Bis(2,6-dinitroaryl)platinum Complexes. 1. Synthesis through Transmetalation Reactions

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Complexes *cis*-Q[Pt(κ^2-Ar)(κ^1-Ar)Cl] [Q = Ph_3PCH_2Ph (**1**), Me_4N (**2**); 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*] have been prepared by reacting [$HgAr_2$] [Ar = $C_6(NO_2)_2$-2,6-$(OMe)_3$-3,4,5] and $Q_2[Pt_2Cl_6]$ (4:1) in acetone at 100 °C. Complex **2** could be prepared by reacting [$HgAr_2$] (i) with $[Me_4N]_2[Pt_2Cl_6]$ (2:1) in the presence of an excess of $[Me_4N]Cl$ or (ii) with $[Me_4N]_2[PtCl_4]$ (1:1). The reaction of equimolecular amounts of **2** and Tl(acac) or $AgClO_4$ gave, respectively, *cis*-Me_4N[Pt(κ^1-Ar)$_2$(acac-κ^2-*O,O*)] (**3**) or *cis*-[Pt(κ^2-Ar)(κ^1-Ar)(OH_2)] (**4**), which in turn reacts with neutral ligands to give *cis*-[Pt(κ^2-Ar)-(κ^1-Ar)L] [L = PhCN (**5**), tetrahydrothiophene (**6**)]. $Hg(O_2CCF_3)_2$ reacts with an equimolar amount of **2** to give *cis*-Me_4N[Pt(κ^2-Ar)(κ^1-Ar){OC(O)CF_3}] (**7**). The structures of complexes **1**, **4**·Et_2O, **4**·CH_2Cl_2, and **7** have been solved by X-ray diffraction studies.

Introduction

The use of organomercurials as transmetallating agents has several advantages over the use of the classical organolithium and Grignard reagents in the synthesis of organometallic compounds,[1] notably the possibility of preparing functionalized derivatives. Thus, we have reported the synthesis of aryl complexes containing *ortho*-substituents such as $-NO_2$ [Pd(II),[2−6] Pt(II),[7] Pt(IV),[8] Au(I),[9] Au(III),[10] Rh(III)[11]], $-NH_2$ [Pt-(II)[12]], −CHO [Pd(II)[13]], −C(O)Me [Pd(II)[14]], −C(O)NHR [Pd(II)[15]], and −N═NR [Au(III),[10] Sn(IV),[16] Tl(III)[17]] using the corresponding diaryl mercurials. Two main types of reactions have been used: transmetalation reactions, i.e., Cl[M] + [HgR_2] → Ar[M] + [Hg(R)Cl], or redox-transmetalation reactions, i.e., [M] + [Hg(R)Cl] (or [HgR_2]) → [M](R)Cl (or [M]R_2) + Hg. Mono-, homodi-, or heterodiarylcomplexes have been thus prepared. We have reported the synthesis of two triarylgold(III) complexes starting from $[AuCl_4]^-$ and using only mercurials as transmetalating agents.[18] Other authors have also found mercurials useful in preparing functionalized aryl complexes.[19] In a few cases diaryl derivatives are isolated, even when equimolecular amounts of the reagents are used, because a double transmetalation occurs, i.e., Cl_2[M] + [HgR_2] → [M]R_2 + $HgCl_2$. We have observed this behavior when R = 2-nitroaryl, [M] = $AuCl_2^-$,[20] Pt;[7] R = 2-arylazoaryl, [M] = $AuCl_2^-$.[21] In the case of M = Pd and R = 2-nitroaryl, the reaction leads first to [PdR_2], and this reacts with the other reaction product ($HgCl_2$) to give $[PdR(\mu\text{-Cl})]_2$.[4] In this paper, we report a new example of this type of double transmetalation in the reaction between [$HgAr_2$] [Ar = $C_6(NO_2)_2$-2,6-$(OMe)_3$-3,4,5] and $[Pt_2Cl_6]^{2-}$, giving a diaryl platinum-(II) complex. We have reported that the related reaction

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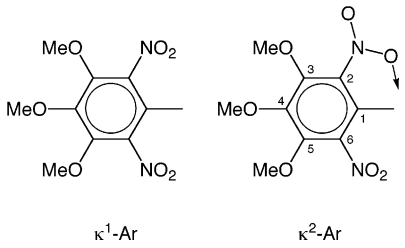
with $[Pd_2Cl_6]^{2-}$ leads only to monoaryl-palladium(II) complexes even when using an excess of the mercurial.[2]

The interest in nitroaryl complexes is well documented. Thus, in addition to those we have prepared using organomercurials,[2,7−11] others have been obtained using organo-lithium or -tin derivatives,[22] oxidative addition reactions,[23] arylhydrazonium salts,[24] direct metalation of arenes,[25] or nitration of aryl complexes.[26] Our interest in the synthesis of nitroaryl complexes is based on the great stability of these complexes—allowing, for example, the synthesis of one of the few carbonyl arylpalladium(II) complexes[5]—and on the study of the coordination ability of the *ortho* nitro group. In this paper we report the synthesis and reactivity toward neutral and anionic ligands of some 2,6-dinitro-3,4,5-trimethoxyphenyl platinum(II) complexes. In the following article we will describe the reactivity of some of these complexes toward carboxylate salts of mercury and of the oxidative addition of $[HgAr_2]$ to Pt(0) to give di- and trinuclear containing Pt−Hg compounds.[27]

Experimental Section

The reactions were carried out without precautions to exclude 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.[28] NMR spectra were recorded in Varian Unity 300 or Bruker AC 200, Avance 300, or Avance 400 spectrometers at room temperature unless otherwise stated. Chemical shifts were referred to TMS or H_3PO_4 (^{31}P) or $CFCl_3$ (^{19}F). The synthesis of HgR_2 was reported previously.[2] 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).

