Synthesis and Structural Studies of Platinum Complexes Containing Monodentate, Bridging, and Chelating Formamidine Ligands

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The reactions of K_2PtCl_4 with *N,N′*-diphenylformamidine (HDPhF) and *N,N′*-di-*p*-tolylformamidine (HDTolF) produce the trans square-planar compounds $PtCl_2(HDPhF)_2$, **1a**, and $PtCl_2(HDTolF)_2$, **1b**. Compound **1a** crystallizes as yellow parallelepipeds in the space group $P2_1/c$ with two independent molecules in the asymmetric unit and unit cell dimensions $a = 23.427(7)$ Å, $b = 16.677(6)$ Å, $c = 12.980(4)$ Å, and $\beta = 96.10(2)°$. These compounds are soluble in common organic solvents and have been used as starting materials for the preparation of diplatinum compounds. Treatment of **1a** and **1b** with NaOMe and the halide abstraction reagent $TlPF_6$ produces the compounds $Pt_2(\mu\text{-DArF})_2(\eta^2\text{-DArF})_2$, Ar = Ph (**2a**) and Tol (**2b**), respectively. Compound **2a** crystallizes as yellow rods in the space group $P\bar{1}$ with unit cell dimensions $a = 12.296(3)$ Å, $b = 12.310(4)$ Å, $c = 15.374(4)$ Å, $\alpha = 90.75(2)°$, $\beta = 91.02(2)°$, and $\gamma = 110.20(2)°$. Compound **2b** crystallizes with a molecule of THF, as yellow rods in the space group $P2_1/c$ with $a = 17.883(3)$ Å, $b = 14.517(3)$ Å, $c = 22.581(3)$ Å, and $\beta = 98.17(1)°$. These compounds contain two cis bridging formamidinato ligands and two formamidinato ligands that are chelated to separate Pt centers. Upon heating, they further react to give the tetrabridged compounds $Pt_2(\mu\text{-DArF})_4$, Ar = Ph (**3a**), Tol (**3b**). Compound **3a** crystallizes as orange cubes in the cubic space group $I432$ with $a = 19.671(1)$ Å. On going from the bis-bridged, bis-chelate structure in **2a** to the tetrabridged structure in **3a**, the metal−metal separation decreases from 2.910(1) to 2.649(1) Å. Both **2b** and **3b** have been oxidized to give the $Pt^{II}-Pt^{III}$ compound $Pt_2(\mu\text{-DTolF})_4(PF_6)$, **4**. Compound **4** crystallizes as cubes in the tetragonal space group $P4/ncc$ with $a = 14.392(1)$ Å and $c = 14.436(1)$ Å. The Pt−Pt distance in **4** is 2.5304(6) Å.

Introduction

Formamidinato ligands in a paddlewheel arrangement about two metal centers provide a unique opportunity to study many metal−metal interactions within the same structural motif. This type of compound is known for many of the transition metals, including V, Cr, Fe, Co, Ni, Cu, Mo, Tc, Ru, Rh, Pd, W, Re, Os, and Ir.[1] The flexibility of the formamidinato ligand, exemplified by its ability to bridge two metals that are separated at distances as short as 1.930(2) Å[2] and as long as 3.049(1) Å,[3] and its highly basic nature are probably the main reasons that it stabilizes such a variety of dimetal systems.

Within group 10 (Ni, Pd, and Pt) the possibility of a metal−metal bond of order 1 arises if the metal centers have a d^7 electronic configuration, that is, are in a formal oxidation state of +3. The bonding, formally described as $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$, is frequently found in Rh(II),[1a] but it is not as common for Ir(II)[4] and Pt(III).[1a,5] For the d^8 metals, Ni(II) and Pd(II), the formation of a metal−metal bond does not occur, at least with the formamidinato ion as a ligand,[6] because they form the neutral $M_2(RNC(H)NR)_4$ compounds. These can be oxidized by removal of one electron, but studies have shown this to be a ligand-based oxidation in the case of the Pd compound.

The possibility of altering the electronic properties of the ligand by changing the substituents on the nitrogen and methine carbon atoms is another advantage of the amidine ligand. By using *N,N′*-diphenylbenzamidine (DPhBz) in the palladium system, Bear and co-workers found that the neutral $Pd_2(DPhBz)_4$ could be oxidized to the d^7-d^8 species $Pd_2(DPhBz)_4{}^+$.[7] Changing the substituents on the amidine ligand can also influence the mode of binding. For Pd(II), DPhBz is known to form complexes that include a bis-chelate mononuclear species,[8] a bis-chelate, bis-bridged dimetal compound, and a tetrabridged compound.[7] In contrast, for the *N,N′*-di-*p*-tolylformamidine (DTolF) ligand, only the dinuclear tetrabridged species has been observed. For platinum, the DPhBz ligand produces a mononuclear bis-chelate species, with no evidence of other compounds being formed in solution.[9]

