strong rR effects for the ligand stretching modes and only weak effects for the metal–ligand stretching modes upon excitation into the MLCT band. This result confirms the strong MLCT character of the metal to α-diimine transitions in these complexes, which is also evident from the large solvatochromism of these MLCT bands. The rR spectra of the $W(CO)_4$(R–DAB) complexes, on the other hand, do not show any rR effect for μ(s)(CN) of the R–DAB ligand but instead show strong rR effects for metal–ligand stretching and ligand deformation modes. This implies a lack of MLCT character for the transitions involved, which are now strongly metal–ligand bonding to antibonding. This lack of MLCT character is also evident from the absence of any solvent dependence of the position of the MLCT band.

In conclusion it can be said that the rR spectra of these Ru(II) complexes give valuable information not only about the correctness of previous assignments of absorption bands but also about the specific nature of the transitions involved.

Acknowledgment. We thank Dr. E. S. Dodsworth for useful discussion.

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Synthesis and Solvolytic Behavior of *cis*-(1,1′-Bis(diphenylphosphino)ferrocene)platinum(II) and -palladium(II) Complexes. X-ray Structure of Bis(μ-hydroxy)bis(1,1′-bis(diphenylphosphino)ferrocene)diplatinum(II) Tetrafluoroborate

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The fate of cis-platinum(II) drugs inside the cell cytoplasm as well as the mechanism of the selective lesion caused by them to DNA are still open questions.[1] Particularly relevant seems to be the hydrolytic cleavage of the Pt–Cl bonds, the consequent formation of aquo and/or hydroxo species, and their reactivity toward nucleotides.

We have recently reported[2] that (dppf)$PtCl_2$ (**1**-Pt) and $[(dppf)Pt(\mu\text{-}Cl)]_2^{2+}$ (**2**-Pt) (dppf) = 1,1′-bis(diphenylphosphino)ferrocene) are the precursors of the solvato complexes $[(dppf)PtClS]^+$ (**3**-Pt) and $[(dppf)PtS_2]^{2+}$ (**5**-Pt), which exhibit a remarkably high reactivity toward thymidines.

Preliminary in vitro tests on the cytostatic ability of complexes **1**-Pt and **2**-Pt have shown[3] that only the hydrolytically labile complex **2**-Pt, dissolved in DMSO, caused considerable growth inhibition of tumoral cells. Interestingly, the related complex $[(dppf)Pt(\mu\text{-}OH)]_2^{2+}$ (**4**-Pt) herein described turned out to be inactive and this observation prompted us to investigate the solution chemistry, i.e. solvolytic behavior, of complexes $[(dppf)M(\mu\text{-}Cl)]_2^{2+}$ (**2**, M = Pd, Pt) as well as of the related species $[(dppf)PtS_2]^{2+}$ (**5**-Pt, S = dimethylformamide) and $[(dppf)M(\mu\text{-}OH)]_2^{2+}$. We also report on the X-ray structure of **4**-Pt, which is, to the best of our knowledge, the second example of a hydroxo bis(phosphino) complex of platinum(II) for which the molecular structure has been determined by X-ray analysis.[4] Moreover, we herein describe some preliminary voltammetric tests concerning the reported complexes.

Experimental Section

General Procedures and Materials. All solvents were dried by standard procedures. ^1H and ^{31}P NMR spectra were recorded on a JEOL 90 Q spectrometer at 27 °C and were referenced to internal Me_4Si and external H_3PO_4 (85% w/w), respectively. IR spectra were recorded on a Perkin-Elmer Model 599 B spectrometer. UV–vis spectra were taken on a Perkin-Elmer LAMBDA 5 spectrometer. The apparatus used for voltammetry consisted of an Amel Model 551 potentiostat modulated by an Amel Model 566 function generator, while the recording device was a Hewlett-Packard 7040 A X-Y recorder. All experiments were performed at 25 °C in deoxygenated 1,2-dichloroethane (DCE) with 0.2 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte, with use of a conventional three-electrode liquid-jacketed cell. The working electrode was a planar Pt microelectrode (ca. 0.3 mm^2), surrounded by a Pt-spiral counter electrode. A silver/0.1 M silver perchlorate electrode in acetonitrile, separated from the working solution by a fine glass frit, was used as the reference electrode. All potentials are referred to the ferrocenium/ferrocene couple. 1,1′-Bis(diphenylphosphino)ferrocene (dppf) was from Strem Chemicals and was used as received, and (dppf)$PtCl_2$ was prepared as reported elsewhere.[14]