Chart 1



κ^1-Ar κ^2-Ar

Synthesis of *cis*-[Ph$_3$PCH$_2$Ph][Pt(κ^2-Ar)(κ^1-Ar)Cl] (1). To a suspension of $[Ph_3PCH_2Ph]_2[Pt_2Cl_6]$ (153.6 mg, 0.12 mmol) in acetone (10 mL) was added $[HgAr_2]$ (335.4 mg, 0.47 mmol). The suspension was stirred at 100 °C for 2 h in a Carius tube and, after cooling, filtered through Celite. The filtrate was concentrated (3 mL), and addition of Et_2O (2 mL) gave **1** as a violet solid. Yield: 236 mg, 92%. Mp: 213−215 °C. IR (cm^{-1}): ν(Pt−Cl) 310. Λ_M = 97 Ω^{-1} cm^2 mol^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 6.91−7.76 (m, 20 H, Ph), 4.91 (d, 2 H, CH_2, $^2J_{HP}$ = 14.1 Hz), 3.96 (s, 3 H, MeO), 3.95 (s, 6 H, MeO), 3.87 (s, 3 H, MeO), 3.85 (s, 3 H, MeO), 3.80 (s, 3 H, MeO). Anal. Calcd for $C_{43}H_{40}ClN_4O_{14}PPt$: C, 47.02; H, 3.67; N, 5.10. Found: C, 46.97; H, 3.39; N, 5.06. Single crystals of **1** were obtained by slow diffusion of *n*-hexane into a solution of **1** in acetone.

Synthesis of *cis*-Me$_4$N[Pt(κ^2-Ar)(κ^1-Ar)Cl] (2). To a suspension of $[Me_4N]_2[PtCl_4]$ (445 mg, 0.92 mmol) in acetone (10 mL) was added $[HgAr_2]$ (655 mg, 0.92 mmol). The suspension was stirred at 150 °C for 1 h in a Carius tube and then concentrated to dryness. CH_2Cl_2 (20 mL) was added, the suspension filtered, and the resulting solution concentrated (8 mL). Addition of Et_2O (20 mL) gave a suspension that was filtered, and the solid was air-dried to give complex **2** as a dark red solid. Yield: 720 mg, 96%. Mp: 185−188 °C. IR (cm^{-1}): ν(Pt−Cl) 298. Λ_M = 118 Ω^{-1} cm^2 mol^{-1}. ^1H NMR (300 MHz, d_6-acetone): δ 3.99 (s, 3 H, MeO), 3.97 (s, 3 H, MeO), 3.91 (s, 6 H, MeO), 3.89 (s, 3 H, MeO), 3.88 (s, 3 H, MeO), 3.40 (s, 12 H, Me_4N). $^{13}C\{^1H\}$ NMR (75.45 MHz, d_6-acetone): δ 154.92, 154.25, 149.97 (J_{PtC} = 34 Hz), 148.91, 147.00 (J_{PtC} = 77 Hz), 143.00 (J_{PtC} = 15 Hz), 142.53 (J_{PtC} = 9 Hz), 139.06 (J_{PtC} = 55 Hz), 128.68 (J_{PtC} = 1202 Hz, *i*-C Ar), 113.75 (J_{PtC} = 1264 Hz, *i*-C Ar), 62.58 (OMe), 62.17 (OMe), 62.08 (*m*-OMe, κ^1-Ar), 61.46 (OMe), 61.41 (OMe), 56.00 (t {1:1:1}, Me_4N, $^1J_{NC}$ = 4 Hz). Anal. Calcd for $C_{22}H_{30}ClN_5O_{14}Pt$: C, 32.26; H, 3.69; N, 8.55. Found: C, 32.57; H, 3.74; N, 8.56.

Synthesis of *cis*-Me$_4$N[Pt(κ^1-Ar)$_2$(acac-κ^2-*O,O*)] (3). Tl(acac) (37 mg, 0.12 mmol) was added to a solution of **2** (101 mg, 0.12 mmol) in acetone (4 mL). The resulting suspension was stirred for 2 h and then filtered through Celite. The filtrate was concentrated to dryness, and CH_2Cl_2 (1 mL) was added. The suspension was stirred for a few minutes and then was filtered and the solid air-dried to give pale yellow **3**. Yield: 73 mg, 73%. Mp: 252 °C (d). Λ_M = 109 Ω^{-1} cm^2 mol^{-1}. ^1H NMR (300 MHz, d_6-acetone): δ 5.20 (s, 1 H, CH), 3.85 (s, 6 H, MeO), 3.82 (s, 12 H, MeO), 3.40 ("t" (1:1:1), 12 H, Me_4N, $^2J_{NH}$ = 0.6 Hz), 1.60 [s, 6 H, MeC(O)]. $^{13}C\{^1H\}$ NMR (50 MHz, d_6-acetone): δ 183.41 (CO), 152.28 (Ar), 145.92 (Ar, $^2J_{PtC}$ = 73 Hz), 142.07 (Ar), 114.61 (CH), 101.41(Ar, $^1J_{PtC}$ = 62 Hz), 62.09 (OMe), 61.22 (OMe), 55.97 (t (1:1:1), Me_4N, $^1J_{NC}$ = 4 Hz), 26.71 (Me). Anal. Calcd for $C_{27}H_{37}N_5O_{16}Pt$: C, 36.74; H, 4.23; N, 7.93. Found: C, 36.57; H, 4.13; N, 7.60.

Preparation of CH_2Cl_2 Solutions of *cis*-[Pt(κ^2-Ar)(κ^1-Ar)(OH$_2$)] (4). Method a. A mixture of **2** (96 mg, 0.12 mmol) and finely ground $AgClO_4$ (44 mg, 0,21 mmol) in CH_2Cl_2 (3 mL) was stirred (protected from daylight) for 5 h. The resulting suspension was filtered to give a red solution.

