$. As this is the method used to prepare all complexes homologous to **10**, they are all of general formula $[Pt(R)(HgR)(PPh_3)_2]$.[19−21] We have been able to prepare Pt−Hg compounds with other neutral ligands by reacting $[HgAr_2]$, $[Pt(dba)_2]$, and bpy in 1:1.3:1.6 molar ratio to give *cis*-$[Pt(\kappa^1\text{-Ar})\{Hg(\kappa^1\text{-Ar})\}(bpy)]$ (**11**) or by reacting complex **10** with XyNC (1:1) to afford $[Pt(\kappa^1\text{-Ar})\{Hg(\kappa^1\text{-Ar})\}(CNXy)(PPh_3)]$ (**12**). If an excess of XyNC was used, a mixture of unidentified products was obtained.

X-ray Crystal Structures. Trinuclear [Pt−Hg−Pt] Complexes. Crystals apparently suitable for an X-ray crystallographic study were obtained for **6**. Although the structure shown in Scheme 1 was established, a complete crystallographic analysis was not possible. Disorder in the organic ligands was so severe that, despite repeated attempts and data collection at low temperature, no satisfactory refinement was achieved. However, the composition and the position of the acetate ligands acting as bridges were established with certainty. The platinum centers are hexacoordinated and the Ar groups act as chelating ligands, with Pt−C bonds mutually *cis*.

Complete crystallographic analysis was possible for complexes **7** and **9** (Figures 1 and 2, respectively). They can be regarded as containing two octahedra formed by two "$Pt(\kappa^2\text{-Ar})_2(\kappa^1\text{-}O_2CAr)$" fragments with a bridging Hg atom at a common apex. Both samples appeared optically to consist of only one type of crystal, but no specific search for other crystal types was carried out. The crystal selected for the study of complex **9** proved to be the centrosymmetric stereoisomer (*AC*), with a crystallographic inversion center at the mercury atom, whereas both halves of compound **7** display the same chirality (because of the crystallographic glide planes, both enantiomers are present and the compound is a racemate). In both complexes the mercury has a linear or almost linear coordination [Pt−Hg−Pt = 170.471(11)° (**7**), 180° by symmetry (**9**)] and each Pt atom is displaced slightly from the center of its octahedron toward the Hg atom; the Pt deviations from the best equatorial planes are 0.090 and 0.133 Å for **7** and 0.124 Å for **9**. The two Pt−Hg bond distances are somewhat different in complex **7** [2.6093(3), 2.5914(3) Å], although Hg is *trans* to the same ligand, and are slightly longer than that in **9** [2.5898(2) Å]. These Pt−Hg distances lie in the range reported in other complexes containing covalent Pt−Hg bonds (2.666−2.513 Å),[4,6−13] but they are shorter than those in other complexes in which a metal−metal bond was described as Pt → Hg or could be thus formulated (2.835−2.650 Å)[4,5,14,15] or in higher nuclearity clusters