We wish to present the syntheses and X-ray structures of several complexes of Pt with the formamidine ligand. $PtCl_2(HDArF)_2$, Ar = Ph (**1a**), Tol (**1b**), were prepared as a convenient method for solubilizing Pt(II) chloride. $Pt_2(\mu\text{-DArF})_2(\eta^2\text{-DArF})_2$, Ar = Ph (**2a**), Tol (**2b**·THF), were prepared from **1a** or **1b** by deprotonating the formamidine ligand and

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Table 1. Crystallographic Data

	1a	**2a**	**2b**·THF	**3a**	**4**
formula	$C_{52}H_{48}Cl_4N_8Pt_2$	$C_{52}H_{44}N_8Pt_2$	$C_{64}H_{60}N_8OPt_2$	$C_{52}H_{44}N_8Pt_2$	$C_{60}H_{60}F_6N_8PPt_2$
fw	1316.96	1171.13	1347.38	1171.13	1428.31
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$I432$	$P4/nnc$
a, Å	23.427(7)	12.296(3)	17.883(3)	19.671(1)	14.392(1)
b, Å	16.677(6)	12.310(4)	14.517(3)		
c, Å	12.980(4)	15.374(4)	22.581(3)		14.436(1)
α, deg		90.75(2)			
β, deg	96.10(2)	91.02(2)	98.17(1)		
γ, deg		110.20(2)			
V, Å^3	5043(3)	2183(1)	5803(2)	7611.7(7)	2989.9(4)
Z	4	2	4	6	2
d_{calc}, g cm^{-3}	1.735	1.782	1.542	1.533	1.587
μ, mm^{-1}	5.798	6.448	4.864	10.475	4.763
λ, Å	0.710 73	0.710 73	0.710 73	1.541 84	0.710 73
temp, K	293(2)	293(2)	293(2)	293(2)	293(2)
transm factors	0.9981−0.6590	0.9990−0.7108	0.9991−0.8955	1.000−0.7913	0.9987−0.6318
R1[a], wR2[b]	0.033, 0.074	0.021, 0.053	0.030, 0.065	0.050, 0.138	0.019, 0.049
R1[a], wR2[b] (all data)	0.034, 0.077	0.029, 0.054	0.071, 0.087	0.069, 0.194	0.023, 0.052

[a] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $wR2 = [\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$.

abstracting the chloride. Similar to the Pd(II)− benzamidinato compounds, these compounds contain two bridging and two chelating formamidinato ligands and can be converted into the tetrabridged compounds $Pt_2(\mu\text{-DArF})_4$, Ar = Ph (**3a**), Tol (**3b**). The mixed-valence compound $[Pt_2(\mu\text{-DTolF})_4](PF_6)$, **4,** synthesized from the one-electron oxidation of **2b**, is also reported.

Experimental Section

General Procedures. All reactions were carried out under an argon or dinitrogen atmosphere using standard Schlenk techniques. Solvents were purified by conventional methods and distilled under dinitrogen immediately prior to use. *N*,*N*′-diphenylformamidine (HDPhF) was purchased from Aldrich Chemical Co. and used as received; *N*,*N*′-di-*p*-tolylformamidine (HDTolF) was prepared by a slightly modified published procedure.[10] The product was washed extensively with hexanes and recrystallized from toluene/hexanes. ^{1}H NMR studies were performed on a JEOL JNM GX-400 or -200 spectrometer; IR spectra were recorded on a Perkin-Elmer 16PC FT-IR spectrophotometer as Nujol mulls between KBr plates or as KBr pellets. UV−vis spectra were recorded on a Cary 17D spectrometer.

Preparation of *trans*-$PtCl_2(HDPhF)_2$, 1a. Method 1. K_2PtCl_4 (0.5 g, 1.20 mmol) was placed in a round-bottom flask containing HDPhF (0.470 g, 2.41 mmol). Toluene (35 mL) was added, and the mixture was refluxed and stirred for 24 h, or until it was observed that the insoluble pink K_2PtCl_4 had disappeared. While hot, the mixture was filtered to remove KCl, giving a yellow filtrate. The toluene was evaporated under vacuum to give a crude product that was contaminated with a small amount of free ligand. Washing with hot hexanes, followed by recrystallization from toluene/hexanes, gave pure **1a**. Yield: 0.60 g (82%). Anal. Calcd for $C_{26}H_{24}Cl_2N_4Pt$: 47.42% C, 3.67% H, 8.51% N. Found: 47.09% C, 3.19% H, 8.22% N. IR: 1880(m), 1650(s), 1630(s), 1600(s), 1580(s), 1500(s), 1330(s), 1215(s), 1100(w), 1020(m), 990(m), 960(s), 840(m), 720(w), 700(m), 510(s) cm^{-1}. UV−vis (CH_3CN): λ_{max} 285 nm. ^{1}H NMR ($CDCl_3$): δ 7.7, 7.8 (s, C−H), 7.1−7.5 (m, arom), 9.4 (s, br, N−H).