Method b. $AgClO_4$ (39 mg, 0.12 mmol) was added to a solution of **2** (57 mg, 0.07 mmol) in acetone (3 mL). After a

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Table 1. Crystallographic Data for Complexes 1, 4, and 7

	1	**4**·Et_2O	**4**·CH_2Cl_2	**7**·$CHCl_3$
formula	$C_{43}H_{40}ClN_4O_{14}PPt$	$C_{22}H_{30}N_4O_{16}Pt$	$C_{19}H_{22}Cl_2N_4O_{15}Pt$	$C_{25}H_{31}Cl_3F_3N_5O_{16}Pt$
M_r	1098.30	801.59	812.40	1015.99
habit	red tablet	red tablet	red tablet	red tablet
cryst size (mm)	0.6 × 0.4 × 0.15	0.6 × 0.6 × 0.25	0.24 × 0.22 × 0.05	0.27 × 0.14 × 0.07
crystal system	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
cell constants				
a (Å)	10.7880(10)	8.606(3)	10.4998(6)	16.0619(6)
b (Å)	18.1386(16)	11.552(5)	9.3162(6)	13.1120(5)
c (Å)	22.673(2)	14.680(4)	27.0169(16)	17.5245(6)
α (deg)	90	93.59(3)	90	90
β (deg)	93.020(7)	102.60(3)	90.890(3)	94.589(3)
γ (deg)	90	91.88(3)	90	90
V (Å^3)	4430.6(7)	1419.9(9)	2642.4(3)	3678.9(2)
Z	4	2	4	4
D_x (Mg m^{-3})	1.647	1.875	2.042	1.834
μ (mm^{-1})	3.34	5.02	5.59	4.12
F(000)	2192	792	1584	2000
T (°C)	−100	−130	−140	−140
$2\theta_{max}$	52	50	60	60
no. of reflns measd	10 147	5038	55 628	73 304
no. of indep reflns	8654	5018	7732	10 751
transmns	0.58−0.88	0.45−0.99	0.52−0.89	0.64−0.89
R_{int}	0.032		0.073	0.042
no. of params	577	403	384	520
restraints	520	334	87	129
$wR(F^2$, all reflns)	0.073	0.071	0.070	0.049
$R(F, >4\sigma(F))$	0.037	0.028	0.030	0.022
S	0.87	1.05	1.03	0.95
max $\Delta\rho$ (e Å^{-3})	1.1	1.6	2.22	1.89

few minutes, the solution was concentrated to dryness and CH_2Cl_2 (3 mL) was added. The resulting suspension was filtered to give a red solution.

Red single crystals of **4**·CH_2Cl_2 were obtained by slow diffusion of *n*-hexane into a solution of **4** in dichlomethane.

Preparation of Et_2O Solutions of 4. A CH_2Cl_2 solution of **4** (from 0.12 mmol of **2** and 0.21 mmol of $AgClO_4$) was concentrated to dryness, and Et_2O (5 mL) was added to give a red solution.

Synthesis of *cis*-[Pt(κ^2-Ar)(κ^1-Ar)(OH_2)]·Et_2O (4·Et_2O). Addition of *n*-pentane to an Et_2O (5 mL) solution of **4** (0.12 mmol) gave a suspension, which was filtered, and the solid air-dried to give red complex **4**·Et_2O. Yield: 75 mg, 75%. Dec point: 153−166 °C (see Discussion). IR (cm^{-1}): ν(OH) 3430. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.03 (s, 12 H, MeO), 3.87 (s, 6 H, MeO), 3.51 (q, 4 H, CH_2, $^3J_{HH}$ = 6.9 Hz), 1.21 (t, 6 H, Me, $^3J_{HH}$ = 6.9 Hz) (See Discussion). ^{1}H NMR (300 MHz, $CDCl_3$, −30 °C): 6.03 (s, 1 H, H_2O), 4.06 (s, 6 H, MeO), 4.04 (s, 3 H, MeO), 4.02 (s, 3 H, MeO), 3.91(s, 3 H, MeO), 3.82 (s, 3 H, MeO), 3.54 (q, 4 H, CH_2, $^3J_{HH}$ = 7 Hz), 2.38 (s, 1 H, H_2O), 1.22 (t, 6 H, Me, $^3J_{HH}$ = 7 Hz). Red single crystals of **4**·Et_2O were obtained by slow diffusion of *n*-pentane into a solution of **4**·Et_2O in Et_2O. Anal. Calcd for $C_{22}H_{30}N_4O_{16}Pt$: C, 32.97; H, 3.77; N, 6.99 Found: C, 33.09; H, 3.59; N, 7.36.

