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Cyclometalated Complexes of Palladium(II) and Platinum(II): *cis*-Configured Homoleptic and Heteroleptic Compounds with Aromatic C⁀N Ligands

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The palladium(II) and platinum(II) bis-homoleptic complexes M(C⁀N)$_2$, where C⁀N is benzo[*h*]quinoline (H-bhq), 2-phenylpyridine (H-phpy), 2-(2′-benzothienyl)pyridine (H-bthpy), 2-(2′-thienyl)quinoline (H-thq), and 2-(2′-thienyl)pyridine (H-thpy), were prepared by metal exchange of the lithiated ligands C⁀N with M(Et$_2$S)$_2$Cl$_2$. The palladium(II) bis-heteroleptic complexes, Pd(C⁀N)(C′⁀N′), were synthesized from Pd(C⁀N)$_2$ bis-homoleptic complexes, which were converted by HCl into the dichloro-bridged compounds [Pd(C⁀N)Cl]$_2$. By addition of Et$_2$S, the Pd(C⁀N)(Et$_2$S)Cl complexes were formed, which were allowed to react with Li(C′⁀N′), yielding M(C⁀N)(C′⁀N′) compounds. An alternative way for obtaining the bis-heteroleptic molecules is by ligand exchange, according to the equilibrium M(C⁀N)$_2$ + M(C′⁀N′)$_2$ = 2M(C⁀N)(C′⁀N′). The crystal structures of Pt(bhq)$_2$ (**1**) and Pt(thq)$_2$ (**3**) present an important distortion of the square planar (SP-4) geometry toward a two-bladed helix. Bis-homoleptic and some bis-heteroleptic complexes of palladium(II) have also been synthesized. In both cases, the steric interactions between the two ligands cause again a helical distortion rather than yielding *trans* compounds. For *cis*-bis(benzo[*h*]quinoline)platinum(II) (**1**), in the crystal (monoclinic, space group $P2_1/n$, $a = 13.728(3)$ Å, $b = 6.9537(15)$ Å, $c = 19.701(5)$ Å, $\beta = 106.17(2)°$, $Z = 4$, $\rho_{\mathrm{calcd}} = 2.028\ \mathrm{g{\cdot}cm^{-3}}$; diffractometer measurements, block-matrix least-squares refinement, $R = 0.043$, $R_{\mathrm{w}} = 0.047$) the average Pt−N and Pt−C distances are 2.151(6) and 1.988(7) Å, respectively. One benzo[*h*]quinoline ligand is significantly less planar than the other. For *cis*-bis[2-(2′-thienyl)quinoline]platinum(II) (**3**), in the crystal (trigonal, space group $P3_221$, $a = b = 9.373(1)$ Å, $c = 20.152(3)$ Å, $Z = 3$, $\rho_{\mathrm{calcd}} = 2.022\ \mathrm{g{\cdot}cm^{-3}}$; diffractometer measurements, full-matrix least-squares refinement, $R = 0.010$, $R_{\mathrm{w}} = 0.010$) the molecule has C_2 symmetry and is chiral. The Pt−N and Pt−C bond lengths are 2.156(2) and 1.984(3) Å, respectively. The quinoline moitey is not planar but bent about the fused bond by 6.8°. The thiophene moiety is inclined to the best plane through the quinoline moiety by 24.4°.

Introduction

Cyclometalated complexes have recently found widespread interest as species with promising properties in various fields.[4,5] The original method for preparing metallocycles is the spontaneous deprotonation of a C−H group in a suitable position.[6,7] This route generally yields only one metallocycle in a complex. Species containing two metallocycles have been obtained, using lithiated ligands.[8,9] Such compounds, with C⁀N aromatic cycles, show interesting photochemical and photophysical properties.[10−15]

In the present paper we extend our recent investigations of cyclometalated platinum(II) and palladium(II) compounds[16] to related complexes (Figure 1): *cis*-bis(benzo[*h*]quinoline)platinum(II), Pt(bhq)$_2$ (**1**), *cis*-bis[2-(2′-benzothienyl)pyridine]platinum(II), Pt(bthpy)$_2$ (**2**), *cis*-bis[2-(2′-thienyl)quinoline]platinum(II), Pt(thq)$_2$ (**3**), *cis*-bis(benzo[*h*]quinoline)palladium(II), Pd(bhq)$_2$ (**4**), *cis*-bis(2-phenylpyridine)palladium(II), Pd(phpy)$_2$ (**5**), *cis*-bis[2-(2′-thienyl)pyridine]palladium(II), Pd(thpy)$_2$ (**6**), *cis*-bis-[2-(2′-benzothienyl)pyridine]palladium(II), Pd(bthpy)$_2$ (**7**). Three heteroleptic complexes, *cis*-[2-(2′-thienyl)pyridine](2-phenylpyridine)palladium(II), Pd(thpy)(phpy) (**8**), *cis*-[2-(2′-thienyl)-pyridine][benzo[*h*]quinoline]palladium(II), Pd(thpy)(bhq) (**9**), and *cis*-[benzo[*h*]quinoline](2-phenylpyridine)palladium(II), Pd(bhq)(phpy) (**10**), are also described.