Method 2. K_2PtCl_4 (0.5 g, 1.20 mmol) was placed in a round-bottom flask containing HDPhF (0.470 g, 2.41 mmol). 1,2-Dichlorobenzene (20 mL) was then added, and the mixture was refluxed. The reaction was essentially complete in 3 h. KCl was removed by filtration. Addition of hexanes to the filtrate precipitated the product **1a**. The solid was then filtered off and recrystallized from hot toluene/hexanes. Yield: 0.52 g (71%).

Preparation of *trans*-$PtCl_2(HDTolF)_2$, 1b. This compound was prepared in a manner similar to that above, using the HDTolF ligand. Yields were 70−75%. IR: 1640(s), 1600(s), 1580(m), 1515(s), 1490(m), 1320(s), 1200(s), 1020(w), 975(w), 800(s), 515(m) cm^{-1}. UV−vis (CH_3CN): λ_{max} 275 nm. ^{1}H NMR ($CDCl_3$): δ 7.6, 7.7 (s, C−H), 7.1−7.5 (m, arom), 9.2−9.5 (s, br, N−H), 2.0, 2.1 (m, *p*-CH_3).

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $PtCl_2(HDPhF)_2$, **1a**

	x	y	z	U(eq)[a]
Pt(1)	924(1)	586(1)	1131(1)	36(1)
Cl(1)	1031(2)	1587(2)	2358(2)	67(1)
Cl(2)	760(1)	−405(2)	−119(2)	46(1)
N(1)	1054(3)	1421(5)	26(6)	36(2)
N(2)	118(3)	1888(5)	−110(7)	49(2)
N(3)	923(4)	−250(6)	2263(7)	49(2)
N(4)	−58(4)	−330(6)	2390(7)	53(2)
C(1)	651(5)	1911(6)	−362(8)	38(3)
C(2)	478(5)	−519(6)	2683(8)	48(3)
Pt(2)	5893(1)	−5143(1)	4130(1)	36(1)
Cl(3)	5836(1)	−4499(2)	5680(2)	46(1)
Cl(4)	5907(2)	−5811(2)	2592(2)	72(1)
N(5)	6146(3)	−6147(5)	4909(6)	35(2)
N(6)	5273(3)	−6815(5)	4818(6)	35(2)
N(7)	5749(4)	−4096(5)	3340(6)	41(2)
N(8)	4791(4)	−4300(5)	2774(7)	44(2)
C(3)	5831(5)	−6778(6)	5094(7)	36(3)
C(4)	5276(5)	−3892(6)	2826(8)	42(3)

[a] U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Preparation of $Pt_2(\mu\text{-DPhF})_2(\eta^2\text{-DPhF})_2$, 2a. To a THF (10 mL) solution of $PtCl_2(HDPhF)_2$ (0.200 g, 0.30 mmol) were added $TlPF_6$ (0.213 g, 0.61 mmol) and an excess of NaOMe (0.05 g, 0.9 mmol). The reaction mixture was stirred at room temperature for 2 h, during which time the solution color changed from yellow to purple. Filtration was then accomplished through Celite, and a mixture of hexanes was layered on top of the filtrate. Diffusion of the hexanes into the THF solution produced large yellow crystals of **2a**. Yield: 0.015 g (8%) IR: 1630(m), 1610(m), 1585(s), 1500(s), 1370(m), 1280(s), 1220(m), 975(m), 830(w), 825(m), 520(w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 9.50 (s, C−H), 7.70, 7.55, 7.15 (m, arom), 7.8 (s, C−H), 6.95, 6.80, 6.20 (m, arom).

Preparation of $Pt_2(\mu\text{-DTolF})_2(\eta^2\text{-DTolF})_2$·THF, 2b. This compound was prepared in a manner similiar to that used for **2a**, with $PtCl_2(HDTolF)_2$ as the starting material. X-ray-quality crystals were prepared by slow diffusion of hexanes into a solution of **2b** in THF. Yields were only 10−15% due to a small amount of reduction to Pt metal and incomplete reaction. IR: 1645(m), 1615(m), 1580(s), 1540(s), 1500(s), 1345(m, br), 1260(s), 1220(m), 960(m), 840(w), 815(m), 500(w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 9.80 (s, C−H), 7.80, 7.85, 7.20 (m, arom), 7.6 (s, C−H), 6.85, 6,90, 6.50 (m, arom), 2.0, 2.1 (m, *p*-CH_3).

Preparation of $Pt_2(\mu\text{-DPhF})_4$, 3a, and $Pt_2(\mu\text{-DTolF})_4$, 3b. A 15 mL MeOH solution of **2a** (0.10 g, 0.085 mmol) was refluxed for 1 h.