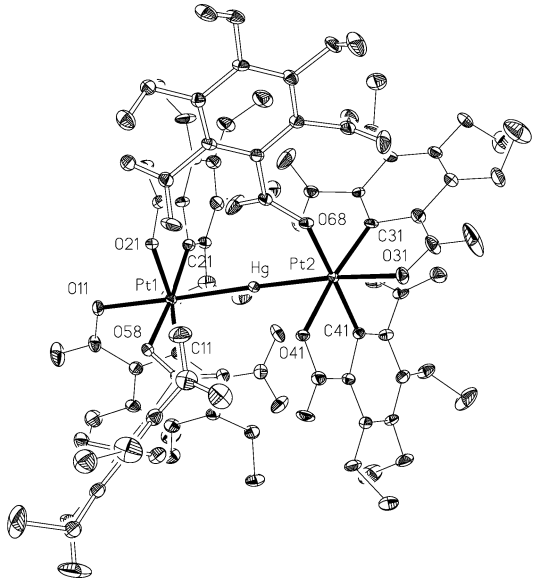


Figure 1. Ellipsoid representation of **7** (50% probability; solvent and H atoms omitted). Selected bond lengths (Å) and angles (deg): Hg−Pt(2) 2.5914(3), Hg−Pt(1) 2.6093(3), Pt(1)−C(21) 2.013(5), Pt(1)−C(11) 2.024(5), Pt(1)−O(21) 2.068(4), Pt(1)−O(58) 2.076(4), Pt(1)−O(11) 2.253(4), Pt(2)−C(41) 2.008(5), Pt(2)−C(31) 2.011(5), Pt(2)−O(41) 2.070(4), Pt(2)−O(68) 2.078(3), Pt(2)−O(31) 2.255(4), O(11)−N(11) 1.268(6), O(12)−N(11) 1.203(6), O(16)−N(12) 1.228(6), O(17)−N(12) 1.230(7), O(21)−N(21) 1.301(6), O(22)−N(21) 1.207(6), O(26)−N(22) 1.203(7), O(27)−N(22) 1.218(6), O(31)−N(31) 1.245(6), O(32)−N(31) 1.199(7), O(36)−N(32) 1.200(7), O(37)−N(32) 1.209(6), O(41)−N(41) 1.290(6), O(42)−N(41) 1.218(6), O(46)−N(42) 1.227(6), O(47)−N(42) 1.208(6), O(51)−N(51) 1.231(6), O(52)−N(51) 1.214(6), O(56)−N(52) 1.230(7), O(57)−N(52) 1.231(7), O(61)−N(61) 1.211(7), O(62)−N(61) 1.215(6), O(66)−N(62) 1.214(6), O(67)−N(62) 1.210(6), N(11)−C(12) 1.435(7), N(12)−C(16) 1.469(7), N(21)−C(22) 1.426(7), N(22)−C(26) 1.478(7), N(31)−C(32) 1.434(8), N(32)−C(36) 1.460(7), N(41)−C(42) 1.427(7), N(42)−C(46) 1.492(7), N(51)−C(52) 1.469(8), N(52)−C(56) 1.451(8), N(61)−C(62) 1.484(7), N(62)−C(66) 1.480(6), Pt(2)−Hg−Pt(1) 170.471(11), C(21)−Pt(1)−C(11) 103.5(2), C(21)−Pt(1)−O(21) 80.24(19), C(11)−Pt(1)−O(58) 85.22(18), O(21)−Pt(1)−O(58) 90.87(15), C(21)−Pt(1)−O(11) 97.7(2), C(11)−Pt(1)−O(11) 77.57(18), O(21)−Pt(1)−O(11) 93.32(15), O(58)−Pt(1)−O(11) 81.99(15), C(21)−Pt(1)−Hg 85.35(16), C(11)−Pt(1)−Hg 107.18(15), O(21)−Pt(1)−Hg 81.72(11), O(58)−Pt(1)−Hg 94.13(11), C(41)−Pt(2)−C(31) 100.0(2), C(41)−Pt(2)−O(41) 80.54(19), C(31)−Pt(2)−O(68) 85.69(17), O(41)−Pt(2)−O(68) 92.93(13), C(41)−Pt(2)−O(31) 91.80(19), C(31)−Pt(2)−O(31) 78.64(19), O(41)−Pt(2)−O(31) 91.23(15), O(68)−Pt(2)−O(31) 84.00(15), C(41)−Pt(2)−Hg 87.56(15), C(31)−Pt(2)−Hg 107.98(16), O(41)−Pt(2)−Hg 82.15(11), O(68)−Pt(2)−Hg 95.84(10), O(12)−N(11)−O(11) 118.6(5), O(16)−N(12)−O(17) 123.9(5), O(22)−N(21)−O(21) 118.9(5), O(26)−N(22)−O(27) 124.4(5), O(32)−N(31)−O(31) 117.7(5), O(36)−N(32)−O(37) 123.3(6), O(42)−N(41)−O(41) 118.1(5), O(47)−N(42)−O(46) 126.1(5), O(52)−N(51)−O(51) 124.8(5), O(56)−N(52)−O(57) 124.3(6), O(61)−N(61)−O(62) 126.0(5), O(67)−N(62)−O(66) 124.8(5).

(3.159−2.671 Å).[26,27] The Ar groups are bonded to platinum as chelating ligands and are mutually *cis*. The four Pt−C distances in **7** are not significantly different [range 2.024(5)−2.008(5) Å], but in **9**, they are slightly different [1.989(4), 2.018(4) Å]. The Pt−O bonds *trans* to the mercury atom are shorter in **7** [2.253(4), 2.255(4) Å] than those in **9** [2.283(3) Å] and both longer than the Pt−O bonds *trans* to the aryl group [2.068(4), 2.070-