$[(dppf)M(\mu\text{-}Cl)]_2(BF_4)_2$ (2: M = Pt, 2-Pt; M = Pd, 2-Pd). A solution of $AgBF_4$ (0.119 g, 0.609 mmol) in acetone (10 mL) was added dropwise to a suspension of (dppf)$PtCl_2$ (0.500 g, 0.609 mmol) in acetone (30 mL). After it was stirred for 30 min, the reaction mixture was filtered and the filtrate was vacuum-evaporated to 5 mL. Addition of Et_2O afforded a burgundy red crystalline precipitate (0.424 g) in 80% yield. **2-Pd** was similarly obtained as a green product in 90% yield. IR (Nujol): 295 and 290 cm^{-1} (ν_{Pd-Cl}); 305 and 295 cm^{-1} (ν_{Pt-Cl}). ^{31}P NMR (CD_2Cl_2, 90 MHz): **2**-Pt, δ 18.30 (s, flanked by ^{195}Pt satellites, J = 3987 Hz); **2**-Pd, δ 46.5 (s). Anal. Calcd for $C_{34}H_{28}BClF_4FeP_2Pd$: C, 52.15; H, 3.60; Cl, 4.53. Found: C, 52.30; H, 3.60; Cl, 4.75. Calcd for $C_{34}H_{28}BClF_4FeP_2Pt$: C, 46.84; H, 3.24; Cl, 4.07. Found: C, 46.10; H, 3.23; Cl, 3.82.

$[(dppf)M(\mu\text{-}OH)]_2(BF_4)_2\cdot 2CH_2Cl_2$ (4: M = Pt, 4-Pt;[5] M = Pd, 4-Pd). A solution of $AgBF_4$ (0.238 g, 1.218 mmol) in CH_3OH (5 mL) was added to a suspension of **1**-Pt (0.50 g, 0.609 mmol) in 25 mL of CH_3OH (reagent grade, 0.1% water content). The reaction mixture was stirred for 12 h in the open atmosphere and the solvent removed under vacuum. The residue was extracted several times with CH_2Cl_2, and the resulting solution was concentrated under vacuum. The complex was isolated as a yellow crystalline product (0.431 g, yield 83%) upon adding CH_3OH and cooling the solution at −20 °C. IR (Nujol): 3550 cm^{-1} (w) (ν_{O-H}). ^1H NMR (CD_2Cl_2): δ 7.42 (complex multiplet (cm), 20 H, C_6H_5), 4.50 and 4.32 (cm, 8 H, C_5H_4), −0.05 (s, broad, 1 H, OH). ^{31}P NMR: δ 6.46 (s, flanked by ^{195}Pt satellites, J = 3857 Hz). Burgundy red crystals of **4**-Pd were isolated from acetone containing 1% water, similarly to **4**-Pt. IR (Nujol): 3580 cm^{-1} (m) (ν_{O-H}). ^1H NMR (CD_2Cl_2): δ 7.7–7.3 (cm, 20 H, C_6H_5), 4.54 and 4.36 (cm, 8 H, C_5H_4), −2.32 (s, broad, 1 H, OH). ^{31}P NMR: δ 38.7 (s). Anal. Calcd for $C_{35}H_{31}BCl_2F_4FeOP_2Pd$: C, 52.09; H, 3.87. Found: C, 51.85; H, 3.85. Calcd for $C_{35}H_{31}BCl_2F_4FeOP_2Pt$: C, 44.81; H, 3.33. Found: C, 44.10; H, 3.40.