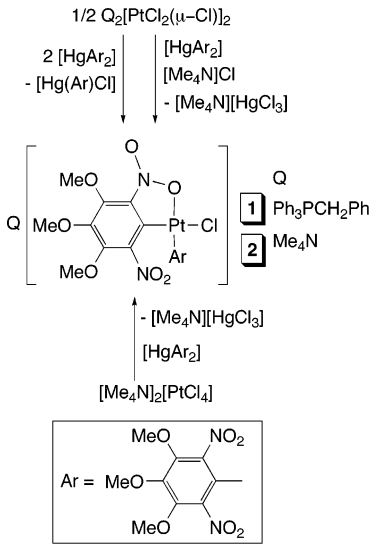
Synthesis of *cis*-[Pt(κ^2-Ar)(κ^1-Ar)(NCPh)] (5). To a solution of **4** (from 0.09 mmol of **2**) in Et_2O (15 mL) was added PhCN (9.7 mg, 0.09 mmol), and the resulting solution was concentrated (3 mL). Addition of *n*-hexane (15 mL) gave a suspension, which was filtered, and the solid air-dried to give **5** as an orange solid. Yield: 73 mg, 96%. Mp: 183−185 °C. IR (cm^{-1}): ν(C≡N) 2272. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80 (dd, 2 H, *o*-H, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.2 Hz), 7.73 (tt, 1 H, *p*-H, $^3J_{HH}$= 8 Hz, $^4J_{HH}$= 1.2 Hz), 7.54 (t, 2 H, *m*-H, $^3J_{HH}$ = 8 Hz), 4.05 (s, 6 H, OMe), 4.022 (s, 3 H, OMe), 4.017 (s, 3 H, OMe), 3.94 (s, 3 H, OMe), 3.84 (s, 3 H, OMe). Anal. Calcd for $C_{25}H_{23}N_5O_{14}Pt$: C, 36.95; H, 2.85; N, 8.62. Found: C, 36.70; H, 2.81; N, 8.58.

Synthesis of *cis*-[Pt(κ^2-Ar)(κ^1-Ar)(tht)] (6). To a solution of **4** (from 0.12 mmol of **2**) in CH_2Cl_2 (3 mL) was added tetrahydrothiophene (tht) (0.12 mmol), and the resulting orange solution was concentrated (1 mL). Addition of Et_2O (15 mL) gave a suspension, which was filtered, and the solid air-dried to give **6** as an orange solid. Yield: 81 mg, 86%. Mp: 207−209 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.05 (s, 6 H, OMe), 4.02 (s, 3 H, OMe), 3.99 (s, 3 H, OMe), 3.93 (s, 3 H, OMe), 3.83 (s, 3 H, OMe), 3.19 (m, 4 H, tht), 2.12 (m, 4 H, tht). Anal. Calcd for $C_{22}H_{26}N_4O_{14}PtS$: C, 33.13; H, 3.29; N, 7.02; S, 4.02. Found: C, 32.95; H, 3.14; N, 6.88; S, 3.75.

Synthesis of *cis*-Me_4N[Pt(κ^2-Ar)(κ^1-Ar){OC(O)CF_3}] (7). To a solution of **2** (68 mg, 0.08 mmol) in CH_2Cl_2 (6 mL) was added $Hg(O_2CCF_3)_2$ (35.4 mg, 0.08 mmol), and the mixture was stirred for 10 min and then filtered through Celite. The filtrate was concentrated to ∼2 mL, and addition of Et_2O (15 mL) gave an oil. By vigorous stirring and cooling in a water/ice bath a suspension was obtained, which was filtered, and the solid air-dried to give **7** as a red solid. Yield: 60 mg, 81%. Mp: 179−181 °C. Λ_M (acetone, 5.2 × 10^{-4} M): 152 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): $\nu_{asym}(CO_2)$ 1696. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.99 (s, 12 H, OMe), 3.92 (s, 3 H, OMe), 3.82 (s, 3 H, OMe), 3.25 (s, 12 H, Me_4N). ^{1}H NMR (400 MHz, $CDCl_3$, −30°C): δ 4.04 (s, 3 H, OMe), 4.02 (s, 6 H, OMe), 4.01 (s, 3 H, OMe), 3.94 (s, 3 H, OMe), 3.81 (s, 3 H, OMe), 3.27 (s, 12 H, Me_4N). ^{19}F{^{1}H} NMR (188.3 MHz, $CDCl_3$): δ −74.05 (s). Anal. Calcd for $C_{24}H_{30}F_3N_5O_{16}Pt$: C, 32.15; H, 3.37; N, 7.81. Found: C, 32.02; H, 3.14; N, 7.61. Crystals of **7**·$CHCl_3$ suitable for X-ray diffraction studies were obtained by slow diffusion of *n*-hexane into a solution of **7** in $CHCl_3$.

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 (**1**: Siemens P4; **4**·Et_2O: Stoe STADI-4; others: Bruker SMART 1000 CCD; with appropriate low-temperature attachments). Measurements were performed with monochromated Mo Kα radiation. Absorption corrections were performed on the basis of psi-scans (**1** and **4**·Et_2O) or multiscans (program SADABS). 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

Scheme 1



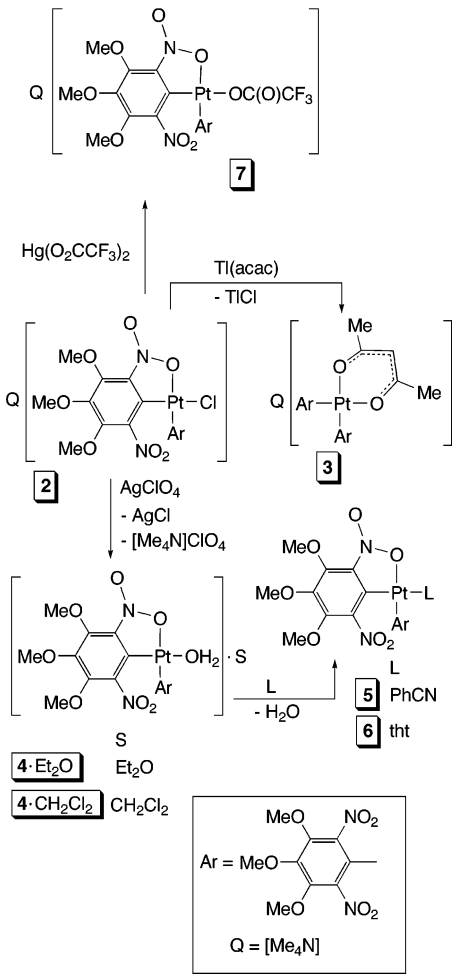
methyl groups or with a riding model. Systems of restraints to local ring symmetry and light atom displacement factor components were employed to improve refinement stability. Special features of refinement: In compound **1** the methoxy group O25−C29 is disordered over two positions, which were refined isotropically in the ratio 1:1. The water hydrogens in both forms of compound **4** were identified in difference syntheses and refined with restrained O−H distances. In compound **7** the CF_3 group is disordered over two positions in the ratio 7:3.