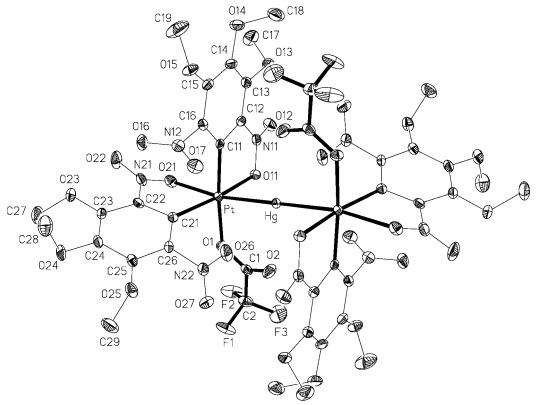


Figure 2. Ellipsoid representation of **9** (30% probability; solvent and H atoms omitted). Selected bond lengths (Å) and angles (deg): Hg−Pt 2.5898(2), Pt−C(11) 1.989(4), Pt−C(21) 2.018(4), Pt−O(11) 2.070(3), Pt−O(1) 2.078(3), Pt−O(21) 2.283(3), O(11)−N(11) 1.295(4), O(12)−N(11) 1.211(4), O(16)−N(12) 1.225(4), O(17)−N(12) 1.220(4), O(21)−N(21) 1.273(4), O(22)−N(21) 1.209(4), O(26)−N(22) 1.220(4), O(27)−N(22) 1.222(5), N(11)−C(12) 1.421(5), N(12)−C(16) 1.479(5), N(21)−C(22) 1.442(5), N(22)−C(26) 1.481(5), Pt−Hg−Pt#1 180.0(4), C(11)−Pt−C(21) 100.79(16), C(11)−Pt−O(11) 80.53(14), C(21)−Pt−O(1) 88.74(14), O(11)−Pt−O(1) 89.43(11), C(11)−Pt−O(21) 89.64(13), C(21)−Pt−O(21) 77.03(13), O(11)−Pt−O(21) 91.62(10), O(1)−Pt−O(21) 89.07(11), C(11)−Pt−Hg 80.87(11), C(21)−Pt−Hg 105.31(11), O(11)−Pt−Hg 86.15(7), O(1)−Pt−Hg 100.15(8), O(12)−N(11)−O(11) 118.8(4), O(17)−N(12)−O(16) 124.6(4), O(22)−N(21)−O(21) 120.5(4), O(26)−N(22)−O(27) 124.9(4)

(4) Å (**7**), 2.070(3) (**9**) Å], showing that the *trans* influence of the mercury atom is even stronger than that of the aryl ligand. This exceptionally large *trans* influence of Hg has been described previously.[8,13] In both complexes, the mercury atom makes four significant intramolecular Hg···O contacts [**7**: to O16, 2.714(4); O59 2.755(4); O69 2.800(4); O37 2.897(5)Å); **9**: to O26, 2.830(3); O2 2.835(3) Å] with the oxygen atoms of two nitro and the two carboxylato ligands (Figures 3 and 4). These contacts (*cis* for **7** and *trans* for **9**) and the Hg−Pt bonds determine a distorted octahedral environment around the mercury atom. The carboxylato ligands in complex **6** form covalent Hg−O bonds. The crystal structures of **7** and **9** have no precedent in the literature. A compound of composition $[\{PtMe_2(O_2CCF_3)(tmeda)\}_2Hg]$ was studied by ^{1}H NMR, but no elemental analyses or other data were reported.[2] More recently the synthesis of two Pt→Hg−Pt compounds, containing one covalent and one donor−acceptor Pt−Hg bond, has been reported.[4]

Crystal Structure of the Dinuclear Pt−Hg Complex 10. The crystal structure of **10** has been deter-

(26) Yamamoto, Y.; Yamazaki, H.; Sakurai, T. *J. Am. Chem. Soc.* **1982**, *104*, 2329. Yamamoto, Y.; Yamazaki, H. *Inorg. Chim. Acta* **1994**, *217*, 121. King, W. D.; Lukehart, C. M. *J. Cluster Sci.* **1998**, *9*, 107. Hao, L. J.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J.; Spivak, G. J.; Vittal, J. J.; Yufit, D. *Inorg. Chim. Acta* **1997**, *265*, 65. Wurst, K.; Strahle, J. *Z. Anorg. Allg. Chem.* **1991**, *595*, 239. Furmanova, N. G.; Bashilov, V. V.; Kurasov, S. S.; Eremenko, N. K.; Sokolov, V. I. *Kristallografiya* **1992**, *37*, 625. Adams, R. D.; Barnard, T. S.; Cortopassi, J. E.; Zhang, L. *Organometallics* **1996**, *15*, 2664. Schoettel, G.; Vittal, J. J.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 6400. Hao, L. J.; Xiao, J. L.; Vittal, J. J.; Puddephatt, R. J.; Manojlovic-Muir, L.; Muir, K. W.; Torabi, A. A. *Inorg. Chem.* **1996**, *35*, 658.

(27) Bour, J. J.; van der Berg, W.; Schlebos, P. P. J.; Kanters, R. P. F.; Schoondergang, M. F.; Bosman, W. P.; Smits, J. M. M.; Beurskens, P. T.; Steggerda, J. J.; van der Sluis, P. *Inorg. Chem.* **1990**, *29*, 2971. Albinati, A.; Dahmen, K. H.; Demartin, F.; Forward, J. M.; Longley, C. J.; Mingos, D. M. P.; Venanzi, L. M. *Inorg. Chem.* **1992**, *31*, 2223.

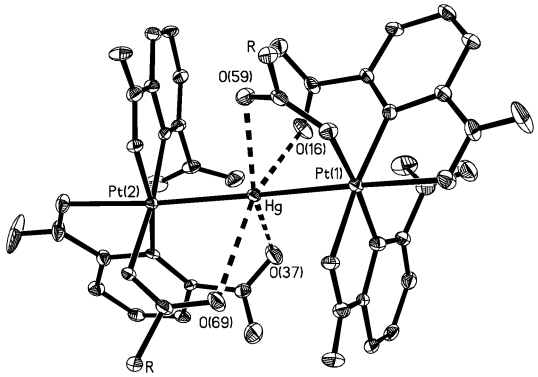


Figure 3. O···Hg contacts in complex **7**. R = $C_6(NO_2)_2$-2,6-$(OMe)_3$-3,4,5.

