

# Mononuclear and Binuclear Palladium(II)/Rhenium(I) Complexes Containing a Sterically Hindered Trinucleating Ligand: 2,3,8,9,14,15-Hexamethyl-5,6,11,12,17,18-hexaazatrinaphthalene (hhtn)

Vincent J. Catalano,<sup>†</sup> Wayne E. Larson, Marilyn M. Olmstead,<sup>‡</sup> and Harry B. Gray<sup>\*</sup>

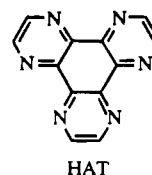
Beckman Institute, California Institute of Technology, Pasadena, California 91125

Received March 2, 1994<sup>⊗</sup>

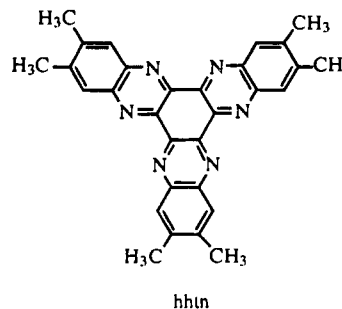
The trinucleating ligand 2,3,8,9,14,15-hexamethyl-5,6,11,12,17,18-hexaazatrinaphthalene (hhtn), **1**, has been obtained in an efficient one-pot synthesis. The reaction of a yellow-green solution of **1** with 1 equiv of Pd(NCPh)<sub>2</sub>Cl<sub>2</sub> gives orange PdCl<sub>2</sub>(hhtn), **2**, which crystallizes with two independent PdCl<sub>2</sub>(hhtn) molecules, a molecule of chlorobenzene, and two molecules of methanol in the triclinic space group *P* $\bar{1}$  with *a* = 12.949(3) Å, *b* = 16.625(4) Å, *c* = 17.062(4) Å,  $\alpha$  = 63.00(2)°,  $\beta$  = 71.39(2)°, and  $\gamma$  = 79.78(2)° at 130 K with *Z* = 4. Refinement of 5551 reflections and 387 parameters yielded *R* = 0.059 and *R*<sub>w</sub> = 0.060. The structure consists of a nearly square planar PdCl<sub>2</sub>(N<sub>2</sub>) complex in a highly-distorted hhtn framework. Unfavorable Cl<sup>−</sup>⋯H interactions force the PdCl<sub>2</sub> unit out of the hhtn plane by 28.1°. The structure indicates that there are  $\pi$ – $\pi$  (ligand–ligand) interactions. Reaction of **2** with another equivalent of Pd(NCPh)<sub>2</sub>Cl<sub>2</sub> produces the binuclear species (PdCl<sub>2</sub>)<sub>2</sub>(hhtn), **5**. Addition of Re(CO)<sub>5</sub>Cl to **1** in refluxing toluene affords deep red crystals of *fac*-Re(CO)<sub>3</sub>Cl(hhtn), **3**. Dark red needles of Re(CO)<sub>3</sub>Cl(hhtn)·CH<sub>3</sub>OH form in the monoclinic space group *P*2<sub>1</sub>/*n* with *a* = 10.515(2) Å, *b* = 27.123(6) Å, *c* = 11.385(2) Å, and  $\beta$  = 110.95(2)° at 130 K with *Z* = 4. Refinement of 5451 reflections and 415 parameters yielded *R* = 0.052 and *R*<sub>w</sub> = 0.052. The structure features a nearly octahedral Re center that is deflected from the hhtn plane by 19.5°. The hhtn in **3** is less distorted than in **2**. Reaction of a dichloromethane solution of **3** with 1 equiv of Pd(NCPh)<sub>2</sub>Cl<sub>2</sub> produces the heterobinuclear (Re(CO)<sub>3</sub>Cl)(PdCl<sub>2</sub>)(hhtn), **4**. Red-brown blocks of **4** cocrystallize with 2.6 molecules of 1,2-dichlorobenzene in the triclinic space group *P* $\bar{1}$  with *a* = 14.540(4) Å, *b* = 14.558(3) Å, *c* = 14.671(4) Å,  $\alpha$  = 64.72(2)°,  $\beta$  = 66.00(2)°, and  $\gamma$  = 63.30(2)° at 130 K with *Z* = 2. Refinement based on full-matrix least squares on *F*<sup>2</sup> using 8481 reflections and 513 parameters yielded *R* = 0.061 and *R*<sub>2</sub> = 0.135. The structure includes a nearly octahedral Re and a square planar Pd coordinated to a highly distorted hhtn ligand. The PdCl<sub>2</sub> fragment is bent out of the ligand plane by 40.2°, whereas the Re unit is distorted by only 10.4°. Complex **4** forms  $\pi$ – $\pi$  stacks exclusively with the 1,2-dichlorobenzene solvate molecules.

## Introduction

Over the last decade, several groups have employed the highly symmetric (*D*<sub>3h</sub>) 1,4,5,8,9,12-hexaazatriphenylene (HAT) ligand as a platform on which to build homo and heteronuclear polymetallic compounds.<sup>1–6</sup> To date, Cr(CO)<sub>4</sub>,<sup>1</sup> Mo(CO)<sub>4</sub>,<sup>1</sup> Re(CO)<sub>3</sub>Cl,<sup>2</sup> Ru(bipyridine)<sub>2</sub>,<sup>3</sup> Ru(HAT)<sub>2</sub>,<sup>4</sup> Ru(1,4,5,8-tetraaza-phenanthrene)<sub>2</sub>,<sup>4</sup> and Rh-<sup>3a</sup> and Ir(2-phenylpyridine)<sub>2</sub><sup>5</sup> fragments have been coordinated to HAT.



The HAT framework also has been used to construct even more elaborate molecular structures, including ones in which Cu<sup>+</sup> is employed as the template around which a multicomponent system containing hexaphenyl HAT assemblies itself.<sup>6</sup> Our work in this area has centered on a related trinucleating ligand, 2,3,8,9,14,15-hexamethyl-5,6,11,12,17,18-hexaazatrinaphthalene, hereafter referred to as hhtn. Hhtn has an advantage over



HAT in that it is the condensation product of two commercially available reagents, hexaketocyclohexane and 4,5-dimethyl-1,2-

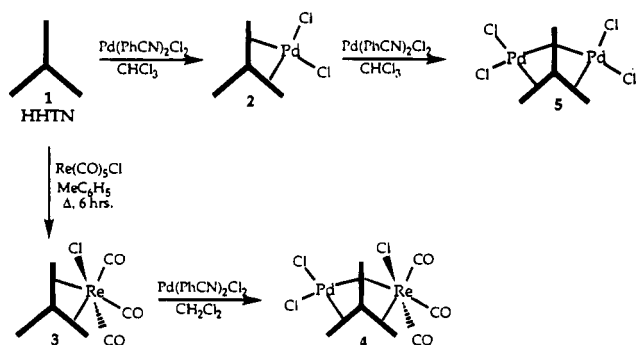
<sup>†</sup> Present address: Department of Chemistry, University of Nevada, Reno, NV 89557.

<sup>‡</sup> Present address: X-ray Crystallographic Structure Center, University of California, Davis, CA 95616.

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, August 15, 1994.

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## Scheme 1



phenylenediamine. While an improved synthetic scheme has made HAT more accessible, the multistep synthesis proceeds through an explosive intermediate, triaminotrinitrobenzene.<sup>7</sup> In view of the ease of preparation of hhtn, it is curious that no work exploring its use as a ligand has hitherto been reported. In this initial paper, we describe the synthesis and characterization of mononuclear and binuclear Pd(II)/Re(I) complexes containing hhtn.

