Synthesis of Bis(2,6-dinitroaryl)palladium(II) and Mono(2,6-dinitroaryl)platinum(II) Complexes. A New Example of the Transphobia Effect and of Transmetalation from Pt to Hg

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The reaction of [Pd(κ^2-Ar)(O,O-acac)] (κ^2-Ar = κ^2-*C,O*-$C_6(NO_2)_2$-2,6-(OMe); **1**) with 1 equiv of RNC gives [Pd(κ^2-Ar)(O,O-acac)(CNR)] [R = Xy (**2a**), ^{t}Bu (**2b**)] and with 4 equiv of XyNC, *trans*-[Pd(κ^1-Ar)$_2$(CNXy)$_2$] (κ^1-Ar = κ^1-*C*-$C_6(NO_2)_2$-2,6-(OMe); **3**). This complex has also been obtained (1) by reacting Tl(acac) with 1 equiv of *trans*-[Pd(κ^1-Ar)Cl(CNXy)$_2$] (**4**), obtained in turn by reacting *trans*-$(NMe_4)_2$[Pd(κ^1-Ar)Cl(μ-Cl)]$_2$ (**5**) with 4 equiv of XyNC or (2) by reacting [Pd(κ^1-Ar)(*C*-acac)(phen)] (**6**) with 4 equiv of XyNC. *cis*-[Pt(κ^2-Ar)(κ^1-Ar)(PPh_3)] (**7**) reacts (1) with $Hg(OAc)_2$ (1:1) to afford a mixture of [Hg(Ar)(OAc)], *cis*-[{Pt(κ^1-Ar)(PPh_3)}$_2$(μ-OH)(μ-OAc)] (**8**), and *trans*-[{Pt(κ^1-Ar)(PPh_3)}$_2$(μ-OH)$_2$] (**9**) or (2) with $HgCl_2$ (1:1) to give *trans*-[{Pt(κ^1-Ar)(PPh_3)}$_2$(μ-Cl)$_2$] (**10**), which reacts with an excess of Ag(OAc) to give **8**. The reaction of **10** with excess of KOH, or with Tl(acac) (1:1) gives **9**. Reaction of palladium complex **5** with 2 equiv of $Hg(OAc)_2$ affords *trans*-[Pd(κ^2-Ar)(μ-OAc)]$_2$ (**11**). The crystal structures of **2a**, **2b**, **3**, **5**, **8**, **9**, and **11** have been determined.

Introduction

We have reported the synthesis of monoaryl palladium complexes [Pd](Ar) (Ar = C_6H_3Me-2,NO_2-6,[1] $C_6(NO_2)_2$-2,6-$(OMe)_3$-3,4,5,[2] $C_6H_4NO_2$-2,[3] $C_6H_4(NO_2)_3$-2,4,6,[4] C_6H(CHO)-2-$(OMe)_3$-3,4,5,[5,6] C_6HR-6-$(OMe)_3$-2,3,4 (R = CHO,[5–7] CH_2OEt,[8] C(O)NHBu^t),[9] C_6H_3R-2-R′-5 (R = R′ = $CH(OMe)_2$, $CH(SCH_2CH_2S)$,[10] CHO, CO_2H, R = CHO, R′ = CO_2H[11]) through transmetalation reactions using the corresponding mercurial [$HgAr_2$] or [Hg(Ar)Cl]. Except for Ar = $C_6H_4NO_2$-2,[3] no diaryl complexes were obtained even when their syntheses were attempted by using an excess of mercurial.[1,10,11] Monoaryl palladium complexes are also the result of the reaction between other aryl mercurials and Pd(II) complexes,[12–14]

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except in one case.[14] In contrast, [Pt](Ar)$_2$ (Ar = $C_6H_4NO_2$-2,[15] $C_6(NO_2)_2$-2,6-(OMe)$_3$-3,4,5)[6] is always the product of the transmetalation reaction and all attempts to obtain [Pt](Ar) by reacting [$HgAr_2$] with $(Me_4N)_2[Pt_2Cl_6]$ or $K_2[PtCl_4]$ in a 1:1 molar ratio were unsuccessful. Instead, [Pt](Ar)$_2$ and the starting platinum complex were isolated.[15,16] However, complexes [Pt](Ar) (Ar = Ph, 2-arylazoaryl, $C_6H_3NH_2$-2-NO_2-5)[12,17,18] and [Pt](Ar)$_2$ (Ar = Ph)[17] have been prepared by using organomercurials. These data suggest that transmetalation reactions with aryl mercurials can only monoarylate palladium complexes, except in a few cases, and mono- or diarylate platinum complexes, depending on the nature of the aryl ligand. The synthetic challenge of preparing [Pd](Ar)$_2$ and [Pt](Ar) when Ar = $C_6(NO_2)_2$-2,6-(OMe)$_3$-3,4,5, for which all attempts with the corresponding mercurial were unsuccessful, is the object of the present article. We have successfully used mercurials to prepare nitrophenyl complexes of other metals such as Au[19] and Rh.[20]

The most general method for the synthesis of [Pd](Ar)$_2$ is the use of the corresponding Li or Mg derivative but we ruled out this method because of the presence of nitro groups in the aryl ligand. In fact, $LiC_6H_4NO_2$-2 is very unstable[21] and has only been used to prepare a family of complexes *cis*-[Pt(Ar)($C_6H_4NO_2$-2)L_2] (L = PPh_3, R = C_6H_4R'-*x* where *x* = 2, 4, R′ = OMe, Me, CF_3, NO_2; L_2 = cod, *x* = 4, R′ = OMe, Me), a synthesis that functions only at very low temperatures.[22] We report here the preparation of [Pd](Ar)$_2$ complexes from a [Pd](Ar) complex by a new method that we have discovered in an experiment designed to study the consequences of forcing two carbon donor ligands to be coordinated mutually trans. We have shown that when a pair of C-donor/P-donor or C-donor/C-donor ligands in a Pd(II) complex is forced to be trans, the resulting species tends to be unstable, and some transformation (*transphobia*[23–25] effect) is expected to prevent the attainment of such an arrangement. For example, a C−P[25,26] or C−S[27] coupling process (or the C−C coupling in the well-known Suzuki, Stille, and other catalytic reactions) or the insertion of dioxygen into a C−Pd bond have been reported.[25] We have also shown that the resistance to being trans (*transphobia*) of C-donor/C-donor ligands pairs is greater than that for C-donor/P-donor ligands. The concept of transphobia is being used successfully by other authors mainly to discuss geometrical preferences in Pd(II) complexes.[28]

With respect to the synthesis of [Pt](Ar) (Ar = $C_6(NO_2)_2$-2,6-(OMe)$_3$-3,4,5) complexes, we report attempts based on oxidative addition reactions of IAr toward Pt(0) and Pt(II) to Hg(II) transmetalation reactions. We are not aware of a Pt to Hg Ar-transmetalation, i.e., [Pt(II)]R + [Hg]X → [Hg(II)]R + [Pt(II)]X for R = aryl, but one example for R = C≡CR′ has been reported.[29] Previous attempts to prepare [Pt](Ar) complexes by reacting [Hg(Ar)$_2$] with Pt(0) complexes led to complexes with Pt−Hg bonds.[30]

Experimental Section

The reactions were carried out without precautions to exclude light or atmospheric oxygen or moisture. The IR (Nujol/polyethylene), C, H, and N analyses, and melting point determinations were carried out as described elsewhere.[31] NMR spectra were recorded in a Varian Unity 300, Bruker AC 200, or Avance 300 or 400 spectrometer at room temperature. Chemical shifts were referred to TMS (^{1}H, ^{13}C{^{1}H}) or H_3PO_4 (^{31}P). The NMR probe temperature was calibrated with use of ethylene glycol ^{1}H NMR standard methods. The ligands κ¹-*C*-$C_6(NO_2)_2$-2,6-(OMe)$_3$ and κ²-*C,O*-$C_6(NO_2)_2$-2,6-(OMe)$_3$ are represented by κ¹-Ar and κ²-Ar. When the coordination mode of this aryl ligand is not known, it is formulated simply as Ar. Complexes [Pd(κ²-Ar)(O,O-acac)] (**1**), $(NMe_4)_2$[Pd(κ¹-Ar)Cl(μ-Cl)]$_2$ (**5**),[2] [Pd(κ¹-Ar)(*C*-acac)(phen)] (**6**), and *cis*-[Pt(κ²-Ar)(κ¹-Ar)(PPh_3)][23] (**7**) were prepared as reported previously. Single crystals of **5**·0.5Me_2CO were obtained by slow diffusion of Et_2O into a Me_2CO solution of **5**.