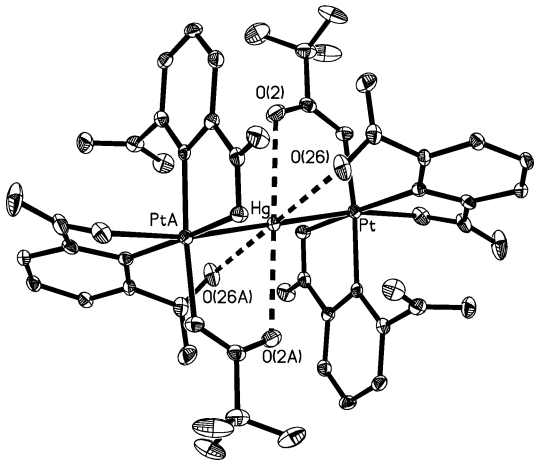


Figure 4. O···Hg contacts in complex **9**.

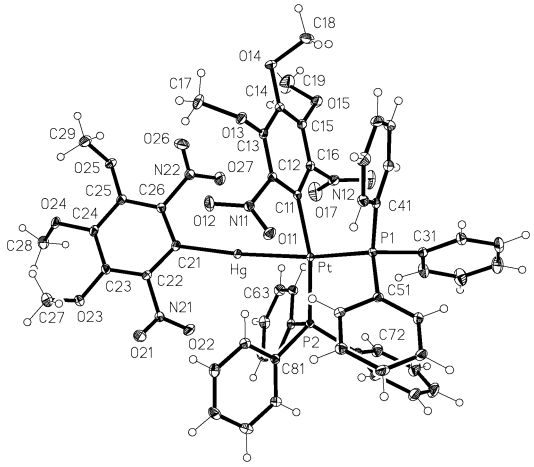


Figure 5. Ellipsoid representation of **10** (50% probability). Selected bond lengths (Å) and angles (deg): Pt−C(11) 2.062(2), Pt−P(2) 2.2923(6), Pt−P(1) 2.3248(6), Pt−Hg 2.57586(19), Hg−C(21) 2.152(2), O(11)−N(11) 1.226(2), O(12)−N(11) 1.230(2), O(16)−N(12) 1.215(3), O(17)−N(12) 1.220(3), O(21)−N(21) 1.224(3), O(22)−N(21) 1.227(3), O(26)−N(22) 1.225(3), O(27)−N(22) 1.218(3), N(11)−C(12) 1.470(3), N(12)−C(16) 1.484(3), N(21)−C(22) 1.477(3), N(22)−C(26) 1.473(3), C(11)−Pt−P(1) 91.72(6), P(2)−Pt−P(1) 103.70(2), C(11)−Pt−Hg 79.91(6), P(2)−Pt−Hg 85.220-(16), C(21)−Hg−Pt 170.25(6), O(11)−N(11)−O(12) 123.0(2), O(11)−N(11)−C(12) 119.72(18), O(12)−N(11)−C(12) 117.23-(19), O(16)−N(12)−O(17) 123.9(2), O(16)−N(12)−C(16) 118.0(2), O(17)−N(12)−C(16) 118.2(2), O(21)−N(21)−O(22) 124.4(2), O(21)−N(21)−C(22) 118.04(19), O(22)−N(21)−C(22) 117.6(2), O(27)−N(22)−O(26) 123.8(2), O(27)−N(22)−C(26) 118.1(2), O(26)−N(22)−C(26) 118.1(2).

mined (Figure 5). The molecule contains a distorted linear P(1)−Pt−Hg−C(21) arrangement. The Pt−P(1) bond distance [2.3248(6) Å] is longer than the Pt−P(2) length [2.2923(6) Å] because of the greater *trans* influence of Hg than the aryl ligand (see above). The P(2)−Pt−P(1) [103.70(2)°] and C(11)−Pt−Hg [79.91(6)°] angles deviate significantly from 90° as a result of the steric repulsion between the *cis* PPh_3 ligands. The Pt−C(11) bond length [2.062(2) Å] is longer than those observed in complexes **7** [2.008(5)−2.024 (5) Å] and **9** [1.989(4) and 2.018(4) Å] in part due to the greater *trans* influence of PPh_3 than the O donor ligands and in part as a consequence of the lower formal oxidation state of the Pt atom in **10** (+1) than in **7** or **9** (+3).[28] The Pt−Hg distance [2.57586(19) Å] in **10** is shorter than those observed in **7** [2.6093(3) and 2.5914(3) Å] and **9** [2.5898-(2) Å], all being in the range of Pt−Hg covalent bond lengths (2.666−2.513 Å).[4,6−13]