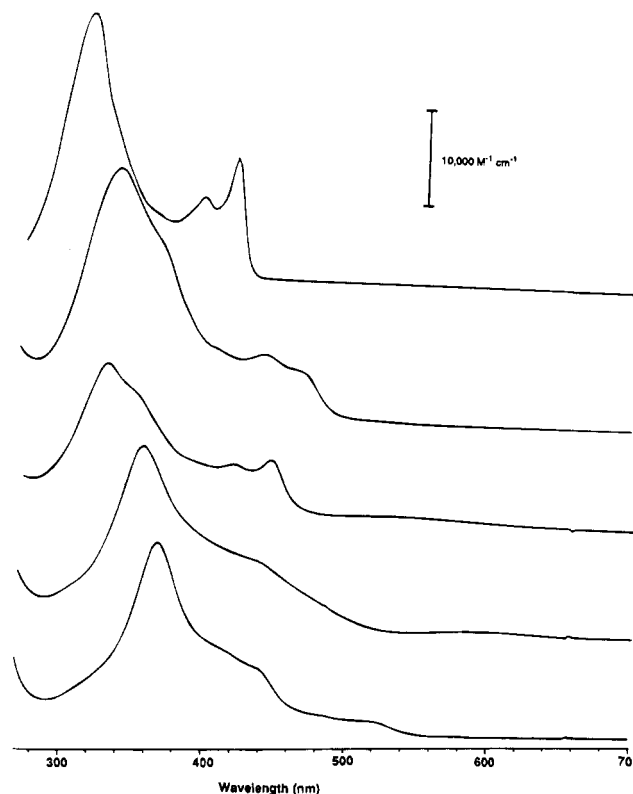
## Results

**Synthesis.** The green-yellow compound hhtn is synthesized in high yield by the condensation of hexaketocyclohexane with 4,5-dimethyl-1,2-phenylenediamine. Several reactions of this compound are shown in Scheme 1. When an orange chloroform solution of Pd(NCPh)<sub>2</sub>Cl<sub>2</sub> is added to the yellow-green chloroform solution of hhtn, a deep orange color appears, and orange microcrystals of PdCl<sub>2</sub>(hhtn), **2**, can be isolated by addition of diethyl ether. Compound **2** can further react with another equivalent of Pd(NCPh)<sub>2</sub>Cl<sub>2</sub> to produce the deep orange (PdCl<sub>2</sub>)<sub>2</sub>(hhtn), **5**. Addition of Re(CO)<sub>3</sub>Cl to **1** in refluxing toluene affords red-brown crystals of *fac*-Re(CO)<sub>3</sub>Cl(hhtn), **3**, after 6 h. The reaction of 1 equiv of Pd(NCPh)<sub>2</sub>Cl<sub>2</sub> with a dichloromethane solution of **3** produces (Re(CO)<sub>3</sub>Cl)(PdCl<sub>2</sub>)(hhtn), **4**, which can be isolated as a brown solid upon addition of diethyl ether.

Hhtn is very soluble in chloroform, moderately soluble in other chlorinated hydrocarbons, slightly soluble in toluene, benzene, and acetone, and insoluble in most alcohols and hydrocarbons. Compounds **2** and **3** are readily soluble in chlorinated hydrocarbons, slightly soluble in acetone, tetrahydrofuran, and acetonitrile, and insoluble in ether, while **4** is considerably less soluble in the aforementioned solvents. (PdCl<sub>2</sub>)<sub>2</sub>(hhtn), **5**, is much less soluble than the previous compounds, but readily dissolves in *N*-methylpyrrolidinone. The lack of solubility hindered the isolation and purification of any trinuclear complexes.

**Characterization.** The <sup>1</sup>H NMR spectrum of each compound displays the appropriate number of signals, all of which are singlets with the proper integration (Experimental Section). All hhtn resonances shift downfield upon metal coordination. Compounds **2**, **3**, and **5** show the expected 3 signals for the methyl groups as well as three signals for the aromatic protons in a 3:1 ratio. The spectrum of **4** shows six independent signals for the methyl protons along with six signals for the aromatic protons.

The infrared spectra of compounds **3** and **4** show similar absorptions attributable to CO stretching for the three CO ligands (**3**, 1915, 1977, 2030 cm<sup>-1</sup>; **4**, 1910, 1980, 2020 cm<sup>-1</sup>). It is



**Figure 1.** Electronic absorption spectra of **1** (top) to **5** (bottom) in CHCl<sub>3</sub> solution [wavelength, nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): **1**, 312 (91 000), 332 (44 000), 394 (29 000), 416 (51 000); **2**, 338 (74 000), 336 (54 000), 440 (20 000), 466 (15 000); **3**, 328 (46 000), 346 (37 000), 416 (17 500), 444 (19 000); **4**, 358 (59 000), 438 (24 000), 570 (2800); **5**, 370 (57 000), 412 (27 500), 440 (21 000), 520 (5600).

evident that the presence of the PdCl<sub>2</sub> unit does not significantly perturb the electronic structure of the Re center.

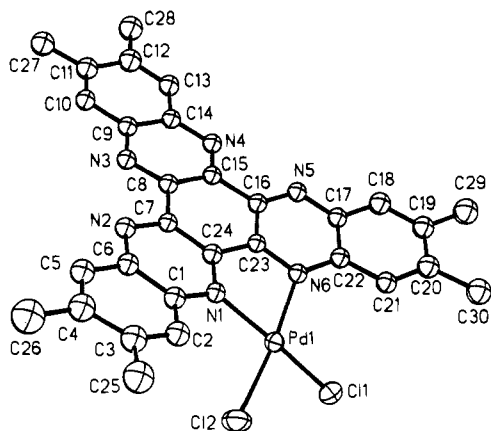
The electronic absorption spectra of chloroform solutions of **1**–**5** are shown in Figure 1. The hhtn spectrum is dominated by intense  $\pi$ – $\pi^*$  absorptions between 300 and 420 nm; these features broaden and red shift in complexes **2**–**5**. In **3** the red shift is not quite as pronounced as in **2**, and the spectrum resembles that of the free ligand more closely. Spectral features become poorly resolved upon coordination of a second metal center.

A chloroform solution of **1** displays a single emission centered at 455 nm (366 nm excitation) at room temperature. The same spectrum is seen for a 77 K frozen solution of **1**. Emission spectra of metal complexes were obtained with 436 nm excitation. A dichloromethane solution of Re(CO)<sub>3</sub>Cl(hhtn) displays emissions at 580 and 710 nm. PdCl<sub>2</sub>(hhtn) shows only one emission band at 620 nm, nearly identical with the 620 nm emission of **5**. At low temperature the heterobinuclear complex, **4**, shows a very broad, asymmetric emission band at 660 nm.

A dichloromethane solution of the hhtn ligand exhibits a reversible reduction at –1.09 V, a quasi-reversible reduction at –1.40 V, and an irreversible oxidation at 1.52 V vs. Ag/AgCl at room temperature. In **3**, the two ligand reductions shift to less negative values (–0.48 and –0.75 V), and four new irreversible reduction waves are observed out to the solvent limit. An irreversible oxidation is also observed toward the positive solvent limit. All the palladium-containing compounds (**2**, **4**, **5**) decompose upon oxidation or reduction as evidenced by their irreversible electrochemistry; reliable cyclic voltammetric data were not obtained.

**Structure of {PdCl<sub>2</sub>(hhtn)}<sub>2</sub>·C<sub>6</sub>H<sub>5</sub>Cl·2CH<sub>3</sub>OH, **2**.** The asymmetric unit consists of two molecules of this complex, one

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**Figure 2.** Perspective view of the Pd(1)-containing species of  $2\text{PdCl}_2(\text{hhtn})\cdot\text{C}_6\text{H}_5\text{Cl}\cdot 2\text{CH}_3\text{OH}$ , **2**, with 50% thermal contours.

**Table 1.** Crystallographic Data<sup>a</sup>

2, $\{\text{PdCl}_2(\text{hhtn})\}_2\cdot\text{C}_6\text{H}_5\text{Cl}\cdot 2\text{CH}_3\text{OH}$	
$\text{C}_{34}\text{H}_{30.5}\text{Cl}_{2.5}\text{N}_6\text{OPd}$	fw = 734.1
$a = 12.949(3) \text{ \AA}$	$P\bar{1}$ , triclinic
$b = 16.625(4) \text{ \AA}$	$T = 130 \text{ K}$
$c = 17.062(4) \text{ \AA}$	$\lambda(\text{Mo K}\alpha) = 0.710 73 \text{ \AA}$
$\alpha = 63.00(2)^\circ$	$\mu(\text{Mo K}\alpha) = 0.85 \text{ mm}^{-1}$
$\beta = 71.39(2)^\circ$	$d_{\text{calc}} = 1.57 \text{ Mg/cm}^3$
$\gamma = 79.78(2)^\circ$	transm factors = 0.86–0.90
$V = 3099(2) \text{ \AA}^3$	
$Z = 4$	
$R = 0.059$	
$R_w = 0.060$	