Synthesis of [Pd(κ¹-Ar)(acac)(CNXy)] (2a). XyNC (7.5 mg, 0.06 mmol) was added to a solution of [Pd(κ²-Ar)(O,O-acac)] (26.5 mg, 0.06 mmol) (**1**) in Me_2CO (6 mL). After 45 min, the resulting solution was concentrated (1 mL) and addition of *n*-pentane (4 mL) gave a suspension that was filtered off and air-dried to give complex **2a** as a pale yellow solid. Yield: 29.1 mg, 86%. Mp: 162.5–163.7 °C. IR (cm^{-1}): ν (CN) 2202; ν (CO) 1566. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (t, 1 H, *p*-H, $^2J_{HH}$ = 7.62 Hz), 7.09 (d, 2 H, *m*-H, $^2J_{HH}$ = 7.53 Hz), 5.40 (s, 1 H, CH), 3.99 (s, 6 H, OMe), 3.90 (s, 3 H, OMe), 2.38 (s, 6 H, Me Xy), 1.99 (s, 3 H, Me acac), 1.95 (s, 3 H, Me acac). Anal. Calcd for $C_{23}H_{25}N_3O_9Pd \cdot C_2H_5O_{0.5}$: C, 47.44; H, 4.78; N, 6.64. Found: C, 47.51; H, 4.78; N, 6.64. Single crystals

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of **2a**·0.5Et_2O were obtained by slow diffusion of *n*-pentane into an Me_2CO/Et_2O solution of **2a**.

Synthesis of [Pd(κ^1-Ar)(acac)(CN^{t}Bu)] (2b). ^{t}BuNC (8.9 μL, 0.08 mmol) was added to a solution of **1** (35.6 mg, 0.08 mmol) in Me_2CO (5 mL). After 50 min, the resulting solution was concentrated (1 mL) and addition of *n*-pentane (4 mL) gave a suspension that was filtered off and air-dried to give complex **2b** as a pale yellow solid. Yield: 29.7 mg, 71%. Mp: 153–154 °C. IR (cm^{-1}): ν (CN) 2218; ν (CO) 1580. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 5.35 (s, 1 H, CH), 3.99 (s, 6 H, OMe), 3.90 (s, 3 H, OMe), 1.97 (s, 3 H, Me), 1.91 (s, 3 H, Me), 149 (s, 9 H, ^{t}Bu). Anal. Calcd for $C_{19}H_{25}N_3O_9Pd$: C, 41.80; H, 4.58; N, 7.70. Found: C, 41.43; H, 4.80; N, 7.67. Single crystals of **2b** were obtained by slow diffusion of *n*-pentane into a Et_2O solution of **2b**.

Synthesis of *trans*-[Pd(κ^1-Ar)$_2$(CNXy)$_2$] (3). XyNC (39.5 mg, 0.30 mmol) was added to a solution of **1** (34.8 mg, 0.075 mmol) in Me_2CO (6 mL). After 1 h of stirring the solution was concentrated (3 mL) and the resulting solid was filtered off and washed with Et_2O to give **3** as a colorless solid. Concentration of the filtrate afforded a second crop of **3**. Yield: 27.2 mg, 82%. Mp: 260–261 °C dec. IR (cm^{-1}): ν (CN) 2204. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.19 (t, 2 H, *p*-H, $^2J_{HH}$ = 7.5 Hz), 7.05 (d, 4 H, *m*-H, $^2J_{HH}$ = 7.5 Hz), 3.96 (s, 12 H, OMe), 3.89 (s, 6 H, OMe), 2.30 (s, 12 H, Me). Anal. Calcd for $C_{36}H_{36}N_6O_{14}Pd$: C, 48.96; H, 4.11; N, 9.52. Found: C, 48.61; H, 4.15; N, 9.56. Single crystals of **3** were obtained by slow diffusion of *n*-pentane into a $CHCl_3$ solution of **3**.

Synthesis of *trans*-[Pd(κ^1-Ar)Cl(CNXy)$_2$] (4). XyNC (98.5 mg, 0.75 mmol) was added to a suspension of **5** (191 mg, 0.19 mmol) in CH_2Cl_2 (7 mL). After 1 h of stirring, the reaction mixture was filtered through anhydrous $MgSO_4$. The filtrate was concentrated (2 mL) and *n*-pentane was added (1 mL). The suspension was filtered and the filtrate was concentrated (ca. 2 mL) to give a solid that was filtered off, washed with *n*-pentane, and air-dried to give **11** as a colorless solid. Yield: 137.9 mg, 55%. Mp: 150–151 °C. IR (cm^{-1}): ν (CN) 2203; ν (PdCl) 314. ^{1}H RMN (400 MHz, $CDCl_3$): δ 7.25 (t, 2 H, *p*-H, $^2J_{HH}$ = 7.7 Hz), 7.10 (d, 4 H, *m*-H, $^2J_{HH}$ = 7.6 Hz), 3.99 (s, 6 H, OMe), 3.91 (s, 3 H, OMe), 2.37 (s, 12 H, Me). Anal. Calcd for $C_{27}H_{27}N_4ClO_7Pd$: C, 48.99; H, 4.11; N, 8.47. Found: C, 48.97; H, 4.31; N, 8.51. Single crystals of **4** were obtained by slow diffusion of *n*-pentane into a $CDCl_3$ solution of **4**.

Synthesis of ArI (6). A solution of [Hg(Ar)$_2$] (204 mg, 0.29 mmol) and I_2 (213 mg, 0.84 mmol) in dimethylformamide (10 mL) was heated for 1 h. When the solution was cooled, a 1 M aqueous solution of NaBr (50 mL) was added and the resulting suspension was filtered. The solid was washed with water and air-dried to give **6** as a colorless solid. Yield: 191 mg, 87%. Mp: 175–177 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.03 (s, 6 H, OMe), 3.99 (s, 3 H, OMe). Anal. Calcd for $C_9H_9IN_2O_7$: C, 28.14; H, 2.36; N, 7.29. Found: C, 28.54; H, 2.28; N, 7.31.

Synthesis of *cis*-[{Pt(κ^1-Ar)(PPh$_3$)}$_2$(μ-OH)(μ-OAc)]·2CH_2Cl_2 (8). Ag(OAc) (20 mg, 0.12 mmol) was added to a solution of **10** (42 mg, 0.03 mmol) in CH_2Cl_2 (5 mL). After 48 h of stirring, the suspension was filtered, the filtrate was concentrated (2 mL), and AcOH (1 μL) was added. A crystalline solid was obtained by slow diffusion of *n*-hexane (20 mL) into the resulting solution. The solid was isolated by filtration, washed with *n*-hexane, and air-dried to give **8** as a yellow solid. Yield: 28 mg, 61%. Mp: 170–174 °C. IR (cm^{-1}): ν (OH) 3605. ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 7.73–7.31 (m, 30 H, PPh_3), 3.74 (s, 6 H, OMe), 3.70 (s, 12 H, OMe), 1.78 (br, 1 H, OH), 0.69 (s, 3 H, AcO). ^{1}H NMR (400 MHz, $CDCl_3$, −30 °C): δ 7.95–7.89 (m, 8 H, PPh_3), 7.51–7.47 (m, 14 H, PPh_3), 7.07–7.00 (m, 8 H, PPh_3), 3.75 (s, 6 H, OMe), 3.71 (s, 12 H, OMe), 1.93 (t, 1 H, OH, $^3J_{PH}$ = 2.4 Hz), 0.68 (s, 3 H, AcO). ^{31}P{^{1}H} NMR (81.01 MHz, $CDCl_3$): δ 4.6 (s, PPh_3, $^1J_{PtP}$ = 4292 Hz). ^{31}P{^{1}H} NMR (162.29 MHz, $CDCl_3$): δ 4.08 (s, PPh_3, $^1J_{PtP}$ = 4292 Hz). Anal. Calcd for $C_{58}H_{56}Cl_4N_4O_{17}P_2Pt_2$: C, 41.59; H, 3.37; N, 3.34. Found: C, 41.83; H, 3.40; N, 3.42. Single crystals of **8** were obtained by slow diffusion of *n*-hexane into a CH_2Cl_2 solution of **8**.

Synthesis of *trans*-[{Pt(κ^1-Ar)(PPh$_3$)}$_2$(μ-OH)$_2$] (9). Method a. KOH (85%, 15 mg, 0.23 mmol) was added to a stirred suspension of **10** (38 mg, 0.03 mmol) in thf (10 mL). The mixture was stirred for 24 h, the solvent was evaporated to dryness, and CH_2Cl_2 (5 mL) was added. The resulting suspension was filtered and the filtrated was concentrated to 1 mL. Addition of Et_2O (15 mL) gave a suspension that was filtered off, washed with Et_2O, and air-dried to give complex **9** as a pale yellow solid.Yield: 30 mg, 82%.