Spectroscopic Properties. The structure in the solid state of complex **5** agrees with that depicted in Scheme 1 because its IR spectrum lacks bands in the region 1600−1700 cm^{-1}, as expected for the absence of terminal acetato ligands, and shows an absorption at 302 cm^{-1} assigned to ν(Pt−Cl), cf. those at 298 and 310 cm^{-1} in **1** and the corresponding $(Ph_3PCH_2Ph)^+$ salt,[1] respectively. Its pale salmon-pink color also agrees with this structure (see below under Color of Complexes). Its molar conductivity is consistent with its 1:1 electrolytic nature. The *cis* arrangement of the aryl groups is proposed on the basis of the geometry of all the other complexes. The ^1H and $^{13}C\{^1H\}$ NMR spectra of complex **5** show three singlets due to the *m*-MeO, *p*-MeO, and AcO groups in agreement with the presence of two equivalent κ^1-Ar and μ_2-AcO ligands. However, some resonances due to quaternary carbons of the aryl ligands appear as two broad signals in the region 145−150 ppm, suggesting some type of fluxional behavior. When the temperature was decreased to −50 °C, the resonances due to the methoxy protons appeared as a broad signal, but the methoxy carbon nuclei appear now as three signals, suggesting the conversion of the κ^1-Ar ligands into two equivalent κ^2-Ar ligands. In addition, the $^{13}C\{^1H\}$ NMR resonances due to Me and quaternary carbons of the AcO ligands were duplicated. This suggests the equilibrium $Me_4N[Hg(\mu\text{-}OAc)_2Pt(\kappa^1\text{-}Ar)_2Cl] \leftrightarrow [Hg(OAc)Pt(\kappa^2\text{-}Ar)_2Cl] + [Me_4N]OAc$ in solution, which is shifted to the left when the precipitating agent (Et_2O) is added. The pale salmon-pink color of **5** in the solid state changes to red in $CHCl_3$ or CH_2Cl_2 solutions, which agrees with the existence of such an equilibrium (see below under Color of Complexes). The $^{195}Pt\{^1H\}$ NMR spectrum contains a broad singlet at −1917 ppm with satellites ($^1J_{PtHg}$ = 23600 Hz). The chemical shift is similar to and the coupling constant smaller than those of other related dinuclear complexes (δ = −1981 and −2250 ppm; $^1J_{PtHg}$ = 37 610 and 34 520 Hz, respectively).[4]

(28) The formal oxidation state of Pt or Hg in the heteronuclear complexes has been calculated using the equation $FOS_M = -[\sum q_t + (1/2)\sum q_b]$, where q_t are the charges of ligands only bonded to M, q_b are the charges of all ligands bridging M with other metal centers, except in the anionic complex **7**, where the calculated $FOS_{Pt} = -[\sum q_t + (1/2)\sum q_b] - 1$. Schemes 3 and 4 illustrate the logic of these assignments.

Because each Pt atom in complexes **6**−**9** is a chiral center (as indicated for the structures of **7** and **9** above), a mixture of all stereoisomers (*CA* + *AA* + *CC*) in solution should show up to 12 MeO resonances in the ^{1}H and ^{13}C{^{1}H} NMR spectra due to the κ^2-Ar ligands. In addition, complexes **6** and **7** would show two and four resonances, respectively, due to the methyl groups of AcO and $ArCO_2$ ligands. In solutions of complexes **6**−**8**, only the expected number of MeO resonances (^{1}H and ^{13}C{^{1}H} NMR) for one stereoisomer was observed. However, the presence in complex **9** of 12 different MeO groups (^{1}H and ^{13}C{^{1}H} NMR) reveals the presence of a mixture (approximately 2:1) of diastereoisomers. While the ^{195}Pt{^{1}H} NMR spectra of **6**−**8** (range −1497 to −1549 ppm) show one singlet, that of **9** shows two very close singlets around −1470 ppm, in agreement with the presence of two diastereoisomers in 2:1 molar ratio. The resonances of complexes **7**−**9** show satellites due to Pt−Hg coupling, while in the ^{195}Pt{^{1}H} NMR spectrum of complex **6** satellites could not be detected, possibly because it is less soluble than **7**−**9**. Complexes **7**−**9** exhibit a remarkable $^1J_{HgPt}$ coupling of 28040−26750 Hz, suggesting strong Pt−Hg bonding. As far as we are aware, only two larger Pt−Hg coupling constants have been reported (34520, 37610 Hz), corresponding to dinuclear formally Pt^{+3}−Hg^+ complexes,[4] while most data reported are in the range 11010−1602 Hz and do not correspond to formally Pt^{+3}−Hg^+ complexes.[10,12,15,27,29−31]

The IR spectra of **7**−**9** show absortions in the region 1647−1612 cm^{-1} corresponding to $\nu_{asym}(CO_2)$ of monocoordinated RCO_2^- ligands, as established by the X-ray diffraction studies of **7** and **9**. However, the IR spectrum of **6** does not show absorptions in the 1600−1700 cm^{-1} region, confirming the absence of monocoordinated RCO_2^- ligands, again consistent with the X-ray diffraction study. The IR spectra of complexes **6**−**9** show a very strong band at 1555−1520 cm^{-1}, corresponding to $\nu_{asym}(NO_2)$, and a medium intensity band at 1350−1305 cm^{-1}, assignable to $\nu_{sym}(NO_2)$. However, the expected absorption around 1250 cm^{-1},[23,32] corresponding to $\nu_{sym}(NO_2)$ of the coordinated nitro groups, is probably shifted and could not be assigned.