3, $\text{Re}(\text{CO})_3\text{Cl}(\text{hhtn})\cdot\text{CH}_3\text{OH}$	
$\text{C}_{34}\text{H}_{28}\text{ClN}_6\text{O}_4\text{Re}$	fw = 806.3
$a = 10.515(2) \text{ \AA}$	$P2_1/n$ , monoclinic
$b = 27.123(6) \text{ \AA}$	$T = 130 \text{ K}$
$c = 11.385(4) \text{ \AA}$	$\lambda(\text{Mo K}\alpha) = 0.710 73 \text{ \AA}$
$\beta = 110.95(2)^\circ$	$\mu(\text{Mo K}\alpha) = 4.146 \text{ mm}^{-1}$
$V = 3033(2) \text{ \AA}^3$	$d_{\text{calc}} = 1.78 \text{ Mg/m}^3$
$Z = 4$	transm factors = 0.47–0.75
$R = 0.052$	
$R_w = 0.052$	

4, $(\text{PdCl}_2)(\text{Re}(\text{CO})_3\text{Cl})(\text{hhtn})\cdot 2.6\text{Cl}_2\text{C}_6\text{H}_4$	
$\text{C}_{48.6}\text{H}_{50.4}\text{Cl}_{8.2}\text{N}_6\text{O}_3\text{PdRe}$	fw = 1349.84
$a = 14.540(4) \text{ \AA}$	$P\bar{1}$ , triclinic
$b = 14.558(3) \text{ \AA}$	$T = 130 \text{ K}$
$c = 14.671(4) \text{ \AA}$	$\lambda(\text{Mo K}\alpha) = 0.710 73 \text{ \AA}$
$\alpha = 64.72(2)^\circ$	$\mu(\text{Mo K}\alpha) = 3.376 \text{ mm}^{-1}$
$\beta = 66.00(2)^\circ$	$d_{\text{calc}} = 1.854 \text{ Mg/m}^3$
$\gamma = 63.30(2)^\circ$	transm factors = 0.66–0.89
$V = 2418.3 \text{ \AA}^3$	$R = 0.061$
$Z = 2$	$R_2 = 0.135$

<sup>a</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ .  $R_w = \sum |F_o| - |F_c| |w|^{1/2} / \sum |F_o| |w|^{1/2}$ .  $R_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ .

molecule of chlorobenzene, and two molecules of methanol. A view of the molecule containing Pd(1) is shown in Figure 2, while a complete picture along with atomic coordinates, distances, and angles for the molecule containing Pd(2) are included as supplementary material. Selected atomic coordinates for the Pd(1)-containing species are given in Table 2, and selected atomic distances and angles are given in Table 3.

The complex crystallizes with two crystallographically independent but strongly interacting  $\text{PdCl}_2(\text{hhtn})$  molecules. This intimate association can be seen in Figure 3. The coordination environment around the two metal centers is slightly different; the Pd–Cl distances between the two complexes are uniform and within normal ranges while the Pd–N separations are slightly perturbed ( $\text{Pd}(1)\text{--N}(1) = 2.057(6) \text{ \AA}$  and  $\text{Pd}(1)\text{--N}(6) = 2.059(9) \text{ \AA}$  vs  $\text{Pd}(2)\text{--N}(7) = 2.063(7) \text{ \AA}$  and  $\text{Pd}(2)\text{--N}(12) = 2.038(8) \text{ \AA}$ , and there is a slight cant in the coordination plane

**Table 2.** Atomic Coordinates ( $\times 10^4$ ) and Equivalent Displacement Coefficients ( $\text{\AA}^2 \times 10^3$ ) for  $\{\text{PdCl}_2(\text{hhtn})\}_2\cdot\text{C}_6\text{H}_5\text{Cl}\cdot 2\text{CH}_3\text{OH}$ , **2**

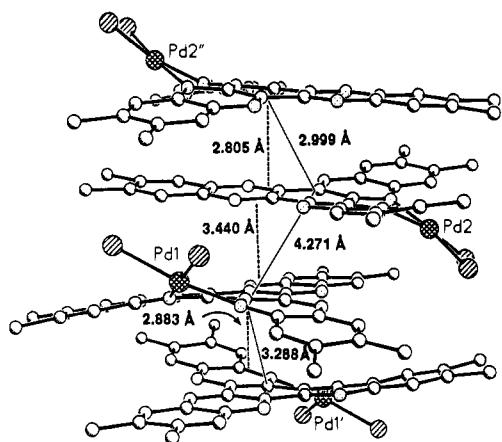
	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Pd(1)	4529(1)	6907(1)	1847(1)	28(1) <sup>a</sup>
Cl(1)	3944(2)	8357(2)	1084(2)	43(1) <sup>a</sup>
Cl(2)	4330(3)	6610(2)	727(2)	51(1) <sup>a</sup>
N(1)	4788(6)	5577(5)	2694(5)	25(2)
N(2)	4324(6)	3855(5)	4178(5)	29(2)
N(3)	3370(6)	3752(5)	5899(5)	27(2)
N(4)	3130(6)	5309(5)	6225(5)	28(2)
N(5)	3878(6)	6931(5)	4782(5)	28(2)
N(6)	4534(6)	7059(5)	2978(5)	26(2)
C(1)	5087(8)	4813(6)	2551(6)	30(2)
C(2)	5716(8)	4844(7)	1702(6)	35(2)
C(3)	6030(9)	4075(7)	1580(7)	41(2)
C(4)	5658(9)	3210(7)	2317(7)	43(3)
C(5)	5080(8)	3178(7)	3149(7)	37(2)
C(6)	4819(8)	3950(6)	3319(6)	30(2)
C(7)	4127(7)	4614(6)	4299(6)	25(2)
C(8)	3663(7)	4552(6)	5232(6)	27(2)
C(9)	2942(7)	3695(6)	6755(6)	29(2)
C(10)	2608(7)	2857(6)	7491(6)	31(2)
C(11)	2180(8)	2786(7)	8355(7)	38(2)
C(12)	2090(9)	3567(7)	8538(7)	43(3)
C(13)	2372(8)	4384(6)	7832(6)	34(2)
C(14)	2823(7)	4494(6)	6915(6)	28(2)
C(15)	3546(7)	5345(6)	5396(6)	26(2)
C(16)	3888(7)	6223(6)	4623(6)	27(2)
C(17)	4258(7)	7697(6)	4046(6)	28(2)
C(18)	4334(8)	8456(6)	4200(7)	37(2)
C(19)	4750(8)	9449(7)	3476(7)	37(2)
C(20)	5149(8)	9313(7)	2563(7)	38(2)
C(21)	5047(8)	8590(6)	2408(6)	31(2)
C(22)	4602(7)	7778(6)	3141(6)	28(2)
C(23)	4246(7)	6269(5)	3722(5)	23(2)
C(24)	4356(7)	5477(6)	3561(6)	28(2)
C(25)	6800(9)	4104(7)	687(7)	51(3)
C(26)	5946(10)	2365(8)	2155(8)	63(3)
C(27)	1794(9)	1893(7)	9126(7)	47(3)
C(28)	1619(9)	3489(7)	9495(7)	50(3)
C(29)	4827(9)	10037(7)	3661(7)	51(3)
C(30)	5653(9)	10172(7)	1793(7)	46(3)

<sup>a</sup> Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

**Table 3.** Selected Bond Lengths ( $\text{\AA}$ ) and Angles (deg) for  $\{\text{PdCl}_2(\text{hhtn})\}_2\cdot\text{C}_6\text{H}_5\text{Cl}\cdot 2\text{CH}_3\text{OH}$ , **2**

Bond Lengths			
Pd(1)–Cl(1)	2.283(2)	Pd(1)–Cl(2)	2.277(4)
Pd(1)–N(1)	2.057(6)	Pd(1)–N(6)	2.059(9)
N(1)–C(1)	1.369(14)	N(1)–C(24)	1.345(12)
N(6)–C(22)	1.367(15)	N(6)–C(23)	1.353(9)
Bond Angles			
Cl(1)–Pd(1)–Cl(2)	87.6(1)	Cl(1)–Pd(1)–N(1)	169.9(2)
Cl(2)–Pd(1)–N(1)	95.1(3)	Cl(1)–Pd(1)–N(6)	95.5(2)
Cl(2)–Pd(1)–N(6)	172.1(2)	N(1)–Pd(1)–N(6)	80.7(3)
Pd(1)–N(1)–C(24)	117.8(7)	Pd(1)–N(6)–C(23)	108.1(7)
N(1)–C(24)–C(23)	117.3(7)	N(6)–C(23)–C(24)	116.8(8)

of Pd(2). The geometry around the Pd center is nearly square planar with the sum of the angles around Pd(1) approaching  $359^\circ$ . There is a contraction of the N(1)–Pd(1)–N(6) angle to  $80.7(3)^\circ$ , owing to the rigid bite of the hhtn ligand. Expansions of the N(1)–Pd(1)–Cl(2) and N(6)–Pd(1)–Cl(1) angles to  $95.1(3)$  and  $95.5(2)^\circ$  are observed. The deflection of  $\text{PdCl}_2$  unit from the hhtn ligand plane, measured as the dihedral angle between the normals of the two planes, is  $28.1^\circ$ . As shown in Figure 4, Pd(1) is  $1.31 \text{ \AA}$  below the calculated ligand plane. The two Cl atoms are in close contact with the hydrogen atoms on C(2) and C(21) ( $2.66 \text{ \AA}$ , Cl(1)··H(2A);  $2.62 \text{ \AA}$ , Cl(2)··H(21A)).