Method b. Tl(acac) (20 mg, 0.07 mmol) was added to a suspension of **10** (50 mg, 0.03 mmol) in Me_2CO/H_2O (3/0.5 mL). The mixture was stirred for 24 h, then the suspension was concentrated and extracted with CH_2Cl_2 (2 × 5 mL). The resulting solution was stirred with Celite for 12 h. The suspension was filtered and the filtrate was concentrated (1 mL). Addition of Et_2O (1 mL) gave a suspension that was filtered off, washed with Et_2O, and air-dried. Yield: 23 mg, 48%. Mp: 284 °C dec. IR (cm^{-1}): ν (OH) 3602. ^{1}H NMR (400.9 MHz, CD_2Cl_2, 25 °C): δ 7.80–7.29 (m, 30 H, PPh_3), 3.66 (s, 18 H, OMe), −0.71(d, 2 H, OH, $^3J_{PH}$ = 3 Hz). ^{1}H NMR (300.1 MHz, $CDCl_3$, 25 °C): δ 7.78–7.35 (m, 30 H, PPh_3), 3.651 (s, 6 H, OMe), 3.645 (s, 12 H, OMe), −0.75 (d, 2 H, OH, $^3J_{PH}$ = 3 Hz). ^{31}P{^{1}H} NMR (162.29 MHz, CD_2Cl_2, 25 °C): δ 4.29 (s, PPh_3, $^1J_{PtP}$ = 4168 Hz). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): δ 5.15 (s, PPh_3, $^1J_{PtP}$ = 4152 Hz). ^{13}C{^{1}H} NMR (100.81 MHz, CD_2Cl_2, 25 °C): δ 148.64 (s, C_q Ar), 146.82 (s, C_q Ar), 143.16 (s, C_q Ar), 134.70 (d, *o*-C PPh_3, $^2J_{PC}$ = 11 Hz), 131.56 (s, *p*-C PPh_3), 128.93 (d, *m*-C PPh_3, $^3J_{PC}$ = 11 Hz), 128.69 (d, *i*-C PPh_3, $^1J_{PC}$ = 65 Hz), 115.31 (d, C_q Ar, $^2J_{PC}$ = 10 Hz), 62.48 (s, *m*-OMe), 61.49 (s, *p*-OMe). Anal. Calcd for $C_{54}H_{50}N_4O_{16}P_2Pt_2$: C, 44.33; H, 3.44; N, 3.83. Found: C, 44.06; H, 3.24; N, 3.83. Single crystals of **9**·1.28$CDCl_3$·0.72CH_2Cl_2 were obtained by slow diffusion of *n*-hexane into a $CDCl_3$ + CH_2Cl_2 solution of **9**.

Synthesis of *trans*-[Pt(κ^1-Ar)(PPh$_3$)(μ-Cl)]$_2$ (10). $HgCl_2$ (110 mg, 0.41 mmol) was added to a solution of **7** (357 mg, 0.37 mmol) in CH_2Cl_2 (5 mL) and the resulting suspension was stirred for 24 h. The suspension was filtered and the solid was washed with CH_2Cl_2 (5 mL). The filtrate was concentrated (3 mL) and Et_2O (10 mL) was added. The resulting suspension was filtered and the solid was washed with Et_2O and air-dried to give **10** as a pale yellow solid. Yield: 262 mg, 95%. Mp: 308 °C dec. IR (cm^{-1}): ν (PtCl) 290, 272. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11–6.91 (m, 30 H, PPh_3), 3.68 (s, 18 H, OMe). ^{31}P{^{1}H} NMR (162.29 MHz, $CDCl_3$): δ 8.33 (s, PPh_3, $^1J_{PtP}$ = 4473 Hz). Anal. Calcd for $C_{54}H_{48}Cl_2N_4O_{14}P_2Pt_2$: C, 43.24; H, 3.23; N, 3.75. Found: C, 43.05; H, 3.20; N, 3.80. Crystals apparently suitable for an X-ray crystallographic study were obtained for **10** by slow diffusion of *n*-hexane into a $CDCl_3$ solution of **10**.

Synthesis of *trans*-[Pd(κ^2-Ar)(μ-OAc)]$_2$ (11). Hg(OAc)$_2$ (63.3 mg, 0.20 mmol) was added to a suspension of $(NMe_4)_2$[Pd(κ^1-Ar)Cl(μ-Cl)]$_2$ (**5**) (101.1 mg, 0.10 mmol) in Me_2CO (6 mL). The resulting suspension was stirred for 30 min and then concentrated (2 mL) and filtered. The solid was treated with CH_2Cl_2 (5 mL), the mixture was filtered through Celite, Et_2O (10 mL) was added to the filtrate, and the suspension was filtered to give **11** as a red solid. Yield: 28 mg, 34%. Mp: 210–211 °C. IR (cm^{-1}): ν (CO) 1548, 1530. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.13 (s, 6 H, *p*-OMe), 3.96, 3.89 (two s, 6 H, *m*-OMe), 2.08 (s, 6 H, Me). Anal. Calcd for $C_{44}H_{48}N_8O_{36}Pd_2$: C, 31.24; H, 2.84; N, 6.63. Found: C, 31.26; H, 2.86; N, 6.63. Single crystals of **11** were obtained by slow diffusion of *n*-hexane vapor into a CH_2Cl_2 solution of **11**.

X-ray Structure Determinations. For clarity, solvent contents are omitted here, but are defined in Tables 1 and 2. Compounds **2a**, **2b**, **3**, **5**, and **11** were measured on a Bruker Smart APEX diffractometer. Data were collected with use of monochromated

Table 1. Crystallographic Data for Complexes 2a, 2b, 3, and 5

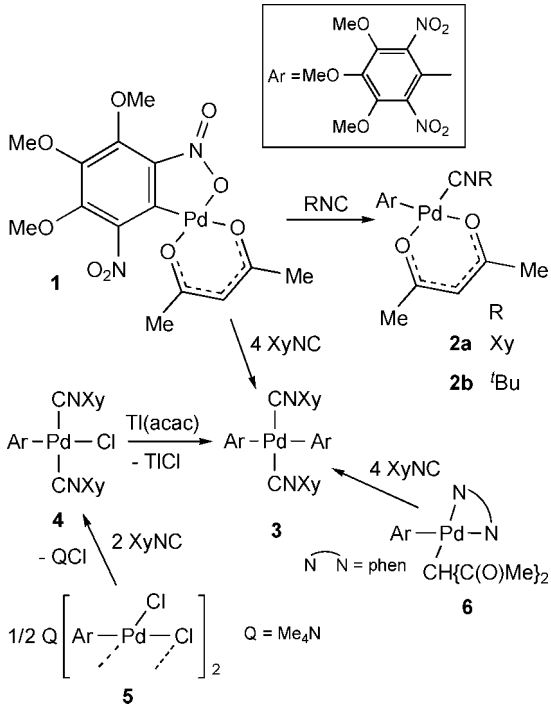
	2a·0.5Et_2O	**2b**	**3**	**5**·0.5Me_2CO
formula	$C_{25}H_{30}N_3O_{9.5}Pd$	$C_{19}H_{25}N_3O_9Pd$	$C_{36}H_{36}N_6O_{14}Pd$	$C_{27.5}H_{45}Cl_4N_6O_{14.5}Pd_2$
M_r	630.92	545.82	883.11	1046.30
cryst habit	colorless block	colorless prism	colorless needle	orange lath
cryst size (mm^3)	0.20 × 0.16 × 0.08	0.24 × 0.12 × 0.08	0.13 × 0.09 × 0.07	0.17 × 0.12 × 0.07
cryst syst	triclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
cell constants				
a, Å	10.0026(5)	16.322(2)	21.1560(9)	14.6377(6)
b, Å	10.5211(5)	8.2938(11)	11.2128(5)	16.8923(7)
c, Å	14.3597(7)	18.474(2)	16.2406(7)	18.0811(7)
α, deg	107.407(2)	90	90	73.573(2)
β, deg	103.434(2	112.011(2)	92.797(2)	88.311(2)
γ, deg	91.700(2)	90	90	71.063(2)
V ($Å^3$)	1394.50(12)	2318.5(5)	3848.0(3)	4046.6(3)
Z	2	4	4	4
λ (Å)	0.71073	0.71073	0.71073	0.71073
ρ(calcd) (Mg m^{-3})	1.503	1.56	1.52	1.72
μ (mm^{-1})	0.72	0.853	0.558	1.222
F(000)	646	1112	1808	2112
T (K)	100(2)	100(2)	100(2)	100(2)
$2\theta_{max}$ (deg)	56	56	56	56
no. of reflns measd	16229	24490	41574	47676
no. of indep reflns	6240	5320	7865	18222
transmissions	0.945, 0.869	0.935, 0.821	0.962, 0.931	0.919, 0.819
R_{int}	0.0232	0.0406	0.0511	0.0299
no. rest/params	40/377	6/296	0/524	26/1007
$R_w(F^2$, all reflns)	0.0775	0.0726	0.0844	0.1006
$R(F, > 4\sigma(F))$	0.0296	0.0306	0.0368	0.0424
S	1.05	1.05	1.07	1.02
max *Δρ* (e $Å^{-3}$)	0.97	0.82	0.64	1.22