The comparison of the palladium(II) compounds with the platinum(II) complexes is of special interest in view of the strong propensity of the latter to undergo highly stereoselective photochemical oxidative addition reactions (**POA**).[16e] The preparation of **2**, **3**, and **4** was undertaken with the aim of

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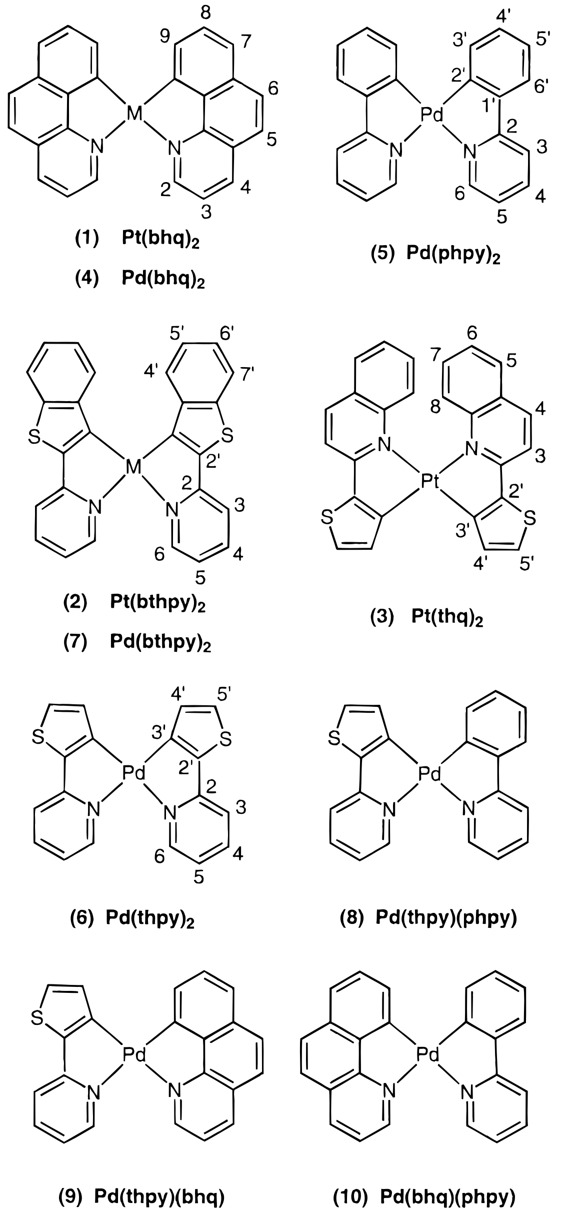

(1) Pt(bhq)$_2$

(4) Pd(bhq)$_2$

(5) Pd(phpy)$_2$

(2) Pt(bthpy)$_2$

(7) Pd(bthpy)$_2$

(3) Pt(thq)$_2$

(6) Pd(thpy)$_2$

(8) Pd(thpy)(phpy)

(9) Pd(thpy)(bhq)

(10) Pd(bhq)(phpy)

Figure 1. Numbering scheme of the platinum(II) and palladium(II) complexes **1**−**10**.

obtaining *trans* complexes with bulky ligands. All attempts to prepare *trans* compounds with sterically less demanding ligands have failed so far.

Experimental Section

Measurements. Infrared and electronic spectra were recorded with Perkin-Elmer 683 and 55 spectrometers, respectively. ^{1}H NMR spectra were obtained with a Bruker M-360 spectrometer. Mass spectra (MS) were measured using a VG Instrument 7070E mass spectrometer.

Solvents and Techniques for Reactions Involving Lithium Reagents. Ether and THF were distilled from a sodium suspension. Ligands and complexes were dried under vacuum for 12 h. All reactions and the transfer of solutions were carried out under a stream of dry nitrogen.