The ^{1}H NMR spectra of complexes **10**−**12** show four different MeO groups, consistent with the presence of two different κ^1-Ar ligands. The ^{31}P{^{1}H} NMR spectrum of **10** shows two doublets, each flanked by ^{195}Pt and ^{199}Hg satellites, indicating a *cis* arrangement of the PPh_3 ligands. The evidence for the linear Ph_3P−Pt−Hg arrangement in **12** comes from the value of $^2J_{PHg}$ (3195 Hz), similar to $^2J_{PHg}$ (3325 Hz) for the P nucleus *trans* to Hg in **10** and greatly different from $^2J_{PHg}$ (291 Hz) corresponding to the P nucleus *cis* to Hg. The ^{195}Pt{^{1}H} NMR spectrum of **10** shows a doublet of doublets, due to coupling to two different P nuclei ($^1J_{PtP}$ = 2530 Hz, $^1J_{PtP}$ = 2647 Hz), that of **11** a singlet and that of **12** a doublet ($^1J_{PtP}$ = 2373 Hz) with the corresponding Hg satellites.

The values of $\delta(^{195}Pt)$ in Pt/Hg complexes follow the order (in ppm) **9** (−1470) > **8** (−1497) > **7** (−1529) > **6** (−1549) > **5** (−1917) ≫ **11** (−3333) ≫ **12** (−4432) > **10** (−4636), which correlates with the formal oxidation state for Pt,[28] +3 (**7**-**9**) > +2.5 (**6**) ≫ +1 (**10**−**12**), with the exception of complex **5** (Pt^{+3}), the anionic nature of which could be the reason for its position behind **6** ($Pt^{+2.5}$), despite its higher formal oxidation state. As chemical shifts reflect effective charges on metals, it seems that the formal oxidation states of Pt, such as we calculate them,[28] are related to their effective charges. The sequence of $\delta(^{195}Pt)$ values **11** ≫ **12** > **10** reflects the different nature of the ligands around the platinum nucleus. The order $\delta(^{195}Pt{-}PR_3) < \delta(^{195}Pt{-}N$ donor ligand) has been empirically established in a series of closely related chloride complexes.[33]

Most reported $^1J_{PtHg}$ values are in the range 1600−11000 Hz, corresponding to complexes with weak Pt−Hg bonds or with coordination number at Pt ≤ 5 or with formal oxidation state for Pt ≤ +2.[12,15,27,30,31] Values as high as 34520 and 37610 Hz have been reported for octahedral complexes at Pt and linear at Hg with strong Pt^{+3}−Hg^+ bonds.[4] The values of $^1J_{PtHg}$ in our complexes follow the order (in Hz) **9** (28040) > **8** (28026) > **7** (26750) ≫ 25828 (**11**) > 23600 (**5**) > 15004 (**12**) > **10** (14945), which is very similar to that correlating the $\delta(^{195}Pt)$ values. The $^1J_{PtHg}$ for Pt(I)−Hg(I) complexes have been reported in the literature only for cationic species, and the values are lower (11010−4322 Hz)[10,12,31] than those in complexes **10**−**12**. The smaller *trans* influence of bpy than that of PPh_3 in complexes **10** and **12** could be the reason for the greater value of its $^1J_{PtHg}$.

The IR spectra of dinuclear complexes show very strong bands at 1550−1520 cm^{-1} [$\nu_{asym}(NO_2)$] and 1350 cm^{-1} [$\nu_{sym}(NO_2)$], medium bands around 1300 cm^{-1} [$\nu_{sym}(NO_2)$], but no absorptions around 1250 cm^{-1}.

Structural Data of Nitroaryl Groups. We discuss here the structural parameters of nitroaryl groups in complexes **9** and **10** as well as those reported in the previous article,[1] **2**·CH_2Cl_2 and **4**, for which the standard deviations of the C−C distances are low ($\sigma \leq 0.006$ Å). Despite the mesomeric effects of nitro and methoxy groups, the average values of the various C−C distances in the three κ^1-Ar ligands present in **2**·CH_2Cl_2, **4**, and **10** (for which $\sigma \leq 0.004$ Å) are almost identical [range of av values: 1.391(4)−1.394(4) Å]. For **2**·CH_2Cl_2, **4**, and **9** ($\sigma \leq 0.006$ Å), three groups of C−C distances have been found for the κ^2-Ar ligands: short, corresponding to C(X1)−C(X6) (see Chart 1) [av 1.377(5) Å] and C(X3)−C(X4) [av 1.376(6) Å], long, C(X1)−C(X2) [av 1.410(5) Å] and C(X2)−C(X3) [av 1.403(6) Å], and intermediate C(X4)−C(X5) [av 1.395(6) Å] and C(X5)−C(X6) [av 1.397(6) Å]. The latter and the average value of all C−C

(29) Catalano, V. J.; Malwitz, M. A.; Noll, B. C. *Inorg. Chem.* **2002**, *41*, 6553.