Table 2. Crystallographic Data for Complexes 8, 9, and 11

	8·2CH_2Cl_2	**9**·1.28$CDCl_3$·0.72CH_2Cl_2	**11**
formula	$C_{58}H_{56}Cl_4N_4O_{17}P_2Pt_2$	$C_{56}H_{52.7}Cl_{5.3}N_4O_{16}P_2Pt_2$	$C_{22}H_{24}N_4O_{18}Pd_2$
M_r	1674.99	1677.04	845.25
cryst habit	pale yellow prism	yellow, irregular	red needle
cryst size (mm^3)	0.28 × 0.22 × 0.10	0.19 × 0.18 × 0.08	0.30 × 0.05 × 0.03
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
cell constants			
a, Å	13.2770(8)	14.1641(8)	10.2492(5)
b, Å	13.5786(8)	14.3015(8)	11.6858(6)
c, Å	18.7001(11)	18.3803(12)	14.5201(8)
α, deg	98.449(4)	68.708(4)	66.848(2)
β, deg	91.862(4)	74.876(4)	72.464(2)
γ, deg	107.581(4)	63.103(4)	64.161(2)
V ($Å^3$)	3168.4(3)	3072.8(3)	1421.30(13)
Z	2	2	2
λ (Å)	0.71073	0.71073	0.71073
ρ(calcd) (Mg m^{-3})	1.76	1.81	1.98
μ (mm^{-1})	4.701	4.90	1.358
F(000)	1644	1641	840
T (K)	133(2)	133(2)	100(2)
$2\theta_{max}$ (deg)	60	60	56
no. of reflns measd	64157	64443	15553
no. of indep reflns	18469	17889	5744
transmissions	0.746, 0.528	0.535, 0.746	0.960, 0.686
R_{int}	0.0333	0.0341	0.0355
no. rest/params	176/800	774/799	0/423
$R_w(F^2$, all reflns)	0.0639	0.0808	0.0756
$R(F, > 4\sigma(F))$	0.0259	0.0294	0.0362
S	0.99	0.99	1.09
max *Δρ* (e $Å^{-3}$)	1.57	1.47	0.666

Mo Kα radiation in *ω* scan mode. Data for compounds **8** and **9** were measured on a Bruker SMART 1000 diffractometer, using monochromated Mo Kα radiation in *ω* and *φ* scan modes. Absorption corrections were based on the multiscan method (program SADABS). All were refined anisotropically on F.[2] Restraints to local aromatic ring symmetry or light atom displacement factor components were applied in some cases. The ordered methyl groups were refined by using rigid groups, and the other hydrogens were refined by using a riding mode. Special features: **2a**, the ether of solvation is disordered over an inversion center; **2b**, one of the nitro groups is disordered over two positions, ca. 60:40%; **5**, NMe_4 cations are disordered over two positions; **8**, one dichloromethane is disordered over two positions; the OH hydrogen was refined freely; and **9**, the solvent content was interpreted as overlapping $CDCl_3$ and CH_2Cl_2; the OH hydrogens were refined freely, but with an O−H distance restraint.

Scheme 1

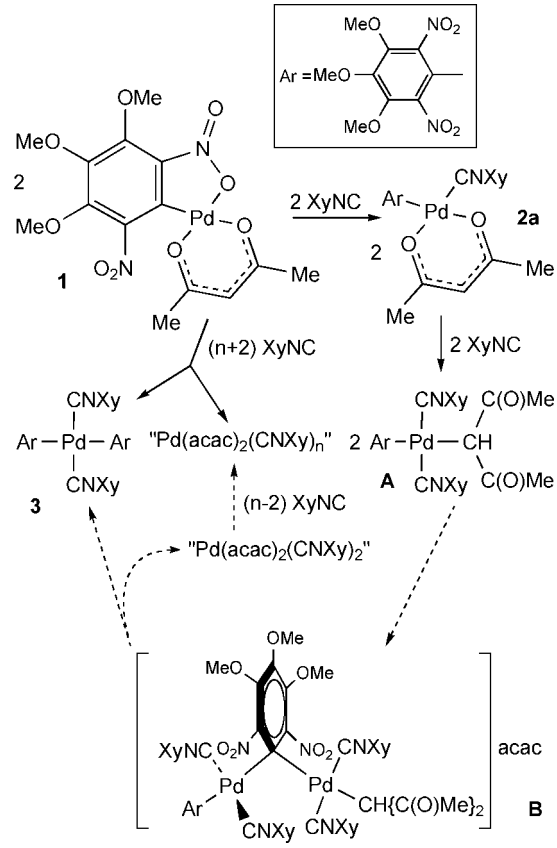


Results and Discussion

[Pd(κ^2-Ar)(*O*,*O*-acac)] (**1**) reacts with 1 equiv of isocyanides to give the adducts [Pd(κ^1-Ar)(*O*,*O*-acac)(CNR)] [R = Xy (**2a**), ^{t}Bu (**2b**); Scheme 1]. We have reported reactions of **1** with other neutral ligands to give adducts [Pd(κ^1-Ar)(*O*,*O*-acac)L] [L = PPh_3, py, tht, bis(diphenylphosphino)methanemonoxide (dppmo)] and [Pd(κ^2-Ar)(*O*,*O*-acac)(phen).[2] When **1** was reacted with 4 equiv of XyNC in acetone, several fast changes of color were observed (to orange via colorless, green, and yellow) and after 5 min a colorless solid begin to precipitate. After 1 h of stirring, concentration of the solution precipitated *trans*-[Pd(κ^1-Ar)$_2$(CNXy)$_2$] (**3**) in 82% yield as a colorless solid. In the orange filtrate, a complex mixture of products was detected by ^{1}H NMR, among which **3** was identified. An X-ray crystallographic study of a few crystals obtained from this filtrate was carried out. Although a complete crystallographic analysis was not possible because of poor data quality, the presence of a palladium atom in a square-planar environment with two cis XyNC ligands was shown with certainty. The other two coordination positions were occupied by a complex chelate ligand apparently resulting from the insertion of XyNC into Pd−C$_{(acac)}$ bonds in which three isocyanides and two acac ligands were involved. When this reaction was carried out in CH_2Cl_2, the same fast changes of color were observed, although the green persisted longer (∼2 min), but complex **3** was also isolated. When **1** was reacted with 2 equiv of XyNC, the yield of **3** decreased (19%) and **2a** also was obtained. Addition of 4 equiv of ^{t}BuNC to an acetone solution of **1** also led to several rapid color changes (to pale yellow via orange and yellow) but only a complex mixture of products was isolated.

The above reactions were designed with the purpose of obtaining a complex with four carbon donor ligands [Pd(κ^1-Ar)(*C*-acac)(XyNC)$_2$] (**A**; Scheme 2). We hypothesize that the great C/C transphobia, *T*(C/C), should destabilize the complex, favoring an isocyanide insertion into the Pd−C$_{acac}$ bond or inducing some C−C coupling process (see Introduction). However, instead, a new transphobia effect was observed in the 1:4 reaction: a disproportionation reaction leading to **3** and

Scheme 2



a mixture in which, at least, a product of stoichiometry "Pd(acac)$_2$(CNXy)$_5$" (**X**) was obtained (see above). Formation of **3** containing four C-donor ligands suggests that *T*(Ar/*C*-acac) in the intermediate complex **A** is greater than *T*(Ar/Ar) or *T*(CNXy/CNXy) in **3**. The formation of **3** as a stable complex in spite of the four C−Pd bonds must be attributed to the strong Ar−M bonds. ^{1}H NMR spectra of complex **3** at 20, 30, 40, 50, and 60 °C in $CDCl_3$ during 45 min show no decomposition or isomerization process. Its platinum homologue, *trans*-[Pt(κ^1-Ar)$_2$(CNXy)$_2$], is obtained by heating the cis isomer at 150 °C. The greater stability of the trans isomer was rationalized in the case of the Pt complex on steric grounds.[23] The low yield of **3** in the 1:2 reaction suggests that formation of **X** is a fast process consuming part of the XyNC required for the synthesis of **3**.