Starting Materials. 2-(2′-Thienyl)pyridine was purchased from Aldrich. 2-(2′-Thienyl)quinoline and 2-(2′-benzothienyl)pyridine were prepared according to Chippendale and Gilman.[17,18] 2-(2-Bromophenyl)pyridine was obtained by a described method.[19] *trans*-Pt(Et$_2$S)$_2$Cl$_2$ and *trans*-Pd(Et$_2$S)$_2$Cl$_2$ were synthesized by following published methods.[20,21] Dinuclear palladium(II) complexes $[Pd(C{\frown}N)Cl]_2$, with benzo[*h*]quinoline as ligands, were prepared according to Cockburn.[22]

10-Bromobenzo[*h*]quinoline, (Br-bhq). Benzo[*h*]quinoline (4.5 g, 25 mmol) and mercuric acetate (8 g, 25 mmol) were heated at 140 °C under vacuum until the acetic acid was completely evaporated. The oily residue was cooled to 20 °C and diluted with 20 mL of CH$_2$Cl$_2$. After dissolution, bromine (4 g, 25 mmol) in 10 mL of CH$_2$Cl$_2$ was added slowly. The reaction mixture was filtered and extracted with water. The organic phase was dried (MgSO$_4$), concentrated, precipitated with petroleum ether, treated by flash chromatography (ethyl acetate/petroleum ether, 1:9), and crystallized from petroleum ether to give 1.9 g of white plates. Yield: 30%.

Mp: 99 °C. $R_f = 0.36$ (silica gel, ethyl acetate/petroleum ether, 1:9). Anal. Calcd for C$_{13}$H$_8$BrN: C 60.49, H 3.12, N 5.43; Found: C 60.77, H 3.29, N 5.54.

Solutions of Lithiated Ligands. Butyllithium (1.3 mL, 1.6 M/hexane) was added slowly to a 20 mL etheral solution (40 mL for the preparation of the heteroleptic complexes) containing 2 mmol of ligand at the indicated temperature

ligand	lithium reagent	temp of reacn, °C	lithiated ligand	ref
Br-bhq	*n*-BuLi	−78	Li-bhq	this work
Br-phpy	*n*-BuLi	−78	Li-phpy	19
H-thpy	*n*-BuLi	+20	Li-thpy	23
H-bthpy	*n*-BuLi	+20	Li-bthpy	this work
H-thq	*t*-BuLi	−78	Li-thq	23

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Palladium(II) Monocyclometalated Complexes. $[Pd(C{\frown}N)Cl]_2$ (1 mmol) was stirred as a suspension in 20 mL of CH$_2$Cl$_2$. Et$_2$S was added slowly until the solution became clear. $Pd(C{\frown}N)(Et_2S)Cl$ crystallized upon reduction of the volume and cooling to 0 °C. Yield: 80%.

Palladium(II) and Platinum(II) Bis-Homoleptic Complexes. M(Et$_2$S)$_2$Cl$_2$ (M = Pd, Pt) (1 mmol) in 20 mL of ether was added slowly to a solution containing 2 equiv of lithiated ligand at −78 °C. The reaction mixture was stirred for 30 min at −78 °C, poured into 100 mL of H$_2$O, and extracted with CH$_2$Cl$_2$. The dried organic phase (MgSO$_4$) was concentrated and filtered through a small alox column in the case of the palladium(II) complexes or purified by flash chromatography with CH$_2$Cl$_2$ in the case of the platinum(II) complexes. The complexes were finally crystallized from CH$_2$Cl$_2$ by addition of diethyl ether through the vapor phase.

Palladium(II) Bis-Heteroleptic Complexes. The solution of the lithiated ligand in ether was added dropwise to a solution containing 1 equiv of $Pd(C{\frown}N)(Et_2S)Cl$ in THF at −78 °C. The further steps were identical to the procedure described for $Pd(C{\frown}N)_2$.

***cis*-Bis(benzo[*h*]quinoline)platinum(II), Pt(bhq)$_2$ (1).** Yield: 16%. Yellow needles. MS *m*/*z* (relative intensity): 554 (12), 553 (16), 552 (73), 551 (M$^+$ = 100), 550 (100), 549 (42), 548 (29), 547 (6). Anal. Calcd for C$_{26}$H$_{16}$N$_2$Pt: C, 56.62; H, 2.92; N, 5.08. Found: C, 56.62; H, 2.97; N, 5.10. ^{1}H NMR (CDCl$_3$, 360 MHz): 9.19, d × d, $J = 5.2$ Hz, $J = 1.3$ Hz, 2H, H−C(2); 8.52, d × d × d, $J = 5.8$ Hz, $J = 2.2$ Hz, $J_{Pt} = 39.3$ Hz, 2H, H−C(9); 8.25, d × d, $J = 8.0$ Hz, $J = 1.3$ Hz , 2H, H−C(4); 7.82, d, $J = 8.7$ Hz, 2H, H−C(6); 7.71−7.65, m, 4H, H−C(7,8); 7.58, d, $J = 8.7$ Hz, 2H, H−C(5); 7.52, d × d, $J = 8.0$ Hz, $J = 5.2$ Hz, 2H, H−C(3).