Results and Discussion

Synthesis of Complexes. When a mixture of $[HgAr_2]$ [Ar = $C_6(NO_2)_2$-2,6-$(OMe)_3$-3,4,5] and $Q_2[Pt_2Cl_6]$ (4:1) in acetone was heated in a Carius tube, a transmetalation reaction occurred leading to *cis*-$Q[Pt(\kappa^2\text{-Ar})(\kappa^1\text{-Ar})Cl]$ [Q = Ph_3PCH_2Ph (**1**), Me_4N (**2**); see Chart 1 and Scheme 1]. These complexes can be easily precipitated from the reaction mixture by addition of Et_2O. The byproduct, [Hg(Ar)Cl], remains soluble and can be isolated by addition of *n*-hexane. However, a better method for preparing complex **2** is to use the same reagents in 2:1 molar ratio in the presence of an excess of $[Me_4N]Cl$. In this way, only half the amount of $[HgAr_2]$ is needed, because Cl^- symmetrizes the byproduct [Hg(Ar)Cl], regenerating $[HgAr_2]$ and giving $Me_4N[HgCl_3]$, which is easily removed from the reaction mixture because of its insolubility in CH_2Cl_2. We have previously reported this transmetalation/symmetrization method for the synthesis of other aryl complexes.[10,13,29] Alternatively, since $[Me_4N]Cl$ reacts with $[Me_4N]_2[Pt_2Cl_6]$ to give $[Me_4N]_2[PtCl_4]$, it is reasonable to assume that in the above reaction $[Me_4N]_2[PtCl_4]$ is the platinum species reacting with the mercurial. In fact, this complex can also be used to prepare **2** by reacting it with $[HgAr_2]$ in a 1:1 molar ratio without adding $[Me_4N]Cl$. $[HgAr_2]$ and $PtCl_2$ do not react when a solution in acetone is heated at 150 °C in a Carius tube.

We have unsuccessfully attempted to prepare monoaryl complexes. Thus, when $[HgAr_2]$ was reacted with $Q_2[Pt_2Cl_6]$ in a 1:1 molar ratio, complex **1** or **2** was isolated along with 50% of unreacted $Q_2[Pt_2Cl_6]$. This result contrasts with that obtained in the reaction between $[HgAr_2]$ and the palladium complex $Q_2[Pd_2Cl_6]$, which gives the complex $Q_2[Pd_2(\kappa^1\text{-Ar})_2Cl_2(\mu\text{-Cl})_2]$ (Q = Ph_3PCH_2Ph, Me_4N) even when using an excess of the mercurial.[2] The behavior of $[HgAr_2]$ is like that of $[HgAr'_2]$ (Ar′ = *o*-nitrophenyl), which reacts with $PtCl_2$ giving $[Pt(\kappa^2\text{-Ar}')_2]$ even when using a 1:1 molar ratio of reagents.[7] Probably, these transmetalation reactions from mercury to platinum involve the simultaneous transfer of both nitroaryl groups and the resulting $HgCl_2$ reacts with $[HgAr_2]$ to give the isolated byproduct [Hg(Ar)Cl].

Scheme 2



The reaction of equimolecular amounts of **2** and Tl(acac) gave *cis*-$Me_4N[Pt(\kappa^1\text{-Ar})_2(\text{acac-}\kappa^2\text{-}O,O)]$ (**3**) (Scheme 2). When complex **2** and an excess of finely ground $AgClO_4$ were stirred at room temperature for 5 h in CH_2Cl_2, a red solution was obtained after removing AgCl, $[Me_4N]ClO_4$, and the excess of $AgClO_4$. This solution can be used as a source of *cis*-$[Pt(\kappa^2\text{-Ar})(\kappa^1\text{-Ar})(OH_2)]$ (**4**). This reaction is almost immediate in acetone, probably because of the greater solubility of $AgClO_4$ in acetone than in CH_2Cl_2. The solutions of **4** in organic solvents (CH_2Cl_2, $CHCl_3$, acetone, Et_2O, toluene) are indefinitely stable at room temperature. However, all attempts to isolate **4** gave products containing some of the solvents used. Thus, addition of *n*-pentane to Et_2O or CH_2Cl_2 solutions of **4** gave the stable aqua complexes *cis*-$[Pt(\kappa^2\text{-Ar})(\kappa^1\text{-Ar})(OH_2)]\cdot Et_2O$ (**4**·Et_2O) or *cis*-$[Pt(\kappa^2\text{-Ar})(\kappa^1\text{-Ar})(OH_2)]\cdot CH_2Cl_2$ (**4**·CH_2Cl_2). Both complexes were

(29) Vicente, J.; Arcas, A.; Chicote, M. T. *J. Organomet. Chem.* **1983**, *252*, 257. Vicente, J.; Arcas, A.; Jones, P. G.; Lautner, J. *J. Chem. Soc., Dalton Trans.* **1990**, 451.