A Proposal for the Reaction Pathway of Formation of 3 from 1. It is reasonable to assume that the first step in this process is formation of complex **2a**, which in turn reacts with XyNC to give the desired complex **A** (Scheme 2). We assume this complex to be trans because, with exclusively C-donor ligands, this seems the geometry with the lower steric hindrance between Ar and acac ligands. Formation of **3** requires an intermolecular transmetalation reaction that could occur through a dinuclear complex such as **B**. The replacement of the acac ligand could be favored by the strong *T*(Ar/*C*-acac) and the trans geometry of **A**. Complexes with bridging aryl ligands have been postulated as intermediates in the formation of diaryl from monoaryl complexes.[32] A few palladium complexes containing bridging aryl ligands have been isolated.[33] Cleavage of the

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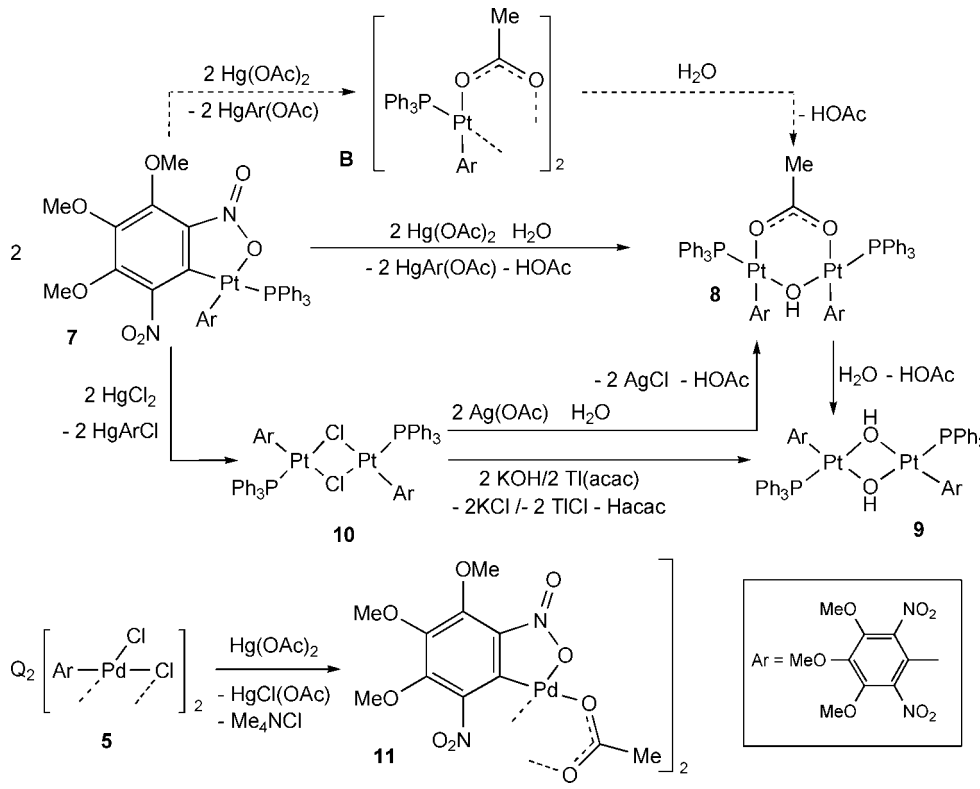
Scheme 3



weakest Ar−Pd bond, i.e., that trans to the acac ligand, and coordination of the replaced acac ligand would give **3** and a highly reactive species *trans*-[Pd(*C*-acac)₂(CNXy)₂] (because of the strong *T*(*C*-acac/*C*-acac)), which would insert XyNC to give, among other products, complex "Pd(acac)₂(CNXy)₅" (**X**). We have studied the reaction between [Pd(acac)₂] and XyNC under different reaction conditions but we have not yet isolated any pure compound from the mixtures of complexes that we obtain. We have reported that isocyanides insert into the C−Pd bond of acetonyl complexes giving β-ketoenamino derivatives.[34] A similar insertion followed by tautomerization could have occurred in the synthesis of **X**.

To support this proposal we have attempted the synthesis of **A** by two other routes. Thus, (1) we have prepared *trans*-[Pd(κ¹-Ar)Cl(CNXy)₂] (**4**) from *trans*-(Me₄N)₂[Pd(κ¹-Ar)Cl(μ-Cl)]₂ (**5**) and excess of XyNC, and reacted it with 1 equiv of Tl(acac) and (2) we have reacted *cis*-[Pd(κ¹-Ar)(*C*-acac)(phen)] (**6**) with 4 equiv of XyNC. In agreement with the above proposed mechanism, both reactions led to the isolation of complex **3** instead of **A**. The low stability of this intermediate contrasts with that of the related complexes **4** and **6** in which, for all trans pairs of groups, *T* < T(Ar/*C*-acac).

Synthesis of Monoaryl Pt Complexes: Oxidative Addition Reactions. To prepare [Pt](Ar) complexes by an oxidative addition reaction, we synthesized IC₆(NO₂)₂-2,6-(OMe)₃-3,4,5 (**6**) by reacting [HgAr₂] with I₂, following the method reported by Deacon.[35] However, **6** did not react at room temperature with 1 equiv of [Pt₂(dba)₃]·dba in toluene under nitrogen and decomposition was observed upon refluxing. Addition of 2,2′-bipyridine to the reaction mixture at room temperature allowed the isolation of an impure sample of [Pt(κ¹-Ar)I(bpy)] in low yield (13%). Therefore, this route to monoaryl derivatives was discarded.

Transmetalation Reactions. The room temperature reaction of *cis*-[Pt(κ²-Ar)(κ¹-Ar)(PPh₃)] (**7**) with Hg(OAc)₂ (1:1) in CH_2Cl_2 gives a mixture of [Hg(Ar)(OAc)] and the dinuclear platinum(II) complexes *cis*-[{Pt(κ¹-Ar)(PPh₃)}₂(μ-OH)(μ-OAc)] (**8**) and *trans*-[Pt(κ¹-Ar)PPh₃(μ-OH)]₂ (**9**; Scheme 3). It is reasonable to assume that the transmetalation reaction took place through the dinuclear complex **B**, containing two bridging acetato ligands, that complex **8** is the result of a partial hydrolysis of **B**, and that **9** is the product of the hydrolysis of **8**. The mixture of **8**, **9**, and [Hg(Ar)(OAc)] could not be separated and all attempts to prevent any hydrolysis failed. The only [Pt](Ar)(μ-OAc) complexes reported, the cycloplatinated derivatives [Pt(C^E)(μ-OAc)]₂ (E = N, P, As), seem to be stable toward moisture.[36,37] The main difference between these complexes and **B** is that the latter has a much more crowded environment around Pt and this could be the reason for its high reactivity toward moisture. This would also explain the facile hydrolysis of complex **8**.

The above reverse transmetalation reaction was unexpected, as we have reported that [Hg(O₂CR)₂] (R = Me, CF_3, C_6F_5) reacts with 1 equiv of *cis*-Me₄N[Pt(κ²-Ar)(κ¹-Ar)Cl] or 0.5 equiv of *cis*-[Pt(κ²-Ar)(κ¹-Ar)L] (L = H_2O, PhCN) to give Pt−Hg

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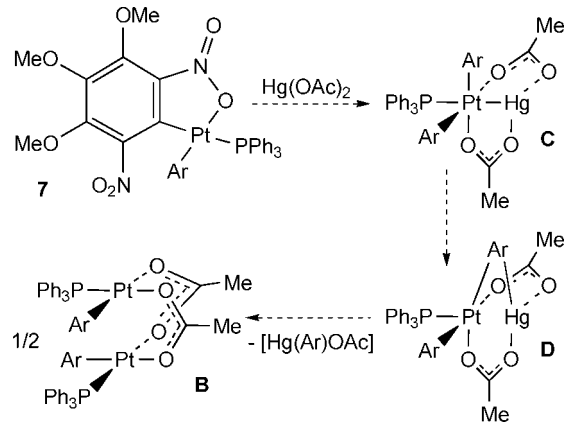
Scheme 4



complexes $Me_4N[Hg(\mu\text{-}OAc)_2\{Pt(\kappa^1\text{-}Ar)_2Cl\}]$, $[Hg(\mu\text{-}OAc)_2\{Pt(\kappa^2\text{-}Ar)_2\}_2]$, $[Hg\{Pt(\kappa^2\text{-}Ar)_2(O_2CR)\}_2]$, or *cis*-$Me_4N[Pt(\kappa^2\text{-}Ar)(\kappa^1\text{-}Ar)(O_2CCF_3)]$.[30] It is possible that some adduct similar to these Pt−Hg complexes is an intermediate (for example, **C** in Scheme 4). As the presence of PPh_3 in the intermediate **C** is the only difference with respect to the stable $Me_4N[Hg(\mu\text{-}OAc)_2\{Pt(\kappa^1\text{-}Ar)_2Cl\}]$, it is possible that this ligand is responsible for the cleavage of the Pt–Hg bond in **C** and the formation of a complex with a bridging aryl group (**D**) finally affording complex **B** and [Hg(Ar)(OAc)].