**Figure 3.** View emphasizing the intermolecular interactions between the  $\text{PdCl}_2(\text{hhtn})$  units of **2**. The solid line represents the distance between the centroids of the hhtn molecule, while the dashed line shows the perpendicular separation between the least-squares planes of the hhtn ligands. The  $\text{Pd}(1)'$  molecule is generated by  $1 - x, 1 - y, 1 - z$ , and  $\text{Pd}(2)'$  is generated by  $-x, 1 - y, 1 - z$ .

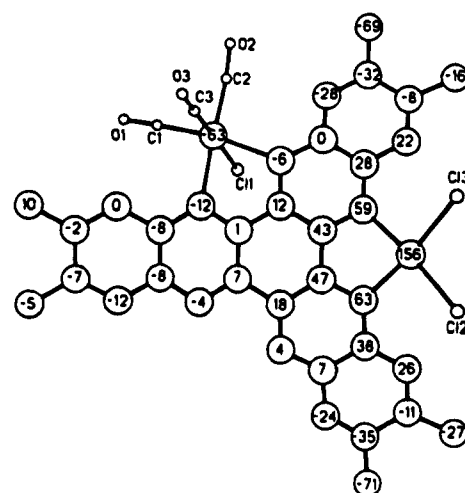
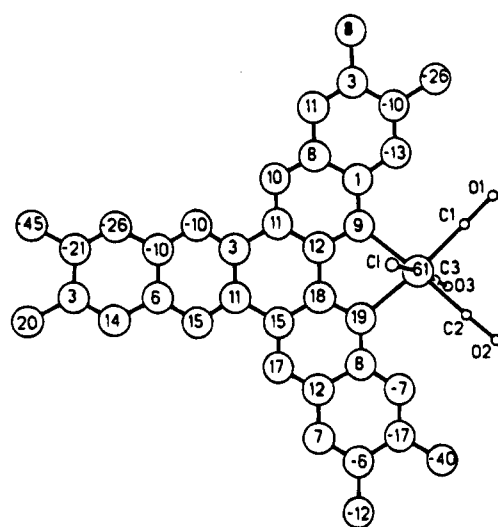
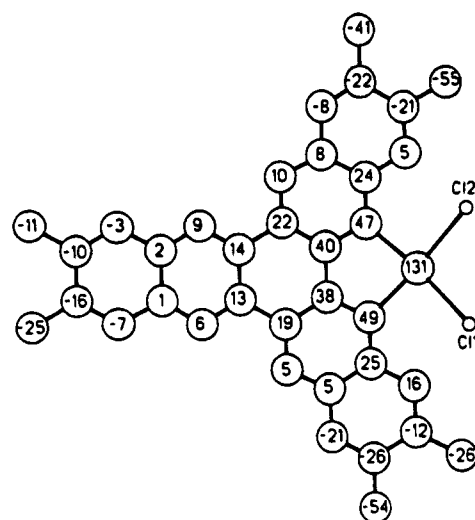
The 24 aromatic C—C distances from the  $\text{Pd}(1)$ -containing molecule range from 1.355(15) to 1.474(10) Å (average value of 1.415 Å), while the 12 C—N distances are somewhat shorter and more uniform, ranging from 1.319(9) to 1.369(14) Å (average value of 1.344 Å). The Pd—Cl distances are within normal ranges.

$\pi$ - $\pi$  interactions take place only between molecules of **2**. The complexes adopt a staggered configuration, with the  $\text{PdCl}_2$  portions directed approximately  $180^\circ$  apart from each other. The molecules (Figure 3) adopt an alternating convex—concave (CV—CC), concave—convex (CC—CV) relationship. The ligands in the CC—CV relationship are staggered, and in the CV—CC arrangement they are eclipsed and offset from each other. The perpendicular separation between the least-squares-calculated planes is 3.44 Å in the CC—CV arrangement; interestingly, this separation is only ca. 2.88 Å in the CV—CC geometry. This shorter distance reflects the fact that few atoms actually lie on the least-squares plane. The 3.44 Å separation is in the normal range for  $\pi$ - $\pi$  (ligand—ligand) interactions.<sup>8</sup>

**Structure of  $\text{Re}(\text{CO})_3\text{Cl}(\text{hhtn})\cdot\text{CH}_3\text{OH}$ , **3**.** The asymmetric unit contains one crystallographically independent molecule of this complex and one methanol solvate. A view of the complex is shown in Figure 5. Selected atomic coordinates are given in Table 4, and selected atomic distances and angles are given in Table 5.

The coordination environment around the Re center is roughly octahedral. The Re—C and Re—Cl separations are normal. The Re—N(1) and Re—N(6) distances of 2.222(6) and 2.203(6) Å are within observed ranges. The N(1)—Re—N(6) angle is contracted to  $75.5^\circ$  as a result of the constrained bite of the hhtn ligand. The C—C and C—N separations are very similar to **2** with the 24 aromatic C—C distances ranging from 1.361(11) to 1.478(10) Å (average value of 1.416 Å). The 12 C—N separations range from 1.315(10) to 1.379(11) Å (average value of 1.345 Å).

The complex crystallizes in an intimate  $\pi$ - $\pi$  association with a second symmetry-related molecule of the complex. This arrangement is best described as an offset head-to-tail geometry with the mean separation between the planes calculated for the hhtn ligands being 2.94 Å. The hhtn ligand in **3** is slightly twisted with an average distortion from planarity of 0.13 Å.

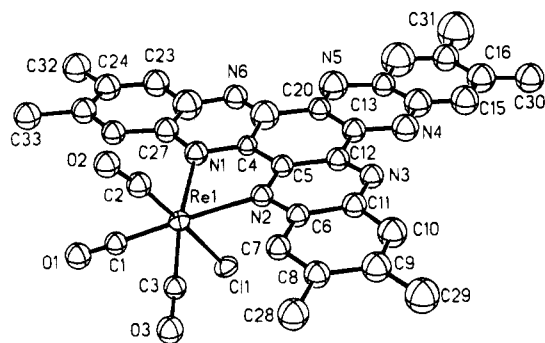


**Figure 4.** Drawing showing the displacements (0.01 Å) from the least-squares plane calculated for the hhtn ligand of **2** (top), **3** (middle), and **4** (bottom).

The Re atom sits 0.61 Å beneath the plane as a result of the sterically hindered coordination pocket. The  $\text{C}(1)\cdots\text{H}(6\text{A})$  and  $\text{C}(2)\cdots\text{H}(25\text{A})$  interactions (2.38 and 2.43 Å) probably account for the  $19.5^\circ$  angle between the hhtn ligand and the Re equatorial coordination plane.

**Structure of  $(\text{Re}(\text{CO})_3\text{Cl})(\text{PdCl}_2)(\text{hhtn})\cdot 2.6(1,2\text{-Cl}_2\text{C}_6\text{H}_4)$ , **4**.** The asymmetric unit consists of the heterobinuclear complex

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**Figure 5.** Perspective view of  $\text{Re}(\text{CO})_3\text{Cl}(\text{hhtn})$ , **3**, with 50% thermal contours.