$[(dppf)Pt(DMF)_2](BF_4)_2$ (5-Pt). A solution of **1** (0.500 g, 0.609 mmol) in 5 mL of anhydrous dimethylformamide was treated with a DMF solution of $AgBF_4$ (0.238 g, 1.218 mmol). After the mixture was stirred for 30 min, the solvent was vacuum evaporated; the oily residue dissolved in CH_2Cl_2 (5 mL), and AgCl filtered off. Upon addition of toluene and cooling at −30 °C the product precipitated as mustard yellow crystals (0.33 g, 51% yield). IR (Nujol): 1640 cm^{-1} (s) (ν_{C-O}). ^1H NMR ($(CD_3)_2SO$): δ 7.96 (s, 2 H, HC(O)), 7.60 (cm, 20 H, C_6H_5), 4.64 and 4.30 (cm, 8 H, C_5H_4), 2.84 and 2.67 (s, 12 H, CH_3). ^{31}P NMR

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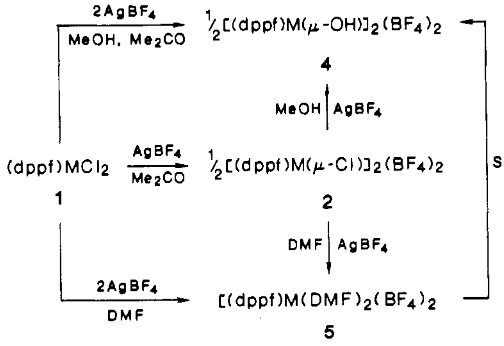
Table I. Crystal Data for $[(dppf)Pt(\mu\text{-}OH)]_2(BF_4)_2{\cdot}2CH_2Cl_2{\cdot}2H_2O$

empirical formula	$C_{70}H_{66}B_2Cl_4F_8Fe_2O_4P_4Pt_2$
color	yellow
cryst dimens, mm	0.12 × 0.12 × 0.18
cryst syst	triclinic
space group	$P\bar{1}$
cell dimens	
a, Å	13.158 (4)
b, Å	12.984 (4)
c, Å	10.990 (3)
α, deg	100.3 (3)
β, deg	104.3 (3)
γ, deg	99.3 (3)
molecules/cell	1
vol, Å^3	1748.0
calcd density, g/cm^3	1.82
wavelength, Å	0.7107
mol wt	1912.5
linear abs coeff, cm^{-1}	49
no. of unique corrected rflns	6132
no. with $I \geq 2\sigma(I)$	4525
final residual R (w = 1)	0.064

Scheme I[a]



[a] M = Pd, Pt; S(H_2O) = wet coordinating solvent for M = Pt. All species are cis complexes.

(CD_2Cl_2): δ 7.00 (s, flanked by ^{195}Pt satellites, J = 4143 Hz). Anal. Calcd for $C_{40}H_{42}B_2F_8FeO_2N_2P_2Pt$: C, 44.93; H, 3.96; N, 2.62. Found: C, 45.49; H, 4.02; N, 2.58.

Crystallography of $[(dppf)Pt(\mu\text{-}OH)]_2(BF_4)_2$. Suitable crystals of **4**-Pt were grown from dichloromethane solution upon slow evaporation, which were analyzed as $[(dppf)Pt(OH)]_2(BF_4)_2{\cdot}2CH_2Cl_2{\cdot}2H_2O$. Characteristics of the data collection (4° ≤ 2ϑ ≤ 50°) processing and refinement are given in Table I.

The data were collected at room temperature on a Philips PW 100 four-circle diffractometer. No absorption correction was applied. The structure was solved by the heavy-atom method and was refined by full-matrix procedures, anisotropically for all non-hydrogen atoms. The programs used were those of the SHELX package.[6] Fractional coordinates and thermal parameters are given in Table II. Additional details, including nonessential bond distances and angles, are available as supplementary material.