This unexpected result opened a route for the synthesis of the desired [Pt](Ar) complexes that we had attempted previously, but without success (see Introduction). However, given the difficulties we encountered in isolating **8** and **9**, we attempted the reaction of **7** with 1 equiv of $HgCl_2$ giving $[Pt(\kappa^1\text{-}Ar)(\mu\text{-}Cl)PPh_3]_2$ (**10**), the homologue of complex **B**. This complex can be easily precipitated from the reaction mixture by addition of Et_2O while the byproduct, [Hg(Ar)Cl], remains soluble. The addition of an excess of Ag(OAc) to a CH_2Cl_2 solution of **10** gave **8**, which must be recrystallized in the presence of acetic acid to avoid formation of traces of **9.** We have unsuccessfully attempted to prepare the intermediate **B** by reacting **8** with a large excess of HOAc; a complex mixture of products resulted. The reaction of **10** with excess KOH in thf or with 2 equiv of Tl(acac) in a mixture of Me_2CO and water (6:1) gave **9** in 82% or 48% yields, respectively.

The reaction of palladium complex **5** with 2 equiv of $Hg(OAc)_2$ does not proceed via transmetalation or formation of a Pd−Hg compound but simply with a ligand substitution of chloro by acetato to give the dinuclear complex $[Pd(\kappa^2\text{-}Ar)(\mu\text{-}O_2CMe)]_2$ (**11**; Scheme 3).

Crystal Structures. Crystals apparently suitable for an X-ray crystallographic study were obtained for **10**. However, although a complete crystallographic analysis was not possible because the rings with the nitro and methoxy groups were badly disordered, the position of the ligands was established with certainty to be that indicated in Scheme 3.

Complete crystallographic analysis was carried out for complexes **2a** (Figure 1), **2b** (Figure 2), **3** (Figure 3), **5** (Figure 4), **8** (Figure 5), **9** (Figure 6), and **11** (Figure 7). Solvent contents are given in Tables 1 and 2. All structures reveal a metal in a distorted square-planar coordination. In the dinuclear complexes **5** and **9**, the coordination planes are almost coplanar (angle between coordination planes: 1.8°, 2.9° (**5**) and 0° by symmetry (**9**)) as has been found and theoretically predicted for most

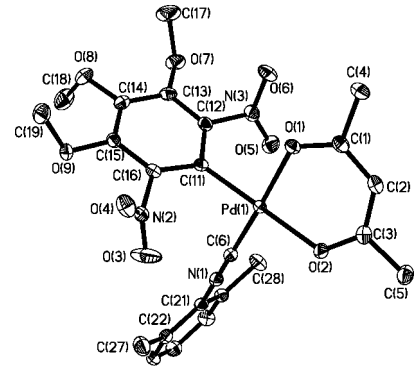


Figure 1. Ellipsoid representation of complex **2a** (50% probability). Selected bond lengths (Å) and angles (deg): Pd(1)–C(6) = 1.925(2), Pd(1)–C(11) = 2.000(2), Pd(1)–O(1) = 2.0130(14), Pd(1)–O(2) = 2.0456(15), O(1)–C(1) = 1.280(3), O(2)–C(3) = 1.275(3), O(3)–N(2) = 1.208(3), O(4)–N(2) = 1.218(2), O(5)–N(3) = 1.227(2), O(6)–N(3) = 1.223(3), N(1)–C(6) = 1.145(3), N(1)–C(21) = 1.405(3), N(2)–C(16) = 1.475(3), N(3)–C(12) = 1.477(3), C(6)–Pd(1)–C(11) = 88.56(8), C(11)–Pd(1)–O(1) = 87.58(7), C(6)–Pd(1)–O(2) = 91.23(7), O(1)–Pd(1)–O(2) = 92.67(6).

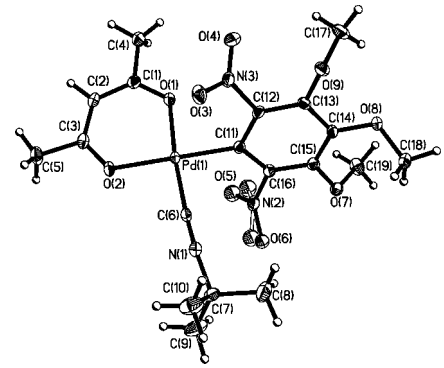


Figure 2. Ellipsoid representation of complex **2b** (50% probability). Selected bond lengths (Å) and angles (deg): Pd(1)–C(6) = 1.927(2), Pd(1)–C(11) = 2.002(2), Pd(1)–O(1) = 2.0098(16), Pd(1)–O(2) = 2.0519(16), N(1)–C(6) = 1.143(3), N(1)–C(7) = 1.474(3), O(1)–C(1) = 1.280(3), O(2)–C(3) = 1.271(3), N(3)–O(4) = 1.222(3), N(3)–O(3) = 1.229(3), N(3)–C(12) = 1.477(3), N(2)–O(6′) 1.126(6), N(2)–O(5) = 1.185(4), N(2)–O(6) = 1.279(4), N(2)–O(5′) = 1.301(6), N(2)–C(16) = 1.482(3), O(7)–C(15) = 1.373(2), O(7)–C(19) = 1.443(3), O(8)–C(14) = 1.363(3), O(8)–C(18) = 1.444(3), O(9)–C(13) = 1.360(3), O(9)–C(17) = 1.449(3), C(6)–Pd(1)–C(11) = 86.68(9), C(11)–Pd(1)–O(1) = 88.02(8), C(6)–Pd(1)–O(2) = 92.92(8), O(1)–Pd(1)–O(2) = 92.36(6).

dinuclear complexes with two single-atom bridges,[38] while in **8** the two coordination planes subtend an angle of 44.3°. A search of the Cambridge Structural Database reveals two platinum complexes containing both carboxylate and OH bridging ligands, $[Pt_2(\mu\text{-carboxylate})(\mu\text{-OH})(NH_3)_4]^{2+}$ (carboxylate = acetate,[39,40] glycolate[40]) and the angles between the coordination planes are 75.5° and 73.0°, respectively. Probably, **8** adopts a wider interplanar angle because of the steric hindrance of the large phosphine and aryl ligands.

Bond distances at palladium in complexes are consistent with the trans influence scale. Thus, we observe (1) similar Pd−O(1)

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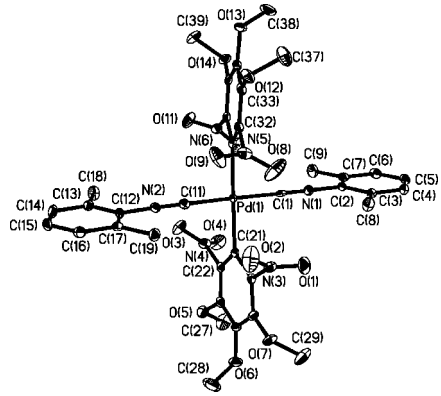