***cis*-Bis[2-(2′-benzothienyl)pyridine]platinum(II), Pt(bthpy)$_2$ (2).** Yield: 30% of orange brown cubes. MS *m*/*z* (relative intensity): 619 (8), 618 (24), 617 (30), 616 (85), 615 (M$^+$ = 100), 614 (76), 613 (18). Anal. Calcd for C$_{26}$H$_{16}$N$_2$PtS$_2$: C, 50.73; H, 2.62; N, 4.55. Found: C, 50.40; H, 2.66; N, 4.42. ^{1}H NMR (CDCl$_3$, 360 MHz): 8.77, d, *J*

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$= 5.7$ Hz, 2H, H−C(6); 7.93, d × d × d, $J = 8.0$ Hz, $J = 7.4$ Hz, $J = 1.4$ Hz, 2H, H−C(4); 7.84, d × d × d, $J = 8.0$ Hz, $J = 1.1$ Hz, $J = 0.8$ Hz, 2H, H−C(3); 7.64, d, $J = 8.0$ Hz, 4H, H−C(4′), H−C(7′); 7.27, d × d × d, $J = 7.4$ Hz, $J = 5.7$ Hz, $J = 1.4$ Hz, 2H, H−C(5); 7.22, d × d × d, $J = 8.1$ Hz, $J = 7.0$ Hz, $J = 1.0$ Hz, 2H; 6.91, d × d × d, $J = 8.1$ Hz, $J = 7.0$ Hz, $J = 1.1$ Hz, 2H.

***cis*-Bis[2-(2-thienyl)quinoline]platinum(II), Pt(thq)$_2$ (3).** Yield: 6% of ruby red cubes. MS m/z (relative intensity): 619 (1), 618 (2), 617 (2), 616 (4), 615 (M$^+$ = 5), 614 (4). Anal. Calcd for $C_{26}H_{16}N_2PtS_2$: C, 50.73; H, 2.62; N, 4.55. Found: C, 50.70; H, 2.72; N, 4.48. ^{1}H NMR (CDCl$_3$, 360 MHz): 8.26, d × d, $J = 8.6$ Hz, $J_{\mathrm{Pt}} = 25.7$ Hz, 2H; 7.81, d × d, $J = 4.8$ Hz, $J_{\mathrm{Pt}} = 21.7$ Hz, 2H, H−C(4′); 7.74, d, $J = 8.0$ Hz, 2H; 7.73, d, $J = 8.6$ Hz, 2H; 7.72, d, $J = 8.6$ Hz, 2H; 7.62, d × d, $J = 4.8$ Hz, $J_{\mathrm{Pt}} = 17.4$ Hz, 2H, H−C(5′); 7.22, d × d × d × d, $J = 8.1$ Hz, $J = 7.0$ Hz, $J = 1.0$ Hz, $J_{\mathrm{Pt}} = 33.3$ Hz, 2H; 6.82, d × d × d × d, $J = 8.6$ Hz, $J = 7.0$ Hz, $J = 1.5$ Hz, $J_{\mathrm{Pt}} = 36.3$ Hz, 2H.

***cis*-Bis(benzo[*h*]quinoline)palladium(II), Pd(bhq)$_2$ (4).** Yield: 67% of yellow needles. MS m/z (relative intensity): 464 (3), 463 (2), 462 (M$^+$ = 4), 461 (4), 460 (2). Anal. Calcd for $C_{26}H_{16}N_2Pd$: C, 67.47; H, 3.48; N, 6.05. Found: C, 67.34; H, 3.52; N, 5.98. ^{1}H NMR (CDCl$_3$, 360 MHz): 9.12, d × d, $J = 5.0$ Hz, $J = 1.3$ Hz, 2H, H−C(2); 8.47, d × d, $J = 6.8$ Hz, $J = 0.8$ Hz, 2H, H−C(9); 8.18, d × d, $J = 8.0$ Hz, $J = 1.3$ Hz, 2H, H−C(4); 7.81, d, $J = 8.7$ Hz, 2H, H−C(6); 7.72, d, $J = 7.8$ Hz, 2H, H−C(7); 7.67, d × d, $J = 7.8$ Hz, $J = 6.8$ Hz, 2H, H−C(8); 7.55, d, $J = 8.7$ Hz, 2H, H−C(5); 7.45, d × d, $J = 8.0$ Hz, $J = 5.0$ Hz, 2H, H−C(3).