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Table 3. Selected Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for $Pt_2(\mu\text{-DPhF})_2(\eta^2\text{-DPhF})_2$, **2a**, and $Pt_2(\mu\text{-DTolF})_2(\eta^2\text{-DTolF})_2$, **2b**·THF

	2a				**2b**·THF			
	x	*y*	*z*	*U*(eq)[a]	*x*	*y*	*z*	*U*(eq)[a]
Pt(1)	2412(1)	1467(1)	1690(1)	29(1)	4374(1)	324(1)	2300(1)	45(1)
Pt(2)	3533(1)	2589(1)	3310(1)	29(1)	4293(1)	2266(1)	1931(1)	41(1)
N(1)	2509(3)	3117(3)	1461(3)	31(1)	3829(3)	222(4)	1446(2)	46(1)
N(2)	933(3)	1342(3)	2331(3)	31(1)	5348(3)	403(4)	1938(2)	47(1)
N(3)	3833(4)	1309(4)	1110(3)	39(1)	3553(3)	292(4)	2839(2)	49(1)
N(4)	2609(4)	−124(4)	1766(3)	39(1)	4723(3)	310(4)	3212(2)	51(1)
N(5)	3662(3)	4067(3)	2673(3)	32(1)	4218(3)	1649(4)	1117(2)	43(1)
N(6)	1895(3)	2495(3)	3534(3)	30(1)	5417(3)	2028(4)	2003(2)	42(1)
N(7)	5114(3)	2405(4)	3237(3)	38(1)	3220(3)	2737(4)	1979(2)	46(1)
N(8)	3692(4)	1169(4)	3890(3)	38(1)	4149(3)	2951(4)	2696(2)	46(1)
C(1)	3050(4)	4037(4)	1951(3)	30(1)	3943(4)	815(5)	1025(3)	49(2)
C(2)	3589(5)	224(5)	1357(4)	44(1)	5705(4)	1198(5)	1923(3)	46(2)
C(3)	965(4)	1953(4)	3051(3)	31(1)	4026(4)	313(5)	3335(3)	55(2)
C(4)	4774(4)	1413(5)	3643(3)	43(1)	3437(4)	3129(5)	2512(3)	49(2)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 4. Selected Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for $Pt_2(\mu\text{-DPhF})_4$, **3a**, and $[Pt_2(\mu\text{-DTolF})_4](PF_6)$, **4**

	3a				**4**			
	x	*y*	*z*	*U*(eq)[a]	x	*y*	*z*	*U*(eq)[a]
Pt(1)	0	4327(1)	0	40(1)	2500	2500	1621(1)	40(1)
N(1)	686(17)	4400(8)	772(19)	46(7)	2358(13)	3907(4)	1694(3)	41(3)
C(1)	934(9)	5000	934(9)	34(5)	2500	4321(5)	2500	48(2)
C(11)	1304(7)	3882(7)	755(8)	32(4)	2082(4)	4433(5)	927(5)	46(2)
C(12)	1996(8)	4024(8)	785(11)	48(9)	2460(1)	4266(4)	56(4)	54(2)
C(13)	2457(6)	3507(12)	927(14)	102(20)	2157(5)	4757(6)	−700(6)	68(3)
C(14)	2226(9)	2849(10)	1038(13)	88(11)	1505(8)	5449(7)	−617(7)	101(3)
C(15)	1534(10)	2707(7)	1007(11)	67(8)	1139(9)	5600(9)	244(7)	133(5)
C(16)	1074(7)	3223(8)	865(9)	47(6)	1402(6)	5109(6)	1002(6)	93(3)
C(17)					1170(1)	5950(1)	−1475(6)	189(1)
P(1)					2500	2500	−2500	70(1)
F(1)					2500	2500	−1398(5)	92(3)
F(2)					3277(3)	1723(3)	−2500	104(2)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

A small amount of platinum metal that formed during heating was removed by filtration, and the MeOH was evaporated under vacuum. The residue was redissolved in toluene (5 mL), and a layer of hexanes (10 mL) was placed on the toluene solution. Slow mixing of the hexanes at −20 °C produced small cubes of **3a**. Yield: 0.030 g (30%). IR: 1610(m), 1585(s), 1540(m), 1510(s), 1355(m), 1230(m), 1000(s), 970(m), 820(m), 540(w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.35 (s, C−H), 7.20, 7.23 (m, arom). A similar route was used to prepare **3b**. Both isomerizations can also be done in CH_3CN or THF.

Preparation of [Pt$_2$(*μ*-DTolF)$_4$](PF$_6$), 4. A 10 mL CH_2Cl_2 solution of **2b** (0.220 g, 0.19 mmol) was treated with $AgPF_6$ (0.05 g, 0.20 mmol). The solution color immediately changed from yellow-orange to brown-red. The reaction mixture was stirred for 8 h. The mixture was filtered through Celite, and Et_2O was layered onto the filtrate. Once the solvents had mixed, the product that formed was collected by filtration (0.109 g, 42%). X-ray-quality crystals were grown after several weeks in the freezer at −20 °C from a THF/hexanes solution. IR: 1585(s), 1560(s), 1480(m), 1415(m), 1325(s), 1295(m), 1270(s), 1200(s), 1165(s, br), 1000(m), 950(m), 850(m), 710(w), 540(m) cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} 442 nm (sh), 685 nm (vbr).