**Table 4.** Atomic Coordinates ( $\times 10^4$ ) and Equivalent Displacement Coefficients ( $\text{\AA}^2 \times 10^3$ ) for  $\text{Re}(\text{CO})_3\text{Cl}(\text{hhtn})\cdot\text{CH}_3\text{OH}$ , **3**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) <sup>a</sup>
Re	489(1)	1041(1)	1531(1)	17(1)
Cl	2622(2)	1409(1)	1543(2)	30(1)
O(1)	534(6)	375(2)	-633(5)	29(2)
O(2)	2123(6)	203(2)	3186(5)	32(2)
O(3)	-2020(7)	561(2)	1748(6)	37(3)
N(1)	-393(6)	1716(2)	440(6)	17(2)
N(2)	-772(7)	2675(2)	-606(6)	19(2)
N(3)	-442(6)	3477(2)	908(6)	18(2)
N(4)	723(7)	3356(2)	3571(6)	18(2)
N(5)	1107(7)	2431(2)	4555(6)	20(2)
N(6)	581(6)	1597(2)	2970(6)	19(2)
C(1)	468(8)	624(3)	169(7)	18(2)
C(2)	1502(8)	517(3)	2587(7)	22(3)
C(3)	-1182(9)	756(3)	1649(7)	21(3)
C(4)	-124(8)	2125(3)	1154(7)	18(3)
C(5)	-919(7)	1782(3)	-837(7)	16(2)
C(10)	-1042(8)	2270(3)	-1342(7)	19(3)
C(11)	-332(8)	2600(3)	623(7)	19(3)
C(12)	127(8)	3038(3)	1441(7)	19(3)
C(13)	-174(8)	3867(3)	1693(7)	17(3)
C(18)	441(8)	3815(3)	3015(7)	20(3)
C(19)	418(8)	2975(3)	2772(7)	16(2)
C(21)	1234(8)	1973(3)	5038(7)	18(2)
C(26)	923(8)	1543(3)	4229(7)	18(3)
C(27)	403(7)	2061(6)	2514(7)	15(2)

<sup>a</sup> Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

and a group equivalent to 2.6 disordered 1,2-dichlorobenzene molecules. A view of this complex is shown in Figure 6, and selected atomic coordinates are given in Table 6. Selected atomic distances and angles are set out in Table 7. The solvent molecules are  $\pi$ -stacked with the binuclear complex at an average separation of 3.34  $\text{\AA}$ .

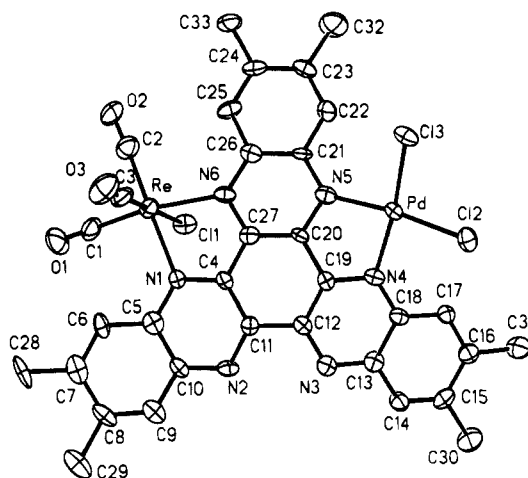
The coordination environments around both metals are similar to those of the respective mononuclear complexes. The Pd—N distances are identical at 2.052(10)  $\text{\AA}$  and the Pd—Cl(2) and Pd—Cl(3) distances are nearly equal at 2.277(3) and 2.276(3)  $\text{\AA}$ . The sum of the angles around the Pd metal totals 358.9°. The PdCl<sub>2</sub> unit is bent (40.2°) out of the hhtn plane and directed to the face opposite Re—Cl. The Re center is more closely coplanar to the hhtn ligand, with the dihedral angle of the normals equaling 10.4°. The Re—N separations (Re—N(1), 2.191(9)  $\text{\AA}$ ; Re—N(6), 2.225(10)  $\text{\AA}$ ) are nearly identical with those seen in **3**. The Re—Cl and Re—C distances in **3** and **4** are also very similar. The N(1)—Re—N(6) with N(4)—Pd—N(5) angles of 75.6(3) and 79.9(4)°, respectively, are consistent with corresponding values for the mononuclear complexes.

The 24 aromatic C—C bond distances in **4** are similar to those of **2** and **3**. They range from 1.36(2) to 1.45(2)  $\text{\AA}$  (average

**Table 5.** Selected Bond Lengths ( $\text{\AA}$ ) and Angles (deg) for  $\text{Re}(\text{CO})_3\text{Cl}(\text{hhtn})\cdot\text{CH}_3\text{OH}$ , **3**

Bond Lengths			
Re—Cl	2.241(2)	Re—C(1)	1.913(8)
Re—C(2)	1.918(7)	Re—C(3)	1.967(9)
Re—N(1)	2.222(6)	Re—N(6)	2.203(6)
C(1)—O(1)	1.158(10)	C(2)—O(2)	1.141(9)
C(3)—O(3)	1.069(12)	N(1)—C(4)	1.344(9)
N(1)—C(5)	1.370(9)	N(2)—C(10)	1.3504(9)
N(2)—C(11)	1.323(9)	N(3)—C(12)	1.324(9)
N(3)—C(13)	1.348(9)	N(4)—C(18)	1.379(9)
N(4)—C(19)	1.338(9)	N(5)—C(20)	1.315(10)
N(5)—C(21)	1.347(9)	N(6)—C(26)	1.356(10)
N(6)—C(27)	1.348(9)	C(4)—C(11)	1.406(10)
C(4)—C(27)	1.457(10)	C(5)—C(10)	1.430(10)
C(11)—C(12)	1.477(10)	C(12)—C(19)	1.426(10)
C(13)—C(18)	1.417(11)	C(19)—C(20)	1.478(10)
C(20)—C(27)	1.417(10)	C(21)—C(26)	1.448(10)

Bond Angles			
Cl—Re—N(1)	82.2(2)	Cl—ReN(6)	85.4(2)
Cl—Re—C(1)	89.5(3)	Cl—Re—C(2)	89.8(3)
N(1)—Re—N(6)	75.5(2)	N(1)—Re—C(1)	98.8(3)
N(6)—Re—C(2)	100.0(3)	C(1)—Re—C(2)	85.1(3)
N(1)—C(4)—C(27)	117.5(6)	N(6)—C(27)—C(4)	118.0(6)



**Figure 6.** Perspective view of  $(\text{PdCl}_2)(\text{Re}(\text{CO})_3\text{Cl})(\text{hhtn})$ , **4**, with 50% thermal contours.

value of 1.42  $\text{\AA}$ ), while the 12 C—N distances range between 1.319(9) to 1.38(2)  $\text{\AA}$  (average value of 1.345  $\text{\AA}$ ).

The intermolecular interactions of  $(\text{Re}(\text{CO})_3\text{Cl})(\text{PdCl}_2)(\text{hhtn})$  including the long-range Pd—Pd' contact of 3.809  $\text{\AA}$  are shown in Figure 7. The hhtn ligand is considerably more distorted in **4** than in either of the mononuclear complexes. The average out-of-plane deviation for the hhtn ligand is 0.38  $\text{\AA}$ . As shown in Figure 4, the Pd atom is a full 1.56  $\text{\AA}$  above the least-squares plane, while the Re center is displaced by 0.63  $\text{\AA}$  in the opposite direction. The <sup>1</sup>H contacts in **4** are similar to those in the mononuclear complexes, with C(1)···H(5) and C(2)···H(25) measuring 2.37 and 2.30  $\text{\AA}$ , while the Cl(2)···H(17) and Cl(3)···H(22) separations are 2.69 and 2.68  $\text{\AA}$ , respectively.

## Discussion

The syntheses of the complexes described here are straightforward; the high-yield, one-pot synthesis of the hhtn ligand is particularly appealing. Hhtn is capable of binding up to three metal atoms in its sterically hindered, dibenzophenanthroline-like coordination pocket. However, we have not been able to characterize any of the trinuclear complexes, owing to their extremely low solubility.