***cis*-Bis(2-phenylpyridine)palladium(II), Pd(phpy)$_2$ (5).** Yield: 25% of yellow plates. MS m/z (relative intensity): 418 (3), 416 (6), 414 (M$^+$ = 8), 413 (6), 412 (3). Anal. Calcd for $C_{22}H_{16}N_2Pd$: C, 63.71; H, 3.89; N, 6.75. Found: C, 63.68; H, 3.88; N, 6.71. ^{1}H NMR (CDCl$_3$, 360 MHz): 8.59, d, $J = 5.4$ Hz, 2H, H−C(6); 8.08, d, $J = 7.6$ Hz, 2H, H−C(3′); 7.85, d, $J = 8.0$ Hz, 2H, H−C(3); 7.79, d × d × d, $J = 8.0$ Hz, $J = 7.2$ Hz, $J = 1.6$ Hz, 2H, H−C(4); 7.62, d × d, $J = 7.6$ Hz, $J = 1.4$ Hz, 2H, H−C(6′).

***cis*-Bis[2-(2′-thienyl)pyridine]palladium(II), Pd(thpy)$_2$ (6).** Yield: 30% of orange plates. MS m/z (relative intensity): 429 (3), 428 (15), 427 (4), 426 (M$^+$ = 17), 425 (13), 424 (6). Anal. Calcd for $C_{18}H_{12}N_2PdS_2$: C, 50.65; H, 2.83; N, 6.56. Found: C, 50.45; H, 2.92; N, 6.66. ^{1}H NMR (CDCl$_3$, 360 MHz): 8.48, d, $J = 5.5$ Hz, 2H, H−C(6); 7.71, d × d × d, $J = 7.9$ Hz, $J = 7.5$ Hz, $J = 1.0$ Hz, 2H, H−C(4); 7.65, d, $J = 4.8$ Hz, 2H, H−C(4′); 7.47, d × d, $J = 7.9$ Hz, $J = 1.0$ Hz, 2H, H−C(3); 7.45, d, $J = 4.8$ Hz, 2H, H−C(5′); 7.07, d × d × d, $J = 7.5$ Hz, $J = 5.5$ Hz, $J = 1.0$ Hz, 2H, H−C(5).

***cis*-Bis[2-(2′-benzothienyl)pyridine]palladium(II), Pd(bthpy)$_2$ (7).** Yield: 10% of orange cubes. MS m/z (relative intensity): 524 (16), 525 (37), 526 (M$^+$ = 51), 527 (17), 528 (43), 529 (14), 539 (22), 531 (6). Anal. Calcd for $C_{26}H_{16}N_2PdS_2$: C, 59.26; H, 3.06; N, 5.32. Found: C, 59.19; H, 3.04; N, 5.36. ^{1}H NMR (CDCl$_3$, 360 MHz): 8.57, d, $J = 5.2$ Hz, 2H, H−C(6); 7.86−7.82, m, 4H; 7.63−7.58, m, 4H; 7.22−7.17, m, 4H; 6.91, d × d × d, $J = 8.1$ Hz, $J = 7.0$ Hz, $J = 1.0$ Hz, 2H.

***cis*-[(2-(2-Thienyl)pyridine)(2-phenylpyridine)]palladium(II), Pd(thpy)(phpy) (8).** Yield: 17% of orange plates. MS m/z (relative intensity): 416 (14), 418 (20), 420 (M$^+$ = 40), 422 (35), 424 (23), 426 (20), 428 (17). Anal. Calcd for $C_{20}H_{14}N_2PdS$: C, 57.09; H, 3.35; N, 6.66. Found: C, 56.80; H, 3.29; N, 6.71. ^{1}H NMR (CDCl$_3$, 360 MHz): 8.56, d, $J = 5.4$ Hz, 1H, H−C(6)phpy; 8.46, d, $J = 5.4$ Hz, 1H, H−C(6)thpy; 8.11, d, $J = 7.6$ Hz, 1H, H−C(3′)phpy; 7.81−7.78, m, 2H, H−C(3), H−C(4)phpy; 7.69, d × d × d, $J = 8.0$ Hz, $J = 7.4$ Hz, $J = 1.7$ Hz, 1H, H−C(4)thpy; 7.64, d, $J = 4.8$ Hz, 1H, H−C(4′)thpy; 7.61, d × d, $J = 7.6$ Hz, $J = 1.5$ Hz, 1H, H−C(6′)phpy; 7.48, d, $J = 8.0$ Hz, 1H, H−C(3)thpy; 7.46, d, $J = 4.8$ Hz, 1H, H−C(5′)thpy; 7.24, d × d × d, $J = 7.6$ Hz, $J = 7.6$ Hz, $J = 1.5$ Hz, 1H, H−C(4′)phpy; 7.19, d × d × d, $J = 7.3$ Hz, $J = 5.4$ Hz, $J = 1.6$ Hz, 1H, H−C(5)phpy; 7.14, d × d × d, $J = 7.6$ Hz, $J = 7.6$ Hz, $J = 1.3$ Hz, 1H, H−C(5′)phpy; 7.05, d × d × d, $J = 7.4$ Hz, $J = 5.4$ Hz, $J = 1.3$ Hz, 1H, H−C(5)thpy.