Results and Discussion

Synthesis and Solvolytic Behavior. Complexes **2**-**5** were obtained in good yields by stepwise removal of the chloride ligands from compounds **1** in the appropriate solvents (Scheme I).

The structure of **2** in the solid state is supported by IR data and that of **4**-Pt by X-ray analysis (see Figure 1). The nature of complexes **2** and **4** in solution is supported by the combination of NMR data with their solvolytic behavior. In fact, complexes **2** maintain their dimeric structure in dichloromethane, while just small amounts of coordinating solvents (1% v/v) cause instantaneous bridge splitting and quantitative conversion into mono(solvato) species (**3**), as shown by ^{31}P NMR data.[7] Interestingly, while **3**-Pt exhibits two sharp resonances due to the different trans ligands, **3**-Pd is stereochemically nonrigid at room temperature (δ 41.7 (s) in dimethylformamide). Moreover, the solvolytic reactions of complexes **2** are accompanied by strong color changes.[8] By contrast, **4**-Pt appears to be quite stable toward solvolysis in both coordinating and noncoordinating solvents, as shown by the invariance of its ^{31}P and ^{1}H NMR and electronic spectra. No evidence of oligomers higher than order 2 could be obtained. The remarkable stability[1a] of **4**-Pt is evidenced also by the extensive conversion of **5**-Pt into **4**-Pt[9] when it is dissolved in wet coordinating solvents.[10] **4**-Pd behaves similarly in dichloromethane, but rapid decomposition occurs in coordinating solvents.

The solvolytic behavior of complexes **2** can be related to that displayed by complexes containing 1,2-bis(diphenylphosphino)-

Table II. Fractional Coordinates and Thermal Parameters for *cis*-$[(dppf)Pt(\mu\text{-}OH)]_2{\cdot}2CH_2Cl_2{\cdot}2H_2O$