Figure 3. Ellipsoid representation of complex **3** (50% probability). Selected bond lengths (Å) and angles (deg): Pd(1)–C(11) 1.965(3), Pd(1)–C(1) 1.966(3), Pd(1)–C(21) 2.069(3), Pd(1)–C(31) 2.071(3), O(1)–N(3) 1.219(3), O(2)–N(3) 1.207(3), O(3)–N(4) 1.220(3), O(4)–N(4) 1.224(3), O(5)–C(23) 1.367(3), O(5)–C(27) 1.440(4), O(6)–C(24) 1.370(3), O(6)–C(28) 1.432(4), O(7)–C(25) 1.369(3), O(7)–C(29) 1.445(4), O(8)–N(5) 1.215(3), O(9)–N(5) 1.215(3), O(10)–N(6) 1.218(3), O(11)–N(6) 1.219(3), O(12)–C(33) 1.371(3), O(12)–C(37) 1.433(4), O(13)–C(34) 1.368(3), O(13)–C(38) 1.444(3), O(14)–C(35) 1.371(3), O(14)–C(39) 1.446(3), N(1)–C(1) 1.149(3), N(1)–C(2) 1.405(3), N(2)–C(11) 1.151(3), N(2)–C(12) 1.404(3), N(3)–C(26) 1.479(3), N(4)–C(22) 1.474(3), N(5)–C(32) 1.472(3), N(6)–C(36) 1.477(3), C(11)–Pd(1)–C(21) 89.37(10), C(1)–Pd(1)–C(21) 89.97(10), C(11)–Pd(1)–C(31) 90.89(10), C(1)–Pd(1)–C(31) 89.73(10),

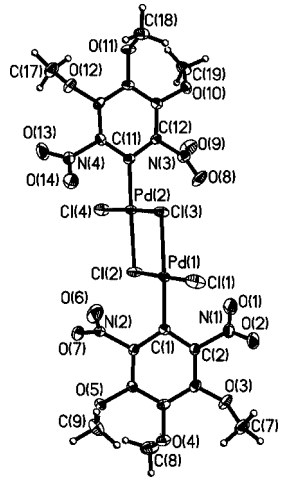

Figure 4. Ellipsoid representation of one of the two independent anionic complexes $[Pd_2(\kappa^1\text{-Ar})_2Cl_2(\mu\text{-Cl})_2]^{2-}$ (**5a**) (50% probability). Selected bond lengths (Å) and angles (deg) for the two independent complexes **5a** and **5b**. **5a**: Pd(1)–C(1) 1.979(3), Pd(1)–Cl(1) 2.2931(8), Pd(1)–Cl(2) 2.3199(8), Pd(1)–Cl(3) 2.4323(8), Pd(2)–C(11) 1.981(3), Pd(2)–Cl(4) 2.2943(8), Pd(2)–Cl(3) 2.3464(8), Pd(2)–Cl(2) 2.4230(8), C(1)–Pd(1)–Cl(1) 89.58(8), C(1)–Pd(1)–Cl(2) 90.94(8), Cl(1)–Pd(1)–Cl(3) 92.97(3), Cl(2)–Pd(1)–Cl(3) 86.50(3), C(11)–Pd(2)–Cl(4) 89.28(9), C(11)–Pd(2)–Cl(3) 92.53(9), Cl(4)–Pd(2)–Cl(2) 92.09(3), Cl(3)–Pd(2)–Cl(2) 86.13(3). **5b**: Pd(1)–C(1) 1.970(3), Pd(1)–Cl(1) 2.3113(8), Pd(1)–Cl(2) 2.3222(8), Pd(1)–Cl(3) 2.4262(8), Pd(2)–C(11) 1.972(3), Pd(2)–Cl(4) 2.3055(8), Pd(2)–Cl(3) 2.3395(8), Pd(2)–Cl(2) 2.4089(9), C(1)–Pd(1)–Cl(1) 91.09(9), C(1)–Pd(1)–Cl(2) 87.99(9), Cl(1)–Pd(1)–Cl(3) 93.50(3), Cl(2)–Pd(1)–Cl(3) 87.45(3), C(11)–Pd(2)–Cl(4) 90.59(9), C(11)–Pd(2)–Cl(3) 89.75(9), Cl(4)–Pd(2)–Cl(2) 92.18(3), Cl(3)–Pd(2)–Cl(2) 87.46(3).

distances trans to XyNC and ^{t}BuNC [**2a** 2.0130(14) Å, **2b** 2.0098(16) Å], (2) Pd−O bond distances trans to Ar [**2a** 2.0456(15) Å, **2b** 2.0519(16) Å] longer than those trans to isocyanide [**2a** 2.0130(14) Å, **2b** 2.0098(16) Å], (3) Pt−O bond

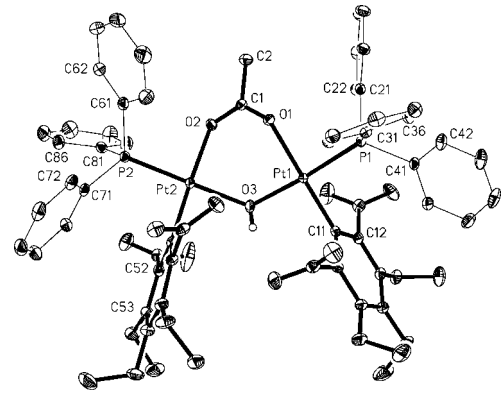

Figure 5. Ellipsoid representation of complex **8** (50% probability). Selected bond lengths (Å) and angles (deg): Pt(1)–C(11) 1.984(3), Pt(1)–O(3) 2.063(2), Pt(1)–O(1) 2.1162(19), Pt(1)–P(1) 2.2192(7), Pt(2)–C(51) 1.985(3), Pt(2)–O(3) 2.069(2), Pt(2)–O(2) 2.0890(19), Pt(2)–P(2) 2.2069(7), N(11)–O(12) 1.211(3), N(11)–O(11) 1.212(3), N(11)–C(12) 1.468(4), N(12)–O(17) 1.215(3), N(12)–O(16) 1.225(3), N(12)–C(16) 1.467(4), N(51)–O(51) 1.193, N(51)–O(52) 1.205(3), N(51)–C(52) 1.478(4), N(52)–O(56) 1.226(3), N(52)–O(57) 1.231(3), N(52)–C(56), 1.472(4), O(1)–C(1) 1.271(3), O(2)–C(1) 1.254(3), C(11)–Pt(1)–O(3) 89.84(10), O(3)–Pt(1)–O(1) 90.20(8), C(11)–Pt(1)–P(1) 94.06(8), O(1)–Pt(1)–P(1) 85.84(6), C(51)–Pt(2)–O(3) 89.35(10), O(3)–Pt(2)–O(2) 87.98(9), C(51)–Pt(2)–P(2) 92.47(8), O(2)–Pt(2)–P(2) 90.09(6).

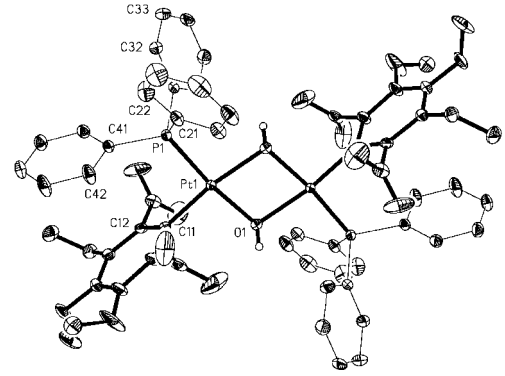

Figure 6. Ellipsoid representation of complex **9** (50% probability). Selected bond lengths (Å) and angles (deg): Pt(1)–C(11) 1.983(3), Pt(1)–O(1) 2.067(3), Pt(1)–O(1)#1 2.087(3), Pt(1)–P(1) 2.2085(9), Pt(1)–Pt(1)#1 3.2228(4), O(1)–Pt(1)#1 2.087(3), N(11)–O(11) 1.184(4), N(11)–O(12) 1.199(5), N(12)–O(16) 1.179(5), N(12)–O(17) 1.232(5), Pt(2)–C(11′) 1.994(3), Pt(2)–O(2)#2 2.081(3), Pt(2)–O(2) 2.095(3), Pt(2)–P(2) 2.2137(9), Pt(2)–Pt(2)#2 3.2161(3), O(2)–Pt(2)#2 2.081(3), N(11′)–O(11′) 1.213(4), N(11′)–O(12′) 1.230(4), N(12′)–O(16′) 1.194(4), N(12′)–O(17′) 1.219(5), C(11)–Pt(1)–O(1) 94.07(12), O(1)–Pt(1)–O(1)#1 78.24(11), C(11)–Pt(1)–P(1) 92.69(10), O(1)#1–Pt(1)–P(1) 95.07(8), O(1)–Pt(1)–Pt(1)#1 39.35(8), O(1)#1–Pt(1)–Pt(1)#1 38.90(7), P(1)–Pt(1)–Pt(1)#1 133.94(2), C(11′)–Pt(2)–O(2)#2 92.43(11), C(11′)–Pt(2)–O(2) 171.70(11), O(2)#2–Pt(2)–O(2) 79.27(11), C(11′)–Pt(2)–P(2) 93.42(9), O(2)#2–Pt(2)–P(2) 173.94(7), O(2)–Pt(2)–P(2) 94.89(7), C(11′)–Pt(2)–Pt(2)#2 132.23(9), O(2)#2–Pt(2)–Pt(2)#2 39.80(7), O(2)–Pt(2)–Pt(2)#2 39.47(7), P(2)–Pt(2)–Pt(2)# 134.34(2).