(30) Hao, L. J.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1996**, *15*, 3115. Dahmen, K. H.; Imhof, D.; Venanzi, L. M.; Gerfin, T.; Gramlich, V. *J. Organomet. Chem.* **1995**, *486*, 37. Grishin, Y. K.; Roznyatovsky, V. A.; Ustynyuk, Y. A.; Titova, S. N.; Domrachev, G. A.; Razuvaev, G. A. *Polyhedron* **1983**, *2*, 895.

(31) Handler, A.; Peringer, P.; Muller, E. P. *J. Organomet. Chem.* **1990**, *389*, C23.

(32) Vicente, J.; Chicote, M. T.; González-Herrero, P.; Grünwald, C.; Jones, P. G. *Organometallics* **1997**, *16*, 3381. Vicente, J.; Bermúdez, M. D.; Carrión, F. J.; Jones, P. G. *Chem. Ber.* **1996**, *129*, 1395. Vicente, J.; Arcas, A.; Borrachero, M. V.; Molíns, E.; Miravitlles, C. *J. Organomet. Chem.* **1992**, *441*, 487. Vicente, J.; Abad, J. A.; Lahoz, F. J.; Plou, F. J. *J. Chem. Soc., Dalton Trans.* **1990**, 1459. Vicente, J.; Martin, J.; Solans, X.; Font-Altaba, M. *Organometallics* **1989**, *8*, 357. Vicente, J.; Chicote, M. T.; Martin, J.; Artigao, M.; Solans, X.; Font-Altaba, M.; Aguiló, M. *J. Chem. Soc., Dalton Trans.* **1988**, 141. Vicente, J.; Chicote, M. T.; Martin, J.; Jones, P. G.; Fittschen, C. *J. Chem. Soc., Dalton Trans.* **1987**, 881. Vicente, J.; Chicote, M. T.; Martin, J.; Jones, P. G.; Fittschen, C.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1986**, 2215.

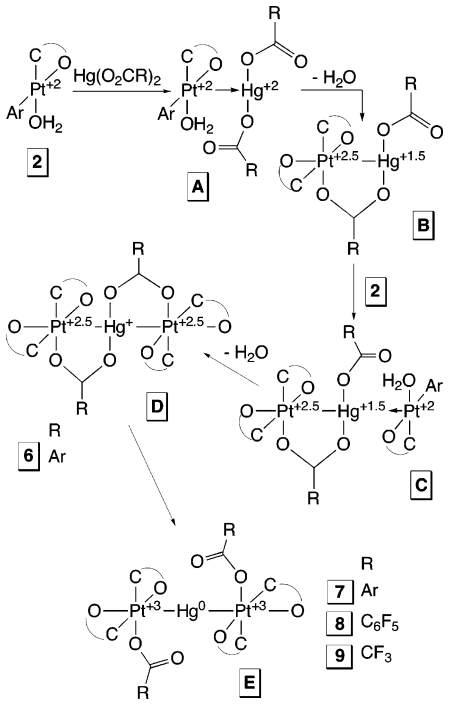
(33) Pregosin, P. S. *Coord. Chem. Rev.* **1982**, *44*, 247.

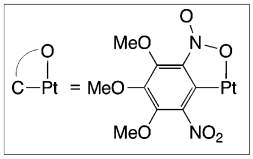
bond distances in κ^2-Ar ligands [av 1.393(6) Å] are the same as that in κ^1-Ar ligands. The strengthening of the C(X1)−C(X6) and C(X3)−C(X4) bonds and the weakening of the C(X1)−C(X2) and C(X2)−C(X3) bonds in the κ^2-Ar ligands are as expected for the −M effect of the −N(O)O(Pt) group, which seems however not to operate for uncoordinated NO_2 groups in κ^1-Ar ligands. Correspondingly, the C−N(O)O(Pt) bond distances ($\sigma \leq 0.006$ Å) are shorter [range: 1.412(6)−1.435(4) Å] than C−NO_2 lengths in κ^2-Ar [1.470(5)−1.486(3) Å] or κ^1-Ar ligands [1.463(5)−1.484(3) Å]. The coordination of a nitro group to Pt increases the N−O(Pt) bond lengths ($\sigma \leq 0.006$ Å) [range: 1.231(6)−1.301(6) Å] with respect to the N−O bond distances in uncoordinated nitro groups [1.201(5)−1.229(5) Å] or in the other N−O bond lengths of κ^2-Ar ligands [1.203(6)−1.219(5) Å].

Color of Complexes. In agreement with previous observations,[23] the intense violet, yellow, orange, or red color of complexes **1**−**4** and **6**−**9** is due to the presence of at least one κ^2-Ar ligand. These colors fade to pale yellow or salmon-pink for **5** and **10**−**12**, where only κ^1-Ar ligands are present. However, solutions of complex **5** in $CHCl_3$ or CH_2Cl_2 have an intense red color, suggesting that in such solutions one or both aryl ligands are present as κ^2-Ar, which agrees with their $^{13}C\{^1H\}$ NMR spectra (see above).