X-ray Crystallographic Procedures. Geometric and intensity data were collected on the following diffractometers: Syntex P3 (**1**, **2a**), Enraf-Nonius CAD-4 (**2b**·THF, **4**), and Rigaku AFC5R (**3**). Detailed procedures have previously been described.[11]

Each crystal was attached to the tip of a glass fiber. Reflections for cell indexing were found by an automated search routine (CAD-4 and Rigaku) or a 360° ϕ-rotation photograph (P3). In each case the cell dimensions and Laue group were verified by axial photography. Data were corrected for Lorentz and polarization effects and an absorption correction was applied based on a series of ψ scans. The positions of the platinum atoms for all of the structures were found in direct-methods *E* maps using the structure solution program in SHELXS-86.[12] The positions of the remaining non-hydrogen atoms were found using subsequent sets of least-squares refinement cycles followed by difference-Fourier syntheses using the program SHELXL-93.[12] In each model, except **3a**, hydrogen atoms were introduced in idealized positions for the calculation of structure factors.

For compound **3a**, the structure was initially solved in the centrosymmetric cubic space group $Im\bar{3}m$. The solution showed the structure to be disordered in two ways: the molecule resided on 4*mm* site symmetry, in which mirror planes contained the ligands. Because the orientation of the phenyl groups in the ligand does not allow for this, they were disordered on either side of the mirror plane. Additionally, peaks corresponding to a second ligand orientation came up at 45° relative to the first ligand set. It was found that moving to a noncentrosymmetric space group (*I*432) with the same systematic absences improved the refinement and removed the first disorder because the molecule resided on a 422-symmetry site. This however did not remove the second ligand orientation, and subsequently each orientation was refined at 50% occupancy. To keep the number of parameters low, only the Pt, N, and methine carbon atoms were refined anisotropically, and the phenyl groups were constrained to be perfect hexagons (C−C 1.395 Å). This gave a final agreement factor of R1 = 0.05. Other information pertinent to data collection and structure solution is given in Table 1. Selected bond distances and angles are

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Table 5. Selected Bond Lengths (Å) and Angles (deg) for **1a**

Pt(1)−Cl(1)	2.302(3)	Pt(2)−Cl(3)	2.297(3)
Pt(1)−Cl(2)	2.319(3)	Pt(2)−Cl(4)	2.289(3)
Pt(1)−N(1)	2.045(8)	Pt(2)−N(5)	2.014(8)
Pt(1)−N(3)	2.026(9)	Pt(2)−N(7)	2.033(8)
N(1)−Pt(1)−N(3)	171.5(3)	N(5)−Pt(2)−Cl(4)	90.1(2)
N(3)−Pt(1)−Cl(1)	90.4(3)	N(7)−Pt(2)−Cl(4)	89.7(3)
N(1)−Pt(1)−Cl(1)	88.7(2)	N(5)−Pt(2)−Cl(3)	89.4(2)
N(3)−Pt(1)−Cl(2)	90.2(3)	N(7)−Pt(2)−Cl(3)	91.0(2)
N(1)−Pt(1)−Cl(2)	91.2(2)	Cl(4)−Pt(2)−Cl(3)	177.2(1)
Cl(1)−Pt(1)−Cl(2)	176.8(1)	N(6)−C(3)−N(5)	122.9(9)
N(1)−C(1)−N(2)	123.0(9)	N(7)−C(4)−N(8)	126(1)
N(3)−C(2)−N(4)	125(1)	N(5)−Pt(2)−N(7)	172.5(3)

Table 6. Selected Bond Lengths (Å) and Angles (deg) for **2a** and **2b**·THF

	2a	**2b**·THF
Pt(1)−Pt(2)	2.9128(9)	2.9376(7)
Pt(1)−N(1)	2.028(4)	2.040(5)
Pt(1)−N(2)	2.043(4)	2.032(5)
Pt(1)−N(3)	2.043(4)	2.035(5)
Pt(1)−N(4)	2.060(4)	2.066(5)
Pt(2)−N(5)	2.037(4)	2.032(5)
Pt(2)−N(6)	2.012(4)	2.023(5)
Pt(2)−N(7)	2.038(4)	2.054(5)
Pt(2)−N(8)	2.039(4)	2.042(5)
N(1)−Pt(1)−N(2)	85.0(2)	86.8(2)
N(1)−Pt(1)−N(3)	104.8(2)	106.0(2)
N(2)−Pt(1)−N(3)	170.3(2)	167.1(2)
N(1)−Pt(1)−N(4)	168.2(2)	168.2(2)
N(2)−Pt(1)−N(4)	106.8(2)	104.3(2)
N(3)−Pt(1)−N(4)	63.5(2)	63.0(2)
N(6)−Pt(2)−N(5)	85.0(2)	86.3(2)
N(6)−Pt(2)−N(8)	104.9(2)	105.0(2)
N(5)−Pt(2)−N(8)	170.2(2)	168.6(2)
N(6)−Pt(2)−N(7)	168.6(2)	167.7(2)
N(5)−Pt(2)−N(7)	106.3(2)	104.7(2)
N(8)−Pt(2)−N(7)	63.8(2)	64.0(2)
N(1)−C(1)−N(5)	126.5(4)	125.5(6)
N(2)−C(3)−N(6)	125.9(4)	126.1(6)
N(3)−C(2)−N(4)	110.1(5)	109.7(6)
N(7)−C(4)−N(8)	109.5(5)	110.2(6)