***cis*-[(2-(2′-Thienyl)pyridine)(benzo[*h*]quinoline)]palladium(II), Pd(thpy)(bhq) (9).** Yield: 20% of yellow plates. MS m/z (relative intensity): 444 (M$^+$ = 1.5), 446 (1.5). Anal. Calcd for $C_{22}H_{14}N_2PdS$: C, 59.40; H, 3.17; N, 6.30. Found: C, 59.33; H, 3.20; N, 6.28. ^{1}H NMR (CDCl$_3$, 360 MHz): 8.93, d × d, $J = 5.1$ Hz, $J = 1.4$ Hz, 1H, H−C(2)bhq; 8.64, d, $J = 5.3$ Hz, 1H, H−C(6)thpy; 8.36, d × d, $J = 6.4$ Hz, $J = 1.7$ Hz, 1H, H−C(9)bhq; 8.30, d × d, $J = 8.0$ Hz, $J = 1.7$ Hz, 1H, H−C(4)bhq; 7.82, d, $J = 8.7$ Hz, 1H, H−C(6)bhq; 7.80−7.72, m, 2H; 7.66−7.45, m, 4H; 7.60, d, $J = 8.7$ Hz, 1H, H−C(3)bhq; 7.51, d, $J = 4.8$ Hz, 1H, H−C(3′)thpy; 7.13, d × d × d, $J = 7.4$ Hz, $J = 5.4$ Hz, $J = 1.3$ Hz, 1H, H−C(5)thpy.

Table 1. Crystallographic Data for *cis*-Bis(benzo[*h*]quinoline)platinum(II), Pt(bhq)$_2$ (**1**), and *cis*-Bis[2-(2′-thienyl)quinoline]platinum(II), Pt(thq)$_2$ (**3**)

	1	**3**
formula	$C_{26}H_{16}N_2Pt$	$C_{26}H_{16}N_2S_2Pt$
mol wt	551.52	615.64
cryst syst	monoclinic	trigonal
space group	$P2_1/n$	$P3_221$
a, Å	13.728(3)	9.374(1)
b, Å	6.9537(15)	9.374(1)
c, Å	19.701(5)	20.154(3)
α, deg	90	90
β, deg	106.17(2)	90
γ, deg	90	120
V, Å^3	1806.3	1533.2
Z	4	3
ρ_{calcd} g·cm^{-3}	2.028	1.999
λ (Mo Kα), Å	0.710 73	0.710 73
R^{a}	0.043^{b}	0.010
$R_{w}{}^{c}$	0.047	0.010^{d}

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] Dunitz and Seiler (1973) weighting scheme with $R = 18$ Å^2. [c] $R = \sum(w(||F_o| - |F_c||))^{0.5}/\sum(w|F_o|)^{0.5}$. [d] $w^{-1} = \sigma^2(F_o) + 4 \times 10^{-6}(F_o{}^2)$.

***cis*-[(Benzo[*h*]quinoline)(2-phenylpyridine)]palladium(II), Pd(bhq)(phpy) (10).** Yield: 26% of yellow needles. Anal. Calcd for $C_{24}H_{16}N_2Pd$: C, 65.69; H, 3.68; N, 6.38. Found: C, 65.66; H, 3.68; N, 6.39. ^{1}H NMR (CDCl$_3$, 360 MHz): 8.92, d × d, $J = 5.0$ Hz, $J = 1.4$ Hz, 1H, H−C(2)bhq; 8.72, d, $J = 5.2$ Hz, 1H, H−C(6)phpy; 8.33, d × d, $J = 6.5$ Hz, $J = 1.1$ Hz, 1H, H−C(9)bhq; 8.24, d × d, $J = 8.0$ Hz, $J = 1.4$ Hz, 1H, H−C(4)bhq; 8.22, d, $J = 7.4$ Hz, 1H, H−C(3′)phpy; 7.87, d, $J = 8.0$ Hz, 1H, H−C(3)phpy; 7.83−7.77, m, 2H, H−C(4)phpy, H−C(6)bhq; 7.69−7.62, m, 3H, H−C(7)bhq, H−C(8)bhq, H−C(6′)phpy; 7.57, d, $J = 8.6$ Hz, 1H, H−C(5)bhq; 7.53, d × d, $J = 8.0$ Hz, $J = 5.0$ Hz, 1H, H−C(3)bhq; 7.35, d × d × d, $J = 7.4$ Hz, $J = 7.4$ Hz, $J = 1.4$ Hz, 1H, H−C(4′)phpy; 7.21, d × d × d, $J = 7.2$ Hz, $J = 5.2$ Hz, $J = 1.4$ Hz, 1H, H−C(5)phpy; 7.18, d × d × d, $J = 7.4$ Hz, $J = 7.4$ Hz, $J = 1.2$ Hz, 1H, H−C(5′)phpy.