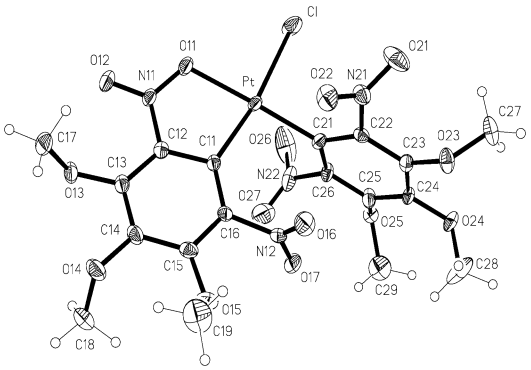


Figure 1. Ellipsoid representation of the anion of **1** (25% probability). Selected bond lengths (Å) and angles (deg): Pt−C(11) 1.978(5), Pt−C(21) 1.985(4), Pt−O(11) 2.088(3), Pt−Cl 2.3367(16), C(12)−N(11) 1.430(6), C(16)−N(12) 1.484-(6), C(22)−N(21) 1.468(6), C(26)−N(22) 1.478(7), N(11)−O(12) 1.213(5), N(11)−O(11) 1.274(5), N(12)−O(17) 1.210-(5), N(12)−O(16) 1.222(5), N(21)−O(22) 1.215(5), N(21)−O(21) 1.216(5), N(22)−O(27) 1.185(7), N(22)−O(26) 1.214(7), C(11)−Pt−C(21) 99.92(19), C(11)−Pt−O(11) 80.10(17), C(21)−Pt−Cl 89.16(14), O(11)−Pt−Cl 91.20(11), O(12)−N(11)−O(11) 118.8(4), O(17)−N(12)−O(16) 125.3(5), O(22)−N(21)−O(21) 123.1(5), O(27)−N(22)−O(26) 122.7(6).

characterized by X-ray diffraction studies, but **4**·CH_2Cl_2 could not be isolated analytically pure. The reaction of a Et_2O or CH_2Cl_2 solution of **4** with benzonitrile or tetrahydrothiophene (tht) afforded the complexes *cis*-[Pt(κ^2-Ar)(κ^1-Ar)(NCPh)] (**5**) and *cis*-[Pt(κ^2-Ar)(κ^1-Ar)-(tht)] (**6**), respectively, which are stable in the solid state and in acetone, CH_2Cl_2, or $CHCl_3$ solutions.

The thermogravimetric analysis of **4**·Et_2O shows that it loses Et_2O at 81 °C, and the low-temperature ^{1}H NMR of the resulting product shows the corresponding signals of **4**, but it is not analytically pure. The molecule of water is removed at 117 °C, but all the attempts to isolate analytically pure [Pt(κ^2-Ar)$_2$] were unsuccessful. Thus, when a sample of **4**·Et_2O was heated at 117 °C for 1 h, a complex mixture of products was obtained. Assuming a *cis* geometry for the hypothetical complex [Pt(κ^2-Ar)$_2$], in accordance with the X-ray crystal structure of *cis*-[Pd(κ^2-Ar′)$_2$] (Ar′ = *o*-nitrophenyl),[4] the unsuccessful attempts to isolate it may be associated with the mutual steric hindrance between the noncoordinated nitro groups. However, the κ^1-coordination of one or two ligands in complexes **1**−**7** releases such steric hindrance around the $PtAr_2$ moiety because the plane of the κ^1-Ar ligands can be located perpendicular to the coordination plane, as is shown in the crystal structures of **4**·Et_2O and **4**·CH_2Cl_2.

While the reaction of **2** with [Hg(OAc)$_2$] (1:1) gave a heterodinuclear Pt/Hg complex (see following article),[27] that with $Hg(O_2CCF_3)_2$ (1:1) proceeds with substitution of chloride by carboxylate to give *cis*-Me_4N[Pt(κ^2-Ar)-(κ^1-Ar){OC(O)CF_3}] (**7**) (Scheme 2).

Structure and Spectroscopic Properties. The crystal structures of complexes **1** (Figure 1), **4** as the diethyl ether (Figure 2) and dichloromethane solvate (Figure 3), and **7** (Figure 4) have been determined. All of them show an approximately square planar coordination around the platinum atom with the ligands κ^2-Ar and a κ^1-Ar mutually *cis*. The C−Pt−C angles are significantly wider than 90° [99.9(2)° (**1**), 102.94(17)° (**4**·Et_2O), 102.30(11)° (**4**·CH_2Cl_2), and 100.02(8)° (**7**)],

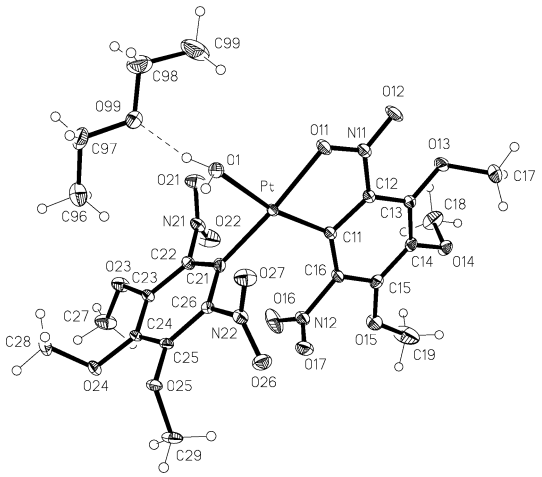


Figure 2. Ellipsoid representation of **4**·Et_2O (30% probability). Selected bond lengths (Å) and angles (deg): Pt−C(11) 1.966(4), Pt−C(21) 1.988(4), Pt−O(11) 2.067(3), Pt−O(1) 2.112(3), O(11)−N(11) 1.291(5), O(12)−N(11) 1.219(5), O(16)−N(12) 1.221(5), O(17)−N(12) 1.215(5), O(21)−N(21) 1.208(5), O(22)−N(21) 1.201(5), O(26)−N(22) 1.217(5), O(27)−N(22) 1.229(5), N(11)−C(12) 1.412(6), N(12)−C(16) 1.470(5), N(21)−C(22) 1.463(5), N(22)−C(26) 1.468(5), C(11)−Pt−C(21) 102.94(17), C(11)−Pt−O(11) 80.43(15), C(21)−Pt−O(1) 88.15(15), O(11)−Pt−O(1) 88.44(13), O(12)−N(11)−O(11) 117.7(4), O(17)−N(12)−O(16) 125.1(4), O(22)−N(21)−O(21) 123.2(4), O(26)−N(22)−O(27) 123.3(4).