The properties of the complexes in solution are consistent with their solid-state structures. Metal coordination systemati-

**Table 6.** Atomic Coordinates ( $\times 10^4$ ) and Equivalent Displacement Coefficients ( $\text{\AA}^2 \times 10^3$ ) for  $(\text{PdCl}_2)(\text{Re}(\text{CO})_3\text{Cl})(\text{hhtn})\cdot 2.6\text{Cl}_2\text{C}_6\text{H}_4$ , **4**

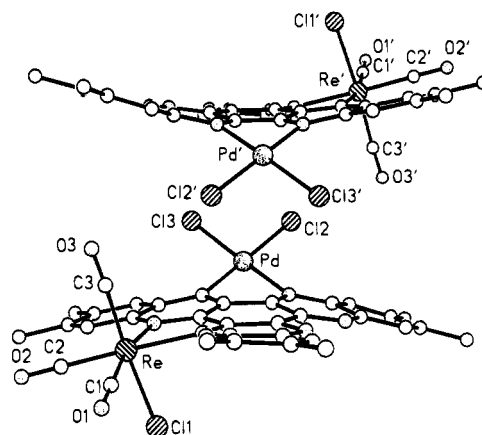
	x	y	z	$U(\text{eq})^a$
Re	1540(1)	1955(1)	3316(1)	30(1)
Pd	3695(1)	6108(1)	348(1)	23(1)
Cl(1)	-86(3)	3381(3)	2866(3)	39(1)
Cl(2)	4835(2)	6929(2)	-1000(2)	34(1)
Cl(3)	4494(2)	6016(2)	1449(2)	34(1)
O(1)	494(10)	289(9)	3906(9)	68(4)
O(2)	617(9)	1702(8)	5662(7)	57(3)
O(3)	3641(9)	253(9)	3758(8)	62(3)
N(1)	2164(7)	2155(7)	1634(7)	23(2)
N(2)	2527(7)	2912(8)	-574(7)	25(2)
N(3)	2751(8)	4925(8)	-1644(8)	30(2)
N(4)	3084(7)	5929(7)	-581(7)	22(2)
N(5)	2781(7)	5183(8)	1463(7)	28(2)
N(6)	2093(7)	3365(8)	2655(7)	26(2)
C(1)	899(12)	912(12)	3684(10)	46(4)
C(2)	965(12)	1844(11)	4778(11)	46(4)
C(3)	2889(12)	884(10)	3573(9)	41(3)
C(4)	2352(8)	3079(8)	1065(8)	21(2)
C(5)	2255(8)	1530(9)	1087(10)	28(3)
C(10)	2407(9)	1932(9)	-10(9)	25(2)
C(11)	2549(9)	3449(9)	-52(9)	24(2)
C(12)	2730(9)	4491(9)	-645(9)	24(2)
C(13)	2851(9)	5915(9)	-2116(9)	29(3)
C(18)	3027(9)	6436(9)	-1584(9)	25(2)
C(19)	2884(8)	4986(8)	-101(9)	21(2)
C(21)	2400(9)	4944(9)	2511(8)	25(3)
C(26)	2088(10)	4008(9)	3124(10)	30(3)
C(27)	2376(9)	3683(9)	1609(9)	25(3)

<sup>a</sup> Equivalent isotropic  $U$  defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

**Table 7.** Selected Bond Lengths ( $\text{\AA}$ ) and Angles (deg) for  $(\text{PdCl}_2)(\text{Re}(\text{CO})_3\text{Cl})(\text{hhtn})\cdot 2.6\text{Cl}_2\text{C}_6\text{H}_4$ , **4**

Bond Lengths			
Re—Cl(1)	2.455(3)	Re—N(1)	2.191(9)
Re—N(6)	2.225(10)	Re—C(1)	1.906(14)
Re—C(2)	1.921(14)	Re—C(3)	1.94(2)
Pd—Cl(2)	2.277(3)	Pd—Cl(3)	2.276(3)
Pd—N(4)	2.052(9)	Pd—N(5)	2.052(10)
C(1)—O(1)	1.16(2)	C(2)—O(2)	1.15(2)
C(3)—O(3)	1.11(2)	N(1)—C(4)	1.328(13)
N(1)—C(5)	1.38(2)	N(2)—C(10)	1.360(14)
N(2)—C(11)	1.323(14)	N(3)—C(12)	1.319(14)
N(3)—C(13)	1.353(14)	N(4)—C(18)	1.354(14)
N(4)—C(19)	1.353(13)	N(5)—C(20)	1.326(14)
N(5)—C(21)	1.347(14)	N(6)—C(26)	1.37(2)
N(6)—C(27)	1.338(14)	C(4)—C(11)	1.44(2)
C(4)—C(27)	1.44(2)	C(5)—C(10)	1.42(2)
C(11)—C(12)	1.47(2)	C(12)—C(19)	1.41(2)
C(13)—C(18)	1.45(2)	C(19)—C(20)	1.44(2)
C(20)—C(27)	1.42(2)	C(21)—C(26)	1.43(2)
Bond Angles			
Cl(1)—Re—N(1)	84.8(2)	Cl—Re—N(6)	81.1(3)
Cl—Re—C(1)	89.0(5)	Cl—Re—C(2)	93.3(4)
N(1)—Re—N(6)	75.6(3)	N(1)—Re—C(1)	97.7(5)
N(6)—Re—C(2)	102.6(5)	C(1)—Re—C(2)	83.8(6)
N(1)—C(4)—C(27)	117.4(10)	N(6)—C(27)—C(4)	119.1(10)
Cl(3)—Pd—Cl(2)	87.92(12)	N(4)—Pd—Cl(2)	95.4(3)
N(5)—Pd—Cl(3)	95.7(3)	N(5)—Pd—N(4)	79.9(4)
N(5)—Pd—Cl(2)	171.4(3)	N(4)—Pd—Cl(3)	170.9(3)
N(4)—C(19)—C(20)	115.3(10)	N(5)—C(20)—C(19)	117.5(10)
C(11)—N(2)—C(10)	116.5(10)	C(12)—N(3)—C(13)	116.9(10)
C(4)—N(1)—C(5)	116.5(10)	C(11)—N(2)—C(10)	116.5(10)
C(12)—N(3)—C(13)	116.9(10)	C(19)—N(4)—C(18)	117.2(9)
C(20)—N(5)—C(21)	116.5(10)	C(27)—N(6)—C(26)	116.2(10)

cally shifts the observed aromatic  $^1\text{H}$  resonances downfield relative to those of the uncomplexed hhtn ligand. The  $\Delta\delta$  ( $\Delta\delta = \delta_{\text{complex}} - \delta_{\text{ligand}}$ ) values for  $^1\text{H}$  in the coordination pocket are larger than  $\text{PdCl}_2$  than for  $\text{Re}(\text{CO})_3\text{Cl}$  complexes ( $\Delta\delta$  in ppm: **2**, 0.87; **3**, 0.43; **4**, 0.92 and 1.04; **5**, 0.97 and 1.0). The

**Figure 7.** View of  $(\text{PdCl}_2)(\text{Re}(\text{CO})_3\text{Cl})(\text{hhtn})$  emphasizing the large hhtn distortion and the long-range Pd...Pd interaction of 2.809  $\text{\AA}$ .

larger shift for **2** relative to **3** is likely due to the greater deshielding effect of the chloride compared to the carbonyl. The  $\Delta\delta$ s for the methyl resonances are considerably less pronounced, with compound **4** exhibiting the largest shift (which is only 0.17 ppm). The downfield trend upon coordination is consistent with the result of related work using phenazine<sup>9</sup> or dipyrdo(2,3-*a*;2',3'-*h*)phenazine (dpop).<sup>10</sup> The corresponding aromatic resonances in *fac*- $\text{Re}(\text{CO})_3\text{Cl}(\text{dpop})$  shift 0.83 ppm.