Table 7. Selected Bond Lengths (Å) and Angles (deg) for **3a** and **4**[a]

	3a	**4**
Pt(1)−Pt(1)^{i}	2.649(2)	2.5304(6)
Pt(1)−N(1)	2.04(2)	2.039(6)
N(1)^{ii}−Pt(1)−N(1)	89.72(7)	89.81(6)
N(1)^{iii}−Pt(1)−N(1)	171.9(9)	174.1(2)
N(1)−C(1)−N(1)^{iv}	129(2)	126.4(8)

[a] Symmetry transformations used to generate equivalent atoms are as follows. **3a**: (i) $-z, -y + 1, -x$; (ii) $-z, y, x$; (iii) $-x, y, -z$; (iv) $z, -y + 1, x$. **4**: (i) $x, -y + {}^1/_2, -z + {}^1/_2$; (ii) $-y + {}^1/_2, x, z$; (iii) $-x + {}^1/_2, -y + {}^1/_2, z$; (iv) $-x + {}^1/_2, y, -z + {}^1/_2$.

given in Table 6 for compound **1a**, Table 7 for compounds **2a** and **2b**·THF, and Table 8 for compounds **3a** and **4**.

Results and Discussion

Table 8. Torsion Angles for Selected Ni, Pd, and Pt Amidine Compounds

compound	angle, deg	ref
$Ni_2(DTolF)_4$	16.8(3)	6
$Ni_2(DTolF)_4(BF_4)$	27.4(4)	6
$Pd_2(DTolF)_4\cdot H_2O$	15.1(6)	6
$Pd_2(DTolF)_4(PF_6)$	17(1)	6
$Pd_2(\mu\text{-DPhBz})_2(\eta^2\text{-DPhBz})_2$	19	7
$Pd_2(\mu\text{-DPhBz})_4$	14	7
$Pt_2(\mu\text{-DTolF})_2(\eta^2\text{-DTolF})_2\cdot THF$	23.9(2)	this work
$Pt_2(\mu\text{-DPhF})_2(\eta^2\text{-DPhF})_2$	9.3(2)	this work
$Pt_2(\mu\text{-DPhF})_4$	6.8(9)	this work
$Pt_2(\mu\text{-DTolF})_4(PF_6)$	11.6(9)	this work

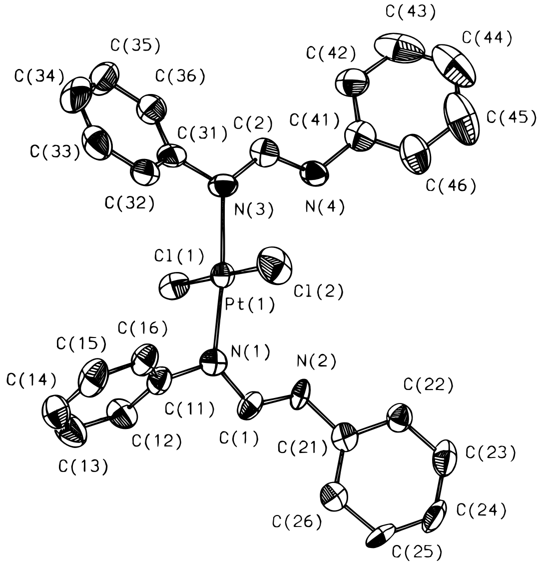

Figure 1. ORTEP diagram for one the two molecules found in the asymmetric unit in the structure of $PtCl_2(HDPhF)_2$.

In a previous paper,[13] we reported the syntheses of several M(II) chloride complexes with formamidine. Because of their solubility properties, they have been used as starting materials in the preparation of metal−metal-bonded compounds in nonaqueous solution. We now report that the reaction of K_2PtCl_4 with 2 equiv of the formamidine ligand produces the mononuclear square-planar compounds **1a** and **1b**. The structure of **1a,** shown in Figure 1, features two trans monodentate formamidine ligands bound to the Pt. These compounds are soluble in a number of organic solvents (toluene, dichloromethane, benzene, THF, and CH_3CN), and because they already contain the correct ratio of formamidine ligands to metal atoms, we considered them good starting materials for the formation of dinuclear compounds of the type $M_2(DArF)_4$. The neutral compounds **2a** and **2b**·THF were prepared by the reactions described in eq 1.