distance trans to the aryl group (**9** 2.087(3) Å) longer than that trans to PPh_3 (**9** 2.067(3) Å), (4) the Pd−O bonds trans to aryl (**11** 2.086(2) Å) longer than those trans to oxygen atoms (**11** 2.005(2)–2.019(2) Å), (5) Pd−CNXy bond distances trans to isocyanide [**3** 1.965(3) and 1.966(3) Å] longer than those trans to O [**2a** 1.925(2) Å], and (6) Pd−Ar bond distances trans to oxygen [**2a** 2.0002(2) Å, **2b** 2.002(2) Å] shorter than trans to Ar [**3** 2.069(3), 2.071(3) Å]. In addition, the Pd−Cl bond

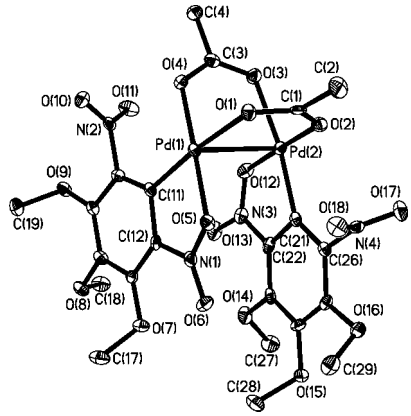

Figure 7. Ellipsoid representation of complex **11** (50% probability). Selected bond lengths (Å) and angles (deg): Pd(1)–C(11) 1.955(3), Pd(1)–O(4) 2.005(2), Pd(1)–O(5) 2.019(2), Pd(1)–O(1) 2.086(2), Pd(1)–Pd(2) 2.8227(4), Pd(2)–C(21) 1.958(4), Pd(2)–O(12) 2.006(2), Pd(2)–O(2) 2.008(2), Pd(2)–O(3) 2.086(2), N(1)–O(6) 1.206(4), N(1)–O(5) 1.294(4), N(1)–C(12) 1.432(4), N(2)–O(10) 1.222(4), N(2)–O(11) 1.226(4), N(2)–C(16) 1.471(4), N(3)–O(13) 1.214(4), N(3)–O(12) 1.284(4), N(3)–C(22) 1.432(4), N(4)–O(18) 1.222(3), N(4)–O(17) 1.221(4), N(4)–C(26) 1.485(4), O(1)–C(1) 1.253(4), O(2)–C(1)1.274(4),O(3)–C(3)1.258(4),O(4)–C(3)1.272(4),C(11)–Pd(1)–O(4) 97.03(12), C(11)–Pd(1)–O(5) 81.29(12), O(4)–Pd(1)–O(1) 89.08(10), O(5)–Pd(1)–O(1) 92.60(9), C(21)–Pd(2)–O(12) 81.28(12), C(21)–Pd(2)–O(2)97.64(12),O(12)–Pd(2)–O(3)91.37(10),O(2)–Pd(2)–O(3) 89.77(10)

distances in **5** follow the expected order: Pd−Cl bridging trans to Ar (2.4323(8), 2.4230(8), 2.4262(8), 2.4089(9) Å) > bridging trans to Cl (2.3199(8), 2.3464(8), 2.3222(8), 2.3395(8) Å) > terminal trans to Cl (2.2931(8), 2.2943(8), 2.3113(8), 2.3055(8) Å).

In **5**, two crystallographically independent, but very similar, units are present. One of them (**5a**) is represented in Figure 4. The anion dimer is not far from approximate inversion symmetry with four chloro ligands, two bridging and two terminal, and two mutually trans κ^1-Ar groups.

The structure of **8** consists of a dimer formed by carboxylato and OH ligands bridging two PtAr(PPh_3) units. The bridging acetato and hydroxo ligands are trans to Ar and PPh_3, respectively. The Pt−OH (2.063(2), 2.069(2) Å) and Pt−C (1.984(3), 1.985(3) Å) bond lengths are similar but the Pt(1)−P (2.2192(7) Å) and Pt(1)−O(1) (2.1162(19) Å) bond distances are significantly greater than Pt(2)−P (2.2069(7) Å) and Pt(1)–O(2) (2.0890(19) Å) in spite of being both trans to OH and Ar ligand. The acetato ligand occupies a strangely asymmetric position, with C(1)–O(1) 1.271(2) Å > C(1)–O(2) 1.254(3) Å and O1···Pt2 3.22 Å > O2···Pt1 3.53 Å, and C(1)–O(1)–Pt(1) 127.6(2)° > C(1)–O(2)–Pt(2) 122.3(2)°. There is no obvious reason for this; in particular, there are no especially short nonbonded interactions involving these atoms (indeed, even the OH group forms no H bonds, presumably for steric reasons).

In the crystals of **9**, two crystallographically independent, but very similar molecules are present, one of which is represented in Figure 5. Both molecules display inversion symmetry. There is a slight difference in the Pt···Pt distances (3.2228(4) and 3.2161(3) Å), which are intermediate between the expected values for a van der Waals interaction (3.44 Å) and a covalent bond (3.00 Å), but are bound to be short in view of the bridging OH groups. Again, the OH groups do not participate in hydrogen bonds.

The crystal structure of **11** consists of dinuclear molecules that adopt an *anti* geometry, with the acetate bridges conferring an open-book shape upon the molecule. The planes of coordination around the Pd centers are stacked with a relatively short Pd−Pd distance of 2.8227(4) Å, which is shorter than that expected for the Pd−Pd covalent bond (3.00 Å) and lies in the range found in some other $[Pd]_2(\mu\text{-OAc})_2$ complexes (2.821–2.936 Å).[37,41]

Spectroscopic Properties. The NMR spectra of all complexes are in agreement with the proposed structures. Thus, at room temperature, the ^{1}H NMR spectra of complexes show the expected two (2:1) or three (1:1:1) methyl singlets per κ^1-Ar or κ^2-Ar groups, respectively, except in **10**, which fortuitously shows only one resonance corresponding to 18 protons. In complex **8**, the Me protons of the acetato ligand (0.68 ppm) are shielded with respect to those in complex **11** (2.08 ppm), certainly because of the proximity of aryl groups of PPh_3 (see Figure 5).

The IR spectra of **8** and **9** show a weak band at 3605 and 3602 cm^{-1}, respectively, assignable to ν(OH). In **10**, bands at 290 and 272 cm^{-1} are assigned to $\nu(PdCl)_{trans\ to\ P}$ and $\nu(PdCl)_{trans\ to\ Ar}$, respectively, in agreement with its crystal structure. The chloro complex **4** shows a band assignable to ν(PdCl) at 314 cm^{-1}.

Conclusions

We report a rare example of disproportionation when [Pd(κ^2-Ar)(*O*,*O*-acac)] is reacted with 4 equivalents of XyNC, yielding *trans*-[Pd(κ^1-Ar)$_2$(CNXy)$_2$]. We attribute this to a new transphobia effect associated with formation of the intermediate [Pd(Ar)(*C*-acac)(XyNC)$_2$], the instability of which arises from the strong *T*(aryl/*C*-acac). We have attempted to prepare this intermediate by two other routes, confirming its instability and observing instead the formation of *trans*-[Pd(κ^1-Ar)$_2$(CNXy)$_2$]. This complex is the first [Pd](Ar)$_2$ with Ar = $C_6(NO_2)_2$-2,6-$(OMe)_3$; we had previously attempted to prepare this compound, unsuccessfully, by a transmetalation using [$HgAr_2$]. A rare example of Pt-to-Hg transmetalation has allowed us to prepare a family of [Pt](Ar)s, by reacting *cis*-[Pt(κ^2-Ar)(κ^1-Ar)(PPh_3)] with $Hg(OAc)_2$ or $HgCl_2$. Such monoaryl platinum complexes could not be prepared by an Hg-to-Pt transmetalation.

Acknowledgment. We thank the Dirección General de Investigación/FEDER for financial support (Grant CTQ2004-05396). M.D.G.-L. and F. J.-H thank Fundación Séneca and Universidad de Murcia, respectively, for grants.

Supporting Information Available: Crystallographic data in CIF format for **2a**, **2b**, **3**, **5**, **8**, **9**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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