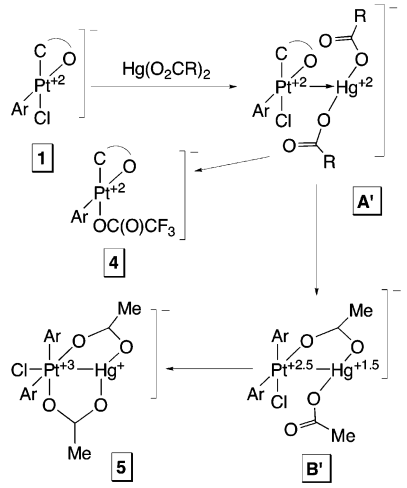
Reaction Mechanism of the Oxidative Addition of Mercury Carboxylates to Diaryl Platinum(II) Complexes. A concerted mechanism for the *cis* oxidative addition of Hg(II) salts to platinum(II) complexes has been suggested.[2,6−8] Starting from complex **2**, we propose the reaction pathway shown in Scheme 3. The first step involves formation of a Pt→Hg bond between the filled d_{z^2} orbital of the platinum atom and an empty orbital of the mercury atom (**A**), with the Pt atom in a square pyramidal coordination and both metals in a formal oxidation state of 2. Complexes with Pt→Hg donor−acceptor bonds have been isolated, or postulated as intermediates, in the formation of Pt−Hg compounds.[4,5,8,14,15] The displacement of the aqua ligand by a carboxylato ligand establishes a bridge between Pt and Hg leading to the intermediate **B**, containing a covalent Pt−Hg bond. The 2.5 formal oxidation state of platinum changes its coordination geometry from square pyramidal to octahedral, concomitant with the change of coordination of the κ^1-Ar ligand to κ^2-Ar. In this intermediate, the mercury atom is still sufficiently electrophilic to form a new Pt→Hg donor−acceptor bond with a second equivalent of **2** to form **C**. Some complexes of type **C**, described as examples of an "arrested" oxidative addition, have been recently isolated.[4] The intermediate **D** results after a new sequence of aqua ligand replacement, carboxylato ligand bridging, and change of coordination of a κ^1-Ar to κ^2-Ar ligand. Complex **6** is an example of this intermediate. The last step is the transfer of carboxylato ligands to platinum to give **E**. Complexes **7**−**9** are examples of the intermediate **E**. This transfer is due to the low charge of Hg in the intermediate **D** and to the low nucleophilic character of the carboxylato ligands when R = Ar, C_6F_5, CF_3. The isolation of the intermediate **D** (**6**) could be explained as a result of the greater nucleophilic character of the acetato ligand. The intramolecular Hg···OC(O)R contacts in **7** and **9** (Figures 3 and 4, respectively) suggest a situation intermediate between **D** and **E** in the solid state in these complexes.

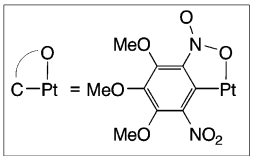
Scheme 3





Scheme 4





For the reaction between the anionic complex **1** and $Hg(OAc)_2$, a similar mechanism could be proposed (Scheme 4). Formation of a Pt→Hg donor−acceptor bond to give the adduct **A′** is also expected in this case. The second step is the formation of one acetato bridge

between Pt and Hg with the concomitant change of coordination of the κ^2-Ar to a κ^1-Ar ligand to give **B′**. When the trifluoroacetate salt was used instead, the bridge with this less nucleophilic carboxylate was not favored and substitution of chloro by trifluoroacetato ligand was preferred to give **4**. Finally, the intermediate **B′** could evolve to complex **5** after formation of a second carboxylato bridge, which would necessitate placing the chloro ligand *trans* to the Hg atom to allow the Pt atom to reach an octahedral coordination.

Conclusions

The first platinum complexes with the aryl group $C_6(NO_2)_2$-2,6-$(OMe)_3$-3,4,5 add oxidatively mercury carboxylates to give three types of complexes: trinuclear Pt−Hg−Pt complexes with (**6**; formally $Pt^{+2.5}-Hg^{+}-Pt^{+2.5}$) or without (**7**−**9**; formally $Pt^{+3}-Hg^{0}-Pt^{+3}$) bridging carboxylato ligands and an anionic dinuclear Pt−Hg complex (**5**; formally $Pt^{+3}-Hg^{+}$). Oxidative addition reactions of $[HgAr_2]$ to $[Pt(dba)_2]$ in the presence of neutral ligands give dinuclear Pt−Hg complexes (**10**−**12**; formally $Pt^{+}-Hg^{+}$).

Acknowledgment. We thank the Ministerio de Ciencia y Tecnología, FEDER (BQU2001-0133), and the Fonds der Chemischen Industrie for financial support. M.D.G.-L. thanks Fundación Séneca (Comunidad Autónoma de la Región de Murcia, Spain) for a grant.

Supporting Information Available: Listing of all refined and calculated atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for **7**, **9**·$CHCl_3$·CH_2Cl_2, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049699Y