$$PtCl_2(HDArF)_2 + 2NaOMe + 2TlPF_6 \rightarrow Pt_2(\mu\text{-DArF})_2(\eta^2\text{-DArF})_2 + 2TlCl + 2MeOH + 2NaPF_6 \quad (1)$$

$$Ar = Ph\ (\mathbf{2a}),\ Tol\ (\mathbf{2b})$$

The deprotonation of the coordinated formamidine ligand was best accomplished with NaOMe. *n*-Butyllithium or other strong bases played noninnocent roles, with reduction to platinum metal usually being the end result. $TlPF_6$ was used as a chloride abstraction reagent; formation of the very insoluble TlCl served as a driving force for the reaction. The structure of **2a** is shown in Figure 2. It consists of two bridging DPhF ligands cis to each other and two DPhF ligands that are chelating different Pt atoms. The structure of **2b** contains a molecule of THF, but the main features are very similar to those in **2a**. The interligand repulsion between the two chelating DPhF ligands is presumably responsible for the long Pt−Pt separations of 2.913(1) and 2.938(1) Å in **2a** and **2b**·THF, respectively. An indication of the repulsion between the two chelating formamidines is given by the dihedral angle of the $Pt(N)_4$ planes. These angles are 23.3(2) and 30.1(1)° for **2a** and **2b**, respectively. They are

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[13] Cotton, F. A.; Daniels, L. M.; Maloney, D. J.; Matonic, J. H.; Murillo, C. A. *Polyhedron* **1994**, *13,* 815.

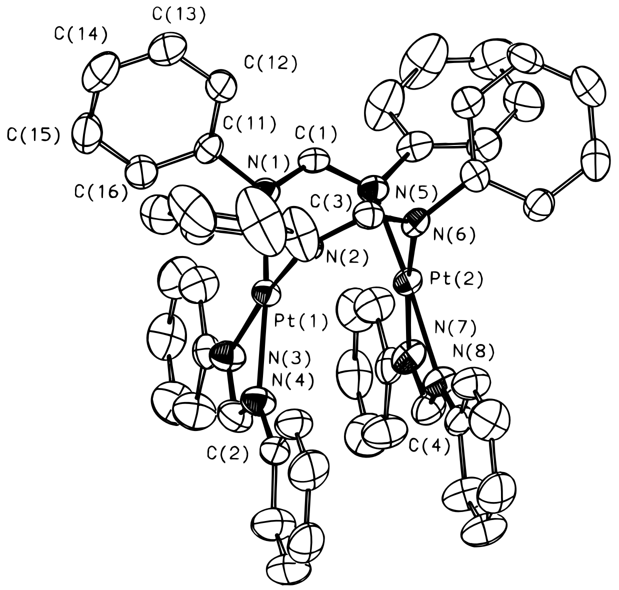

Figure 2. ORTEP drawing of $Pt_2(\mu\text{-}DPhF)_2(\eta^2\text{-}DPhF)_2$. Ellipsoids are drawn at the 40% probability level.

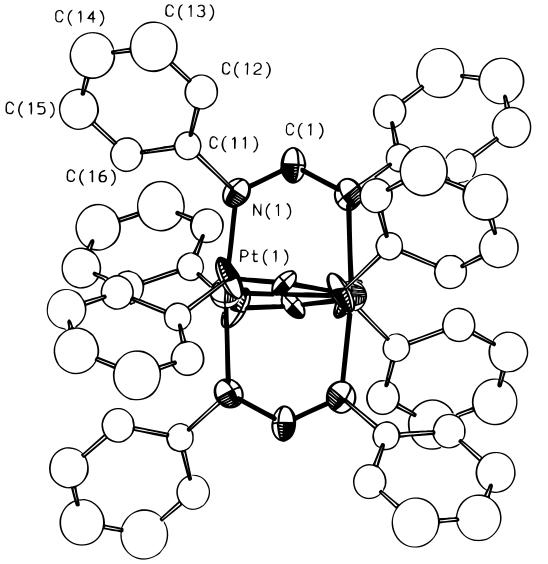

Figure 3. ORTEP drawing of $Pt_2(\mu\text{-}DPhF)_4$, showing one orientation of the ligand. Ellipsoids are drawn at the 40% level.

comparable to that in the $Pd_2(\mu\text{-}DPhBz)_2(\eta^2\text{-}DPhBz)_2$ compound (35°), which also has a similar metal−metal distance of 2.900(3) Å.[6] An interesting difference between the two compounds, **2a** and **2b**, namely, the torsion angles, is shown in Table 4; the twist is considerably less in **2a**, being 9° as compared to 23° in **2b**.

Compounds **2a** and **2b** are reaction intermediates; heating them in weakly coordinating solvents forms the more stable tetrabridged compounds **3a** and **3b**. The structure of **3a** is shown in Figure 3. This isomerization occurs to relieve strain in the four-membered chelate ring. These chelating ligands have N−Pt−N angles of 63.5(2) and 63.8(2)° for **2a** and 63.0(2) and 64.0(2)° for **2b**. Even though they are comparable to those in the very stable tris-chelates,[14] the effect of the nearby metal atom makes the isomerization to a bridging ligand more favorable. On going to the tetrabridged isomer, the metal−metal separation decreases from 2.910(1) Å in **2a** to 2.649(1) Å in **3a**. The distance is very similar to that in $Pd_2(DTolF)_4$, which is 2.622(3) Å. Compared to other $Pt^{II}-Pt^{II}$ distances, that in **3a** is the shortest yet reported. A similar distance was reported for $Pt_2(pyt)_4$, namely 2.680(2) Å;[15] the distance in **3a** is 0.26 Å shorter than that reported in $K_4[Pt_2(H_2P_2O_5)_4]\cdot 2H_2O$ (2.925(1) Å)[16] and 0.10 Å shorter than the Pt−Pt distance in $Pt_2(CH_3CS_2)_4$ (2.767(1)Å).[17]