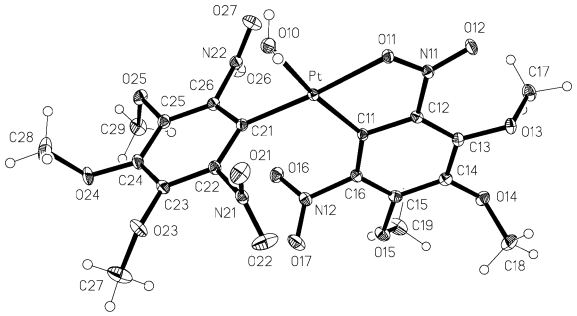


Figure 3. Ellipsoid representation of **4**·CH_2Cl_2 (30% probability; solvent omitted). Selected bond lengths (Å) and angles (deg): Pt−C(11) 1.969(3), Pt−C(21) 1.986(3), Pt−O(11) 2.0737(19), Pt−O(10) 2.147(2), N(11)−O(12) 1.206-(3), N(11)−O(11) 1.288(3), N(11)−C(12) 1.435(4), N(12)−O(17) 1.220(3), N(12)−O(16) 1.224(3), N(12)−C(16) 1.475(4), N(21)−O(22) 1.210(4), N(21)−O(21) 1.220(3), N(21)−C(22) 1.480(3), N(22)−O(27) 1.223(3), N(22)−O(26) 1.227(3), N(22)−C(26) 1.468(4), C(11)−Pt−C(21) 102.30(11), C(11)−Pt−O(11) 80.89(9), C(21)−Pt−O(10) 87.18(10), O(11)−Pt−O(10) 89.84(8), O(12)−N(11)−O(11) 119.8(2), O(17)−N(12)−O(16) 124.9(3), O(22)−N(21)−O(21) 124.1(3), O(27)−N(22)−O(26) 123.9(3).

presumably resulting from steric repulsion between the bulky *cis* aryl ligands. Associated with this is the narrow bite of the chelating ligand; the C−Pt−O angles in the κ^2-Ar ligand are significantly less than 90° [80.1(2)° (**1**), 80.43(15)° (**4**·Et_2O), 80.89(9)° (**4**·CH_2Cl_2), and 80.52(7)° (**7**)]. The Pt−C(κ^1-Ar) bond distances are very similar [1.985(5) Å (**1**), 1.988(4) Å (**4**·Et_2O), 1.986(3) Å (**4**·CH_2Cl_2), and 1.983(2) Å (**7**)]; the same applies to Pt−C(κ^2-Ar) [1.976(5) Å (**1**), 1.966(4) Å (**4**·Et_2O), 1.969(3) Å (**4**·CH_2Cl_2), and 1.973(2) Å (**7**)], although the latter are slightly shorter, suggesting a somewhat greater *trans* influence of the O-nitro ligand than that of chloro, OH_2, or CF_3CO_2 ligands. A comparative study of the nitroaryl

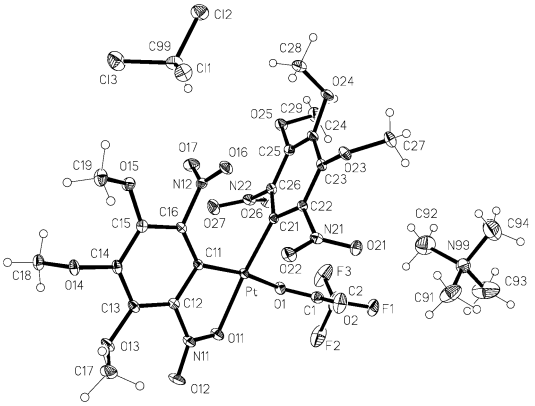


Figure 4. Ellipsoid representation of **7** (30% probability). Selected bond lengths (Å) and angles (deg): Pt−C(11) 1.973(2), Pt−C(21) 1.983(2), Pt−O(1) 2.0774(16), Pt−O(11) 2.0843(15), N(11)−O(12) 1.220(2), N(11)−O(11) 1.284(2), N(11)−C(12) 1.426(3), N(12)−O(16) 1.218(2), N(12)−O(17) 1.221(2), N(12)−C(16) 1.486(3), N(21)−O(22) 1.223(2), N(21)−O(21) 1.232(2), N(21)−C(22) 1.476(3), N(22)−O(27) 1.225(3), N(22)−O(26) 1.228(3), N(22)−C(26) 1.475(3), C(11)−Pt−C(21) 100.02(8), C(11)−Pt−O(1) 168.91(7), C(21)−Pt−O(1) 88.82(7), C(11)−Pt−O(11) 80.52(7), C(21)−Pt−O(11) 174.15(7), O(1)−Pt−O(11) 91.37(6), O(12)−N(11)−O(11) 119.67(19), O(16)−N(12)−O(17) 124.93(19), O(22)−N(21)−O(21) 124.05(19), O(27)−N(22)−O(26) 123.8(2).