atom	x/a	y/b	z/c	U_{eq}, Å^2
Pt	0.0789 (0)	0.4175 (0)	0.4926 (1)	0.0331 (3)
Fe	0.3139 (2)	0.2531 (2)	0.6312 (2)	0.0387 (11)
P(1)	0.2464 (3)	0.4386 (3)	0.4766 (4)	0.0344 (18)
P(2)	0.0529 (3)	0.2434 (3)	0.5010 (4)	0.0341 (19)
O(1)	0.0751 (9)	0.5781 (8)	0.4895 (14)	0.063 (7)
C(1)	0.0211 (13)	0.3103 (13)	0.7410 (16)	0.049 (9)
C(2)	−0.0174 (15)	0.2988 (15)	0.8402 (17)	0.062 (11)
C(3)	−0.0920 (14)	0.2050 (15)	0.8360 (18)	0.059 (11)
C(4)	−0.1228 (13)	0.1246 (12)	0.7235 (17)	0.050 (10)
C(5)	−0.0824 (13)	0.1372 (12)	0.6220 (16)	0.047 (9)
C(6)	−0.0081 (11)	0.2304 (11)	0.6284 (16)	0.043 (9)
C(7)	−0.0179 (15)	0.0904 (13)	0.2651 (17)	0.056 (10)
C(8)	−0.0899 (17)	0.0335 (14)	0.1470 (18)	0.067 (12)
C(9)	−0.1935 (17)	0.0502 (15)	0.1185 (20)	0.071 (12)
C(10)	−0.2225 (14)	0.1216 (15)	0.2054 (22)	0.072 (13)
C(11)	−0.1502 (14)	0.1780 (13)	0.3175 (18)	0.058 (10)
C(12)	−0.0451 (11)	0.1623 (10)	0.3491 (14)	0.038 (8)
C(13)	0.1625 (11)	0.1747 (11)	0.5358 (15)	0.041 (7)
C(14)	0.2348 (12)	0.1495 (10)	0.4610 (17)	0.046 (9)
C(15)	0.3105 (13)	0.1022 (12)	0.5304 (18)	0.052 (10)
C(16)	0.2876 (12)	0.0946 (13)	0.6498 (19)	0.057 (10)
C(17)	0.1951 (11)	0.1403 (12)	0.6565 (16)	0.046 (9)
C(18)	0.3380 (11)	0.4029 (11)	0.6015 (13)	0.035 (7)
C(19)	0.4316 (12)	0.3591 (12)	0.6001 (15)	0.044 (9)
C(20)	0.4694 (12)	0.3339 (13)	0.7224 (18)	0.052 (10)
C(21)	0.4026 (13)	0.3615 (14)	0.8001 (18)	0.055 (10)
C(22)	0.3216 (12)	0.4041 (12)	0.7305 (16)	0.045 (9)
C(23)	0.1679 (12)	0.3048 (12)	0.2282 (16)	0.045 (9)
C(24)	0.1781 (15)	0.2546 (15)	0.1146 (17)	0.057 (11)
C(25)	0.2738 (18)	0.2680 (16)	0.0878 (18)	0.066 (13)
C(26)	0.3639 (15)	0.3363 (16)	0.1771 (18)	0.059 (12)
C(27)	0.3550 (12)	0.3876 (12)	0.2934 (15)	0.044 (9)
C(28)	0.2586 (11)	0.3723 (11)	0.3216 (14)	0.037 (8)
C(29)	0.2757 (12)	0.6229 (13)	0.3796 (16)	0.049 (9)
C(30)	0.3173 (13)	0.7319 (14)	0.3921 (19)	0.053 (11)
C(31)	0.3781 (15)	0.7968 (13)	0.5059 (20)	0.060 (11)
C(32)	0.4018 (13)	0.7536 (12)	0.6154 (19)	0.059 (11)
C(33)	0.3617 (13)	0.6440 (12)	0.6074 (17)	0.051 (10)
C(34)	0.2995 (11)	0.5794 (11)	0.4899 (15)	0.037 (8)
F(1)	0.3524 (12)	0.8669 (10)	0.1450 (14)	0.110 (10)
F(2)	0.4495 (14)	0.9717 (12)	0.3353 (14)	0.124 (11)
F(3)	0.4747 (15)	1.0090 (12)	0.1534 (17)	0.144 (14)
F(4)	0.3306 (14)	1.0295 (13)	0.2083 (17)	0.137 (13)
B	0.4067 (19)	0.9694 (17)	0.2110 (22)	0.061 (13)
Cl(1)	0.8933 (8)	0.3897 (6)	0.1551 (8)	0.137 (13)
Cl(2)	0.7376 (7)	0.4607 (7)	−0.0246 (7)	0.133 (6)
C(35)	0.7621 (25)	0.3585 (18)	0.0623 (29)	0.113 (20)
OW	0.5076 (17)	0.1953 (14)	0.0283 (18)	0.124 (15)

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(7) ^{31}P NMR data for **2**-Pt (J_{Pt-P} and J_{P-P} in parentheses, respectively): δ 18.0 (d, 3860, 19 Hz), 4.1 (d, 4086, 19 Hz), in dimethylformamide-d_7; δ 13.3 (d, 3605, 13 Hz), 5.4 (d, 3982, 13 Hz), in CD_3CN.

(8) UV–vis for **2**-Pt (λ_{max}, nm (ϵ mol^{-1} dm^3 cm^{-1})): 229 (92 000), 487 (1335), in dichloromethane; 206 (231 000), 437 (734), in acetonitrile; 268 (25 000), 435 (830), in dimethylformamide. UV–vis for **2**-Pd: 596 (1950), in dichloromethane; 533 (1500), in acetone; 513 (1300), in acetonitrile.

(9) ^{31}P NMR for **4**-Pt: δ 8.2 (s, J_{Pt-P} = 3813 Hz), in dimethyl-d_6 sulfoxide; δ 8.4 (s, J_{Pt-P} = 3799 Hz), in dimethylformamide. ^{31}P NMR for **4**-Pd: δ 38.0 (s) in dimethyl sulfoxide.