X-ray Crystal Structure Analyses. Crystal data and details of structure refinement for complexes **1** and **3** are given in Table 1.

Pt(bhq)$_2$ (1). Preliminary Weissenberg and precession photographs indicated the crystals to be monoclinic. Intensity data were measured on a Philips PW100 four-circle diffractometer using graphite-monochromated Mo Kα radiation at room temperature. Accurate cell parameters were obtained by least-squares from the setting of 20 high-order reflections. A 3% variation in the intensity of two standard reflections measured every 90 min was observed. No absorption correction was applied. The structure was solved using MULTAN-80[24] and refined by block-matrix least-squares methods using a local (Geneva) version of X-RAY-76.[25] Hydrogen atoms were included in calculated positions (U_{iso}(fixed) = 0.051 Å^2).

Pt(thq)$_2$ (3). Preliminary Weissenberg and precession photographs indicated the crystals to be trigonal. Intensity data were measured on a Stoe-Siemens AED2 four-circle diffractometer using graphite-monochromated Mo Kα radiation at room temperature. The crystal was sealed in a Lindemann glass capillary. Accurate cell parameters were obtained from $\pm\omega$ values of 35 reflections in the 2Θ range 30−40°. There was no significant intensity variation for three standard

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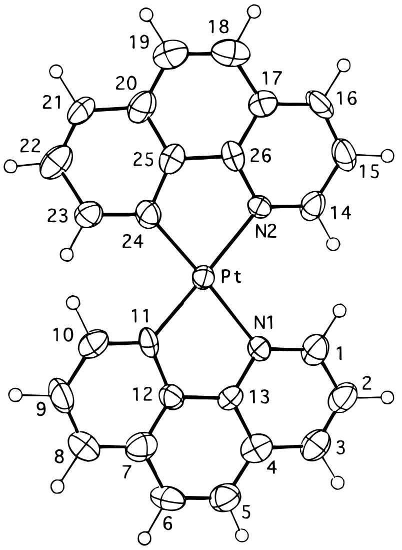


Figure 2. ORTEP plot and crystallographic numbering scheme of Pt(bhq)$_2$ (**1**) (ellipsoids at 50% probability level).

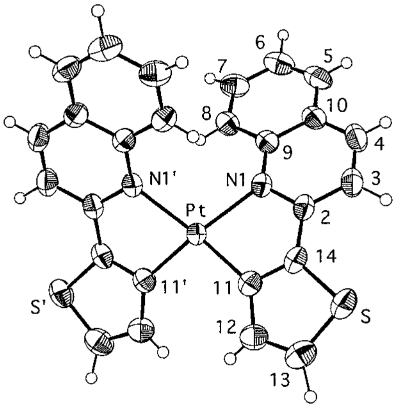


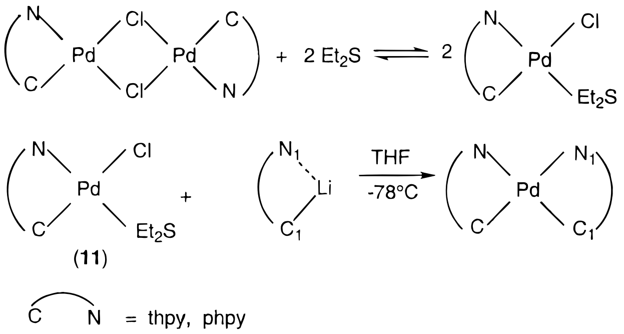
Figure 3. ORTEP plot and crystallographic numbering scheme of Pt(thq)$_2$ (**3**) (ellipsoids at 50% probability level).

reflections measured every hour. A numerical absorption correction was applied to the data with SHELX-76,[26] which was used to solve the structure by Patterson method and for all further calculations. The space group was found to be the enantiomorphous determining space group $P3_221$. This was confirmed by the Patterson and the successful refinement. The majority of H-atoms were located from difference maps and refined isotropically. Atoms H(3) and H(13) were included in calculated positions (U_{iso}(fixed) = 0.053 Å^2). Complex neutral-atom scattering factors not included in XRAY or SHELX-76 were taken from the literature.[27] The crystallographic numbering schemes used for **1** and **3** are given in Figures 2 and 3.