group parameters will appear in the following article reporting other nitroaryl complexes.[27] Complexes **4**·Et_2O and **4**·CH_2Cl_2 show the aqua ligand bonded *trans* to the C(11) atom of the chelating Ar ligand. A search of the Cambridge Structural Database reveals 23 crystal structures of organometallic aqua platinum complexes.[30,31] All of them are monoaqua complexes, and most contain the water molecule *trans* to a carbon donor ligand.[30] The bond distances and angles for complexes **4**·CH_2Cl_2 and **4**·Et_2O are similar. The only exception is the Pt−OH_2 distance, which is significantly longer in **4**·CH_2Cl_2 [2.147(2) Å] than in **4**·Et_2O [2.112(3) Å], possibly as a consequence of the different hydrogen bonds the aqua ligand establishes in each complex. In **4**·Et_2O (Figure 2), the water molecule forms a short[32] hydrogen bond with the Et_2O molecule [H(02)···O(99) 1.79(4) Å, O(1)···O(99) 2.663(5) Å, O(1)−H(02)···O(99) 168(5)°] and a longer[32] hydrogen bond to the *m*-O(25)-Me of the κ^1-Ar ligand of a different molecule [H(01)···O(25) 2.06(4) Å, O(1)···O(25) 2.830(4) Å, O(1)−H(01)···O(25) 146(5)°; acceptor operator (−*x*+2, −*y*+2, −*z*+2)], thus forming inversion-related pairs of units **4**·Et_2O. In **4**·CH_2Cl_2 the water molecule bridges two molecules, establishing two hydrogen bonds with oxygen atoms of two *m*-OMe groups of the same κ^2-Ar ligand (but via different operators; Figure 5). The hydrogen bonding parameters for O(1)−H(01)···O(13) (−*x*, −*y*+1, −*z*+1) are H(01)···O(13) 2.13(3) Å, O(1)···O(13) 2.838(3) Å, O(1)−H(01)···O(13), 168(6)°; and for O(1)−H(02)···O(15) (*x*, *y* + 1, *z*) are H(02)···O(15) 2.24(3) Å, O(1)···O(15) 2.933(3) Å, O(1)−H(02)···O(15) 164(4)°, forming ribbons of molecules parallel to the short *y* axis at $z \approx 0.5$. As would be expected, these compounds also display a considerable number of "weak" hydrogen bonds of the form C−H···O, details of which are given in the Supporting Information.

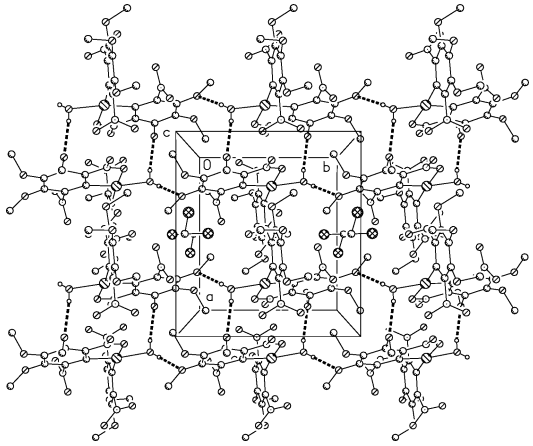


Figure 5. Packing view showing the O−H···OMe hydrogen bonds (broken lines) in **4**·CH_2Cl_2.

As expected, the NMR spectra of complexes **1**, **2**, and **5**−**7** show five different MeO groups, consistent with the structures proposed and with the crystal structure of **1** and **7**. However, the ^{1}H NMR spectra of complexes **4**·Et_2O and **4**·CH_2Cl_2 are not as expected because a fluxional behavior is observed. Thus, at room temperature, the ^{1}H NMR spectrum of **4**·Et_2O in $CDCl_3$ shows only two MeO resonances (2:1) and no signal from the molecule of H_2O. A variable-temperature ^{1}H NMR study was performed on **4**·Et_2O in $CDCl_3$; at −30 °C it shows the expected five singlets for the MeO protons and two broad singlets for the H_2O protons. As the temperature is raised, the MeO singlets broaden, becoming two singlets at room temperature, and the two water signals also broaden, move upfield, and disappear at room temperature. Probably, at room temperature, each aryl ligand is rapidly changing its coordination mode, κ^2-Ar ⇔ κ^1-Ar becoming equivalent, whereas at low temperatures the spectrum shows both different aryl groups, and a hydrogen bond (probably intramolecular) makes the water hydrogens inequivalent.

The ^{1}H NMR and ^{13}C{^{1}H} NMR spectra of **3** show two 2:1 singlets corresponding to the MeO groups of both κ^1-Ar ligands. Its IR spectrum shows a medium intensity band at 452 cm^{-1} assignable to ν(Pt−O),[33] in agreement

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with the chelating nature of the acac ligand. An absorption at 310 or 298 cm^{-1} in complexes **1** or **2**, respectively, can be assigned to ν(PtCl). All complexes show very strong bands in the 1565−1500 cm^{-1} region corresponding to $\nu_{asym}(NO_2)$. A very strong band around 1350−1365 cm^{-1} and a medium intensity band in the 1300−1280 cm^{-1} region are assignable to $\nu_{sym}(NO_2)$ of the noncoordinated nitro groups. Complexes **1**, **2**, and **4**−**7** also show a medium intensity band at around 1250 cm^{-1} that we assign to $\nu_{sym}(NO_2)$ of the coordinated nitro groups.[2,4,6−8,34]

Color of Complexes. In agreement with previous observations,[2] the intense violet, orange, or red color of complexes **1**, **2**, and **4**−**7** is due to the presence of one κ^2-Ar ligand. These colors fade to pale yellow for **3**, where only κ^1-Ar ligands are present.

Conclusions

We report the first platinum complexes with the aryl group $C_6(NO_2)_2$-2,6-$(OMe)_3$-3,4,5. They are obtained through a transmetalation reaction from the corresponding diaryl mercurial [$HgAr_2$]. This process always leads to diaryl platinum complexes.

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Supporting Information Available: Listing of all refined and calculated atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for **1**, **4**·Et_2O, **4**·CH_2Cl_2, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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