(10) Dissolution of **5**-Pt in dimethyl-d_6 sulfoxide containing 1.2% water leads to 65% selective conversion into **4**-Pt (^{31}P NMR) after 24 h at room temperature.

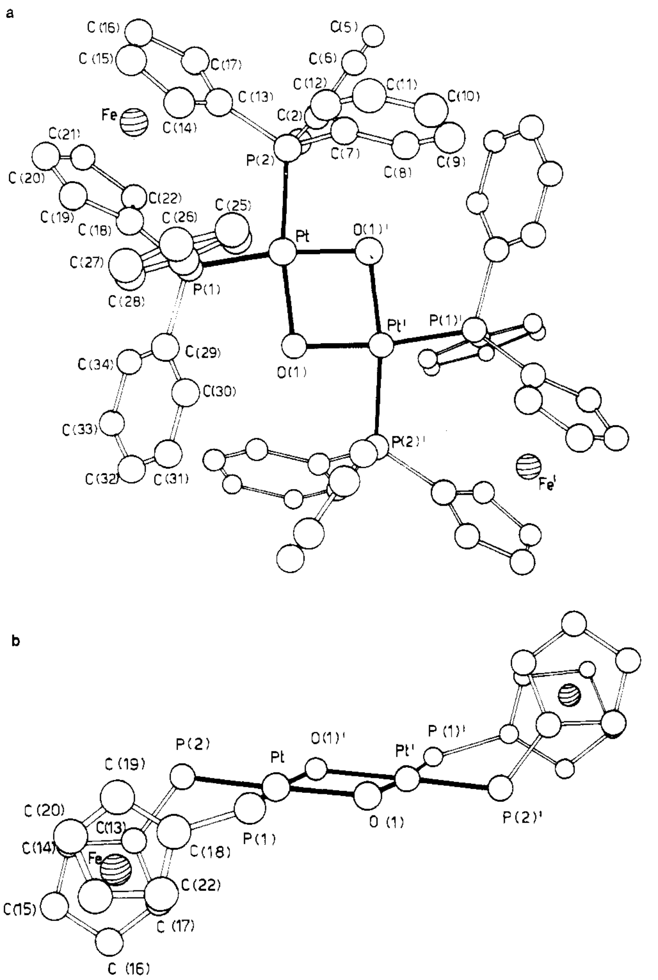

Figure 1. Views of **4**-Pt. The trapped molecules and the anionic counterions are omitted for clarity; in part b the C_6H_5 groups are also omitted. Structural parameters (see also text) are as follows: distances, Pt–P(1) = 2.230 (4), Pt–P(2) = 2.253 (4), Pt–O = 2.100 (11), Pt–Pt = 3.227 (1), Pt–Fe = 4.172 (4), C–Fe = 2.045 (av) Å; angles, Pt–O–Pt = 100.6 (7), P(1)–Pt–P(2) = 98.1 (1), P(1)–Pt–O = 92.3 (3), P(2)–Pt–O = 169.5 (4), P(2)–Pt–O′ = 90.2 (3); O–Pt–O′ = 79.4 (4)°.

ethane $[(dppe)M(\mu\text{-}Cl)]_2^{2+}$.[11] However, two major differences are to be noted: (i) the resistance to bridge splitting appears to be stronger in the dppe complexes, which maintain their dimeric nature in acetonitrile, and (ii) the solvolytic stability toward chloride displacement of the relevant parent complexes, (dppe)MCl_2, appears to be much lower in coordinating solvents (e.g. DMSO) than that observed in complexes **1**. In fact, **1**-Pt appears to be quite unreactive in this last solvent also after heating at 90 °C for 24 h.