The spectroscopic features of **2–5** are analogous to those observed for Pd(II)<sup>11</sup> and Re(I)<sup>10</sup> complexes containing  $\pi$ -acceptor ligands. The lowest energy band of **3** (514 nm) is assigned as  $\text{Re}(\text{d}\pi) \rightarrow \text{hhtn}(\pi^*)$  MLCT, while the higher energy bands (300–450 nm) are attributed to intraligand transitions. For comparison, the MLCT band of  $\text{Re}(\text{CO})_3\text{Cl}(1,10\text{-phenanthroline})$  is at 409 nm ( $4000 \text{ M}^{-1} \text{ cm}^{-1}$ ).<sup>12</sup> The MLCT bands of **2** and **5** (466 and 520 nm, respectively) can be compared to those of  $\text{Pd}(1,10\text{-phenanthroline})\text{Cl}_2$  [ $298 (1930 \text{ M}^{-1} \text{ cm}^{-1})$  and 357 nm ( $1280 \text{ M}^{-1} \text{ cm}^{-1}$ )].<sup>13</sup> The positions of the MLCT bands in **2**, **3**, and **5** indicate that the  $\pi^*$  orbital (LUMO) of hhtn is lower than that of phenanthroline. This finding is supported by CV data: the first reduction of **3** occurs at  $-0.48 \text{ V}$ , while  $\text{Re}(\text{CO})_3\text{Cl}(\text{phenanthroline})$  is reduced at  $-1.3 \text{ V}$ .<sup>14</sup> MLCT emission involving depopulation of the LUMO is shifted to lower energy in a corresponding manner; **3** emits at 710 nm at 77 K, whereas emission from  $\text{Re}(\text{CO})_3\text{Cl}(\text{phenanthroline})$  is observed at 515 nm at 77 K.<sup>10</sup> Assignment of the spectrum of the mixed-metal complex **4** is difficult because the bands are broad and overlapping. However, the redshifting of monomer absorptions upon addition of a second metal center in **4** and **5** is consistent with related observations on binuclear Ru(II) complexes;<sup>15</sup> a similar shift occurs upon binding a second Ru-(bpy)<sub>2</sub> unit to  $\text{Ru}(\text{bpy})_2\text{HAT}$ .<sup>3c</sup>

Owing to severe congestion in the hhtn coordination pocket, the metal center bends away to reduce the unfavorable interaction of  $^1\text{H}$  with the equatorial ligands. The large out-of-plane

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distortions in the structures of **2** (28.1°), **3** (19.5°), and **4** (40.2° for the PdCl<sub>2</sub> unit and 10.4° for the Re(CO)<sub>3</sub>Cl fragment) are manifestations of these interactions. The displacements in **4** (greater for PdCl<sub>2</sub>, smaller for Re(CO)<sub>3</sub>Cl) are due to coupling of the Pd and Re centers. Binding the Re(CO)<sub>3</sub>Cl moiety to hhtn induces a significant out-of-plane distortion on N(4) and N(5) (Figure 4) that predisposes the incoming PdCl<sub>2</sub> center to nitrogen lone pairs that are already greatly displaced out of the hhtn ligand plane; this results in a complex, **4**, where the hhtn ligand is significantly more twisted and cupped compared to the same ligand in **2** and **3**. The twist reduces the steric interaction of the Re equatorial carbonyls, while the cuplike distortion imposes more strain on the Pd center by forcing H(17) and H(22) toward the chlorides. The long-range interatomic Pd···Pd' contact may also contribute to the large PdCl<sub>2</sub> out-of-plane displacement. Structural data on similar highly hindered ligands are lacking; however, in PdCl<sub>2</sub>(*cis*-2,9-bis[2,2-(methoxycarbonyl)ethyl]-1,10-phenanthroline),<sup>16</sup> the PdCl<sub>2</sub> unit is deflected 32.3° out-of-plane. This is presumably due to steric interactions of the methylene protons of the ethyl group with the metal chlorides (H···Cl separations are 2.66 and 2.58 Å). Using 6,6'-dimethyl-2,2'-bipyridine as the chelating ligand leads to a similar distortion.<sup>17</sup> Likewise, in Pd( $\eta^3$ -allyl)(8,8'-dimethyl-2,2'-diquinolyl), the Pd atom is deflected 30.5° from a square planar configuration to minimize the allyl-methyl interactions.<sup>18</sup>

The extended  $\pi$ - $\pi$  interactions in **2**, **3**, and **4** are similar to those of many other  $\pi$ -complexed structures.<sup>6,7,19</sup> The  $\pi$ - $\pi$  interactions in **2** are the most pronounced because the square planar Pd center allows for close intermolecular packing. The Re axial ligands in **3** and **4** disfavor similar  $\pi$ - $\pi$  interactions.

The aromatic hhtn ligand is expected to be planar. Crystal structures of phenazine<sup>20</sup> and its Cu(I) and Ag(I)<sup>7</sup> complexes show very little deviation from planarity of the phenazine ligand. Nor does the related complex, [Cu<sub>3</sub>(qpy)<sub>3</sub>(Ph<sub>6</sub>HAT)]<sup>3+</sup> (qpy is quaterpyridine), show any significant deviation from planarity, with a *maximum* displacement of only 0.19 Å for the HAT portion of the ligand including the three Cu atoms.<sup>4</sup> In contrast, the *average* displacements for the hhtn ligand in **2**, **3**, and **4** are 0.32, 0.13, and 0.39 Å, respectively. The exact cause of the ligand distortion is unclear. Electronic effects are evidenced by the large red-shifts of the MLCT bands, but given the relatively small deviation from planarity in the electronically related HAT complex, these effects must be small. Therefore, we suspect that the deviations in the hhtn complexes are due primarily to the constrained coordination environment.

## Experimental Section

**Preparation of Compounds.** (PhCN)<sub>2</sub>PdCl<sub>2</sub> and Re(CO)<sub>3</sub>Cl (Strem) and hexaketocyclohexane and 4,5-dimethyl-1,2-phenylenediamine (Aldrich) were used as received. Hhtn was prepared by a modification of a standard procedure.<sup>21</sup> The new compounds reported here are stable to moisture and dioxygen and can be prepared without recourse to inert atmosphere techniques.

**2,3,8,9,14,15-Hexamethyl-5,6,11,12,17,18-hexaazatrinaphthalene (hhtn), 1.** To a stirred solution of 200 mL of absolute ethanol

were added 1.0 g (3.20 mmol) of hexaketocyclohexane octahydrate and 1.44 g (10.5 mmol) of 4,5-dimethyl-1,2-phenylenediamine. The solution was brought to reflux. After a few minutes a greenish-brown color formed. After 12 h, the solution was cooled. A yellow-green precipitate formed and was collected by filtration and dried under vacuum (yield: 85%). <sup>1</sup>H NMR (ppm) (300 MHz CDCl<sub>3</sub>):  $\delta$  2.64 (s, 3H, methyl),  $\delta$  8.41 (s, 1H, aromatic).

**PdCl<sub>2</sub>(hhtn), 2.** An orange solution of 163 mg (0.43 mmol) of (PhCN)<sub>2</sub>PdCl<sub>2</sub> in 15 mL chloroform was slowly added to a stirred, yellow-green solution of 200 mg (0.43 mmol) of hhtn in 20 mL of chloroform. A deep orange color immediately formed and the solution was stirred for 20 min. The volume was reduced under vacuum to 10 mL. Addition of diethyl ether afforded an orange microcrystalline solid that was collected by filtration, washed with diethyl ether, and dried in air. The compound was recrystallized from dichloromethane and diethyl ether (yield: 94%). <sup>1</sup>H NMR (300 MHz CDCl<sub>3</sub>):  $\delta$  2.67 (s, 3H, methyl),  $\delta$  2.69 (s, 3H, methyl),  $\delta$  2.70 (s, 3H, methyl),  $\delta$  8.42 (s, 1H, aromatic),  $\delta$  8.45 (s, 1H, aromatic),  $\delta$  9.28 (s, 1H, aromatic).

**Re(CO)<sub>3</sub>Cl(hhtn), 3.** To 355 mg (0.76 mmol) of hhtn suspended in 50 mL of toluene was added 273 mg (0.76 mmol) of Re(CO)<sub>3</sub>Cl. The mixture was brought to reflux. The initial yellow-green color slowly turned deep brown. After 6 h, the solution was cooled, and the toluene was removed under vacuum to yield a brown powder. The powder was dissolved in 30 mL of dichloromethane and filtered through celite. Addition of 20 mL of methanol and removal of the dichloromethane under vacuum yielded deep brown-red crystals that were collected by filtration, washed with diethyl ether, and dried in air (yield: 66%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  2.61 (s, 3H, methyl),  $\delta$  2.71 (s, 3H, methyl),  $\delta$  2.77 (s, 3H, methyl),  $\delta$  8.44 (s, 1H, aromatic),  $\delta$  8.55 (s, 1H, aromatic),  $\delta$  8.84 (s, 1H, aromatic).