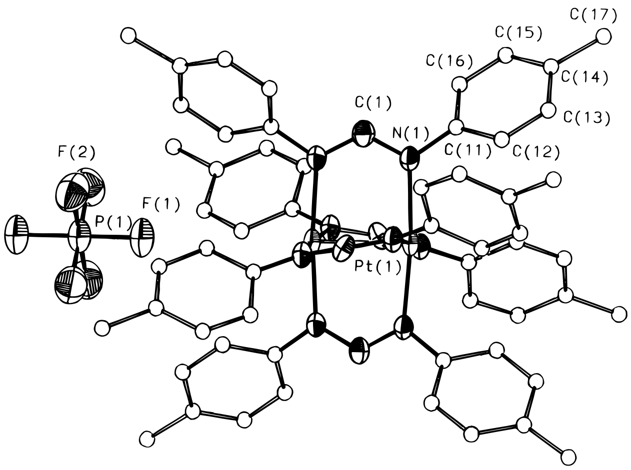

Figure 4. ORTEP diagram of $Pt_2(DTolF)_4(PF_6)$. The tolyl carbon atoms are shown with spheres of arbitrary size.

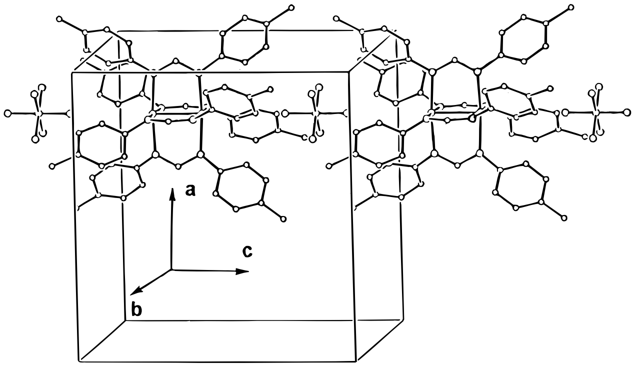

Figure 5. Packing of $Pt_2(DTolF)_4(PF_6)$ along the *c* axis.

A one-electron oxidation of either **2b** or **3b** produces the mixed-valence compound $Pt_2(DTolF)_4(PF_6)$, **4**, as shown in eq 2.

$$\begin{gathered}\mathrm{Pt_2(\mu\text{-}DTolF)_2(\eta^2\text{-}DTolF)_2}\ \text{or}\\ \mathrm{Pt_2(\mu\text{-}DTolF)_4} + \mathrm{AgPF_6} \rightarrow \mathrm{Pt_2(\mu\text{-}DTolF)_4(PF_6)} + \mathrm{Ag^0}\downarrow \quad (2)\end{gathered}$$

The structure of **4** is similar to those of the analogous Ni and Pd di-*p*-tolylformamidinato compounds. The Pt atoms, along with the P atom, lie on a 4-fold axis, forcing the alternation of anions and cations, as shown in Figure 5. The metal−metal distance decreases from 2.649(1) Å in the neutral complex **3a** to 2.5034(6) Å in **4**. This may be explained by the formation of a partial metal−metal bond on going from a $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}\sigma^{*2}$ (BO = 0) electronic configuration in **3a** to $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}\sigma^{*1}$ (BO = 0.5) in **4**. In the palladium system, no such decrease is seen, and in fact the metal−metal distance increases by 0.015(6) Å to 2.637(6) Å. This is consistent with a ligand-based

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(14) Cotton F. A.; Daniels, L. M.; Maloney, D. J. *Inorg. Chim. Acta*, in press.

(15) Umakoshi, K.; Kinoshita, I.; Ichimura, A.; Ooi, S. *Inorg. Chem.* **1987**, *26*, 3551.

(16) Filomena Dos Remedios Pinto, M. A.; Sadler, P. J.; Neidle, S.; Sanderson, M. R.; Subbiah, A.; Kuroda, R. *J. Chem Soc., Chem. Commun.* **1980**, 13.

(17) Bellitto, C.; Flamini, A.; Piovesana, O.; Zanazzi, P. F. *Inorg. Chem.* **1980**, *19*, 3632.

oxidation. In the nickel system, the metal−metal distance does in fact decrease on going from the neutral compound to the oxidized compound, but this may be partly due to a large increase in the torsion angle on going to the oxidized species.

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Supporting Information Available: Tables of crystallographic data, atomic positional and displacement parameters, complete bond distances and angles, anisotropic displacement parameters, and hydrogen positional and thermal parameters for **1a**, **2a**, **2b**·THF, **3a**, and **4** and labeled ORTEP diagrams for **1a** and **2b**·THF (50 pages). Ordering information is given on any current masthead page.

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