Cyclic voltammetric (CV) experiments in 1,2-dichloroethane show that all complexes herein described undergo a reversible one-electron-transfer reaction involving the ferrocene moiety and the relevant standard potentials are significantly sensitive to the nature of the extra ligands.[12] The CV response of complexes **2** does remarkably exhibit the same shape and current values as that of the monomeric species **1**, into which they can be easily converted in situ, upon addition of the stoichiometric amount of Bu_4NCl. This is in full agreement with a complete lack of interaction between the two electroactive centers in the same molecule.[13]

Solid-State Structure of 4-Pt. The molecular structure of the cationic complex is depicted in Figure 1.

The ligand geometry around the Pt atoms is distorted square planar, as shown by the larger P–Pt–P angle (98.1 (1)°), by the smaller P(2)–Pt–O angle (169.5 (4)°), and by the distance of the Pt atoms from the two P and two O mean planes (±0.014 Å). The P(1)–Pt–P(2) angles as well as the Pt–P bond lengths are quite similar to those observed in **1**-Pt.[14] As expected, the $P_4Pt_2O_2$ skeleton is planar and this finding is in striking contrast with the lack of coplanarity observed in the only further example of an X-ray-investigated phosphino–hydroxo–platinum(II) complex, *cis*-$[(PEt_3)_2Pt(\mu\text{-}OH)]_2(BF_4)_2$.[4] In this complex, in fact, the plane normals of the PtP_2O_2 halves form an angle of 36.4°. The Pt–O distance in **4**-Pt (2.100 (11) Å) is significantly longer than that observed in the closely related, i.e. coplanar, bridged hydroxo platinum(II) complex $[(NH_3)_2Pt(\mu\text{-}OH)]_2^{2+}$ (2.03 (1) Å).[15] The Pt–O–Pt angle is also remarkably larger than in the amino complex (100.6 (7) vs 81.3 (4)°), so that also the Pt–Pt distance turns out to be considerably greater (3.227 (1) vs 3.085 (1)°). The Fe atoms are displaced 1.69 Å from the Pt_2O_2 plane, and the two cyclopentadienyl rings, which do not deviate significantly from planarity, are in the staggered configuration and form an angle equal to 5.0°. Similar to what is observed for **1**-Pt,[14] the ring spacing decreases toward the phosphorus atoms.

Water and dichloromethane molecules as well as the BF_4^- ions do not chemically interact with the cationic complex (Pt–Cl distance 3.824 (5) Å and Pt–O distance ≥4 Å). Water molecules are hydrogen-bonded to BF_4^- (O–F = 3.012 (30) Å), while the dichloromethanes are simply trapped inside the crystal lattice.

Single crystals of **4**-Pd were also obtained, and the preliminary X-ray data show that it is isotypic and therefore isostructural with **4**-Pt.

Acknowledgment. We are grateful to Prof. B. Lippert for helpful discussion.

Registry No. **1** (M = Pd), 72287-26-4; **1** (M = Pt), 104413-90-3; **2** (M = Pd), 112220-68-5; **2** (M = Pt), 106354-45-4; **4** (M = Pd), 112220-70-9; **4** (M = Pt), 112220-72-1; **5** (M = Pt), 112295-40-6.

Supplementary Material Available: Listings of selected bond distances and angles, thermal parameters, and mean planes equations (4 pages); a complete listing of structural data (including *F*) (18 pages). Ordering information is given on any current masthead page.

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(12) Standard potentials for two-step charge transfers obtained by comparison of experimental cyclic voltammetry data to the theoretical parameters in Table II of ref 13: **2**-Pd, E°_1 = 0.718 V, E°_2 = 0.754 V; **2**-Pt, E°_1 = 0.707 V, E°_2 = 0.743 V; **4**-Pd, E°_1 = 0.662 V, E°_2 = 0.698 V; **4**-Pt, E°_1 = 0.650 V, E°_2 = 0.686 V.

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Mononuclear and Tetranuclear Diorganotin(IV) Carboxylates from the Reaction of Dimethyltin Oxide with Anthranilic Acid and Its *p*-Amino Isomer

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Hydrolysis of diorganotin compounds, R_2SnX_2, results in the formation of organostannoxanes.[1-5] Although initially this class of compounds was thought to be monomeric,[6] subsequent work

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