**(PdCl<sub>2</sub>)<sub>2</sub>(Re(CO)<sub>3</sub>Cl(hhtn)), 4.** An orange solution of 90 mg (0.23 mmol) of (PhCN)<sub>2</sub>PdCl<sub>2</sub> in 15 mL of dichloromethane was slowly added to the stirred, brown solution of 181 mg (0.23 mmol) of **3** in 20 mL of dichloromethane. The brown solution was stirred for 30 min. An equal volume of methanol was added, and the dichloromethane was removed under vacuum to yield a brown microcrystalline solid. The solid was collected by filtration, washed with diethyl ether, and dried in air. The compound was recrystallized from dichloromethane and ether (yield: 83%). <sup>1</sup>H NMR (300 MHz CDCl<sub>3</sub>):  $\delta$  2.70 (s, 3H, methyl),  $\delta$  2.71 (s, 3H, methyl),  $\delta$  2.74 (s, 3H, methyl),  $\delta$  2.75 (s, 3H, methyl),  $\delta$  2.79 (s, 3H, methyl),  $\delta$  2.81 (s, 3H, methyl),  $\delta$  8.50 (s, 1H, aromatic),  $\delta$  8.60 (s, 1H, aromatic),  $\delta$  8.82 (s, 1H, aromatic),  $\delta$  8.86 (s, 1H, aromatic),  $\delta$  9.33 (s, 1H, aromatic),  $\delta$  9.45 (s, 1H, aromatic).

**(PdCl<sub>2</sub>)<sub>2</sub>(hhtn), 5.** An orange solution of 61 mg (0.16 mmol) of (PhCN)<sub>2</sub>PdCl<sub>2</sub> in 15 mL of chloroform was slowly added to the stirred, orange solution of 100 mg (0.15 mmol) of **2** in 20 mL of chloroform. A deeper orange color appeared, and after 10 min of stirring a deep orange precipitate formed. The precipitate was collected by filtration, washed with diethyl ether, and dried in air (yield: 65%). <sup>1</sup>H NMR (300 MHz CDCl<sub>3</sub>):  $\delta$  2.71 (s, 3H, methyl),  $\delta$  2.73 (s, 3H, methyl),  $\delta$  2.74 (s, 3H, methyl),  $\delta$  8.51 (s, 1H, aromatic),  $\delta$  9.38 (s, 1H, aromatic),  $\delta$  9.41 (s, 1H, aromatic).

**Physical Measurements.** The <sup>1</sup>H NMR spectra were recorded on a General Electric QE-300 NMR spectrometer operating at 300 MHz. Infrared measurements were recorded for hydrocarbon mulls on a Beckman IR-4240 spectrometer. Electronic absorption measurements were made with a Hewlett Packard HP-8452A spectrophotometer; emission data were collected on a home-built instrument.<sup>22</sup>

Electrochemical experiments were performed using a Princeton Applied Research (PAR) Model 173 potentiostat controlled by a Model 175 universal programmer. Cyclic voltammetry was done at ambient temperature with a normal three-electrode configuration consisting of a glassy-carbon working electrode, a platinum-wire auxiliary electrode, and a AgCl/Ag reference electrode containing 1.0 M KCl. The working compartment of the electrochemical cell was separated from the reference compartment by a modified Luggin capillary. All three compartments contained a 0.1 M solution of supporting electrolyte. The dichloromethane (Burdick and Jackson) was distilled from P<sub>2</sub>O<sub>5</sub> prior to use. Tetrabutylammonium hexafluorophosphate ((TBA)PF<sub>6</sub>) (Southwestern Analytical) was used as received.

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All potentials were measured vs aqueous AgCl/Ag and were not corrected for the junction potential. Under conditions identical with those employed here, the ferrocenium/ferrocene couple has an  $E^0$  of 0.45 V.

**X-ray Data Collection:**  $\{\text{PdCl}_2(\text{hhfn})\}_2 \cdot \text{C}_6\text{H}_5\text{Cl} \cdot 2\text{CH}_3\text{OH}$ , **2**. Orange needles were obtained by slow diffusion of diethyl ether through a 2 mm layer of methanol into a chlorobenzene solution of the complex. A single crystal was mounted on a glass fiber with silicon grease and placed in the 130 K nitrogen stream of a Siemens R3m/V diffractometer with a modified Enraf-Nonius low-temperature apparatus. Two check reflections showed only randomly fluctuations (<2%) in intensity throughout the data collection. The data were corrected for Lorentz and polarization effects. Crystal data are given in Table 1.

**$\text{Re}(\text{CO})_3\text{Cl}(\text{hhfn}) \cdot \text{CH}_3\text{OH}$ , **3****. Deep red needles were formed by the slow diffusion of methanol into a tetrahydrofuran solution of the complex. A single crystal was selected and mounted as described above. Two check reflections showed only random fluctuations (<1%) in intensity throughout the data collection. The data were corrected for Lorentz and polarization effects. Crystal data are given in Table 1.

**$\text{Re}(\text{CO})_3\text{Cl}(\text{PdCl}_2)(\text{hhfn}) \cdot 2.6(1,2\text{-Cl}_2\text{C}_6\text{H}_4)$ , **4****. Red-brown blocks were formed by the slow diffusion of diethyl ether into 1,2-dichlorobenzene. A single crystal was selected and mounted as described above. There was no decay in the intensities of the two standard check reflections during the course of the data collection. The data were corrected for Lorentz and polarization effects. Crystal data are given in Table 1.

**Structure Solution and Refinement.**  $\{\text{PdCl}_2(\text{hhfn})\}_2 \cdot \text{C}_6\text{H}_5\text{Cl} \cdot 2\text{CH}_3\text{OH}$ , **2**. Calculations were performed using SHELXTL PLUS (PC and VMS versions) software. Scattering factors and corrections for anomalous dispersion were taken from a standard source.<sup>23</sup> An absorption correction was applied.<sup>24</sup> The structure was solved by direct methods.<sup>25</sup> Hydrogen atoms were added geometrically and refined using a riding model with isotropic thermal parameters equal to 0.05

$\text{\AA}^2$ . The Pd and Cl atoms were assigned anisotropic thermal parameters. The largest feature in the final difference map ( $0.89 \text{ e \AA}^{-3}$ ) is located  $0.97 \text{ \AA}$  from Pd(2).

**$\text{Re}(\text{CO})_3\text{Cl}(\text{hhfn}) \cdot \text{CH}_3\text{OH}$ , **3****. The structure was solved in the monoclinic space group  $P2_1/n$  using direct methods. Hydrogens were added as described above and refined using isotropic thermal parameters of  $0.035 \text{ \AA}^2$ . The hydroxyl hydrogen of the methanol was not located in a Fourier map and was not included in the final model. An absorption correction was applied. All non-hydrogen atoms were refined with anisotropic thermal parameters. The largest peak in the final Fourier difference map corresponded to  $3.2 \text{ e \AA}^{-3}$  at a distance of  $0.9 \text{ \AA}$  from Re. The goodness-of-fit was 1.33.

**$\text{Re}(\text{CO})_3\text{Cl}(\text{PdCl}_2)(\text{hhfn}) \cdot 2.6(1,2\text{-Cl}_2\text{C}_6\text{H}_4)$ , **4****. The structure was solved by a combination of Patterson and difference Fourier methods in the triclinic space group  $P1$  and refined by full-matrix (based on  $F^2$ ) least-squares.<sup>26</sup> Hydrogen atoms were added at calculated positions and refined using a riding model with isotropic thermal parameters equal to 1.2 times the equivalent isotropic  $U$  of the bonded carbons, except for those of the methyl groups, which were assigned multiplicative values of 1.5. Three different sites in the structure with planar electron density were resolved into disordered groupings equivalent to 2.6 molecules of 1,2-dichlorobenzene. An absorption correction was applied. All nonhydrogen atoms of the complex were refined with anisotropic thermal parameters. The largest peak in the final Fourier difference map corresponded to  $1.39 \text{ e \AA}^{-3}$  in the region of the disordered solvent group.

**Acknowledgment.** We thank Mike Hill for assistance with the electrochemistry. This work was supported by the National Science Foundation (Grant CHE-9311587 to H.B.G.; postdoctoral fellowship CHE-9101931 to V.J.C.).

**Supplementary Material Available:** Tables of complete atomic coordinates, bond distances, bond angles, anisotropic thermal parameters, hydrogen atom positions, and crystal data for **2–4** and a perspective view of the Pd(2)-containing species of **2** (29 pages). Ordering information is given on any current masthead page.

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