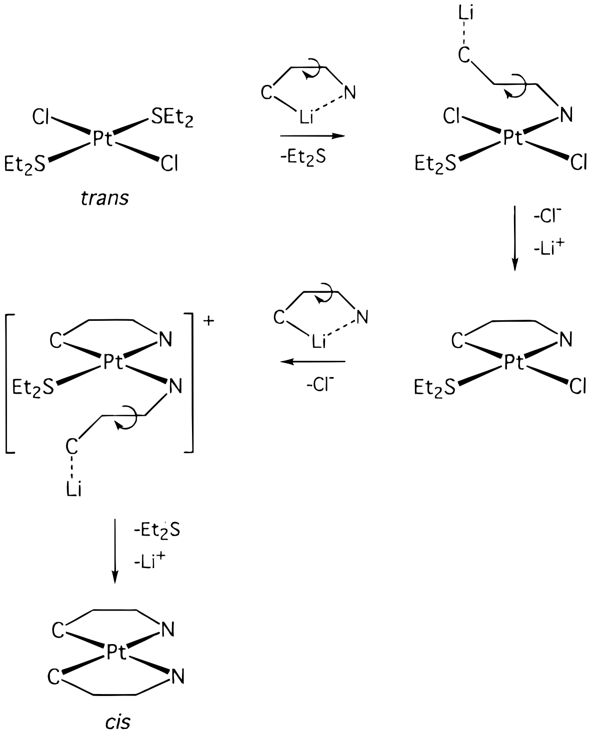
Results and Discussion

Synthesis. The new platinum and palladium complexes were obtained in the same manner as those previously described.[16] The heteroleptic complexes of palladium(II) were prepared according to Scheme 1. The dinuclear chloro-bridged species were obtained by a known method.[22] The second step, reaction of the intermediate **11** with the lithiated ligand, has to be carried out in dilute solution ($<5 \times 10^{-2}$ M) in order to avoid the formation of a bis-homoleptic complex. It is noteworthy that all Pd($\widehat{\mathrm{CN}}$)$_2$ and Pd($\widehat{\mathrm{CN}}$)($\widehat{\mathrm{C'N'}}$) compounds are thermally stable in organic solvents, whereas complexes containing two monodentate σ bonded C-ligands decompose by geminal elimination.[28] This reaction is inhibited by the chelate structure of the two ligands.[16c]

Scheme 1



Scheme 2



Scheme 2 proposes a mechanism for the formation of palladium and platinum bis-homoleptic compounds. Because of a low coordination number, ligand substitutions in the square planar complexes occur almost entirely by associative pathways. In a first step, one lithiated ligand is bounded to the metal center by its nitrogen, causing the consecutive liberation of a diethyl sulfide. The chelation is completed with the formation of a metal−carbon bond, followed by elimination of one chloride. The same mechanism occurs for the coordination of the second ligand, except that the carbon of the first ligand exerts a strong *trans* effect, which directs the coordination of the second nitrogen in *trans* position. The *cis* configuration of the complexes described in this publication is a consequence of the synthetic pathway which was used. Literature reports similar cases, with strongly sterically interacting ligands, where the *cis* configuration is prefered.[16f,16g]

UV−Vis. Compounds Pt(bhq)$_2$ (**1**), Pt(bthpy)$_2$ (**2**), and Pt(thq)$_2$ (**3**) show similar patterns in the low energy region of their UV−vis spectra (Figure 4 and Table 2). As in the analogous compounds prepared earlier, the first strong absorp-

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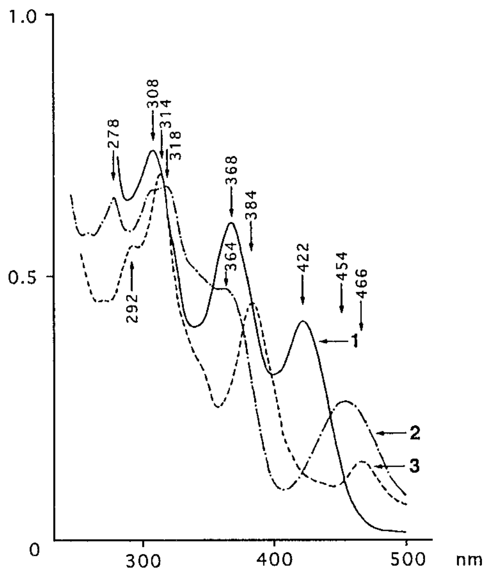


Figure 4. Absorption spectra in CH_2Cl_2 of Pt(bhq)$_2$ (**1**), Pt(bthpy)$_2$ (**2**), and Pt(thq)$_2$ (**3**).

Table 2. Absorption (nm) in CH_2Cl_2 of Homoleptic and Heteroleptic Complexes of Platinum(II) and Palladium(II)

Pt(bhq)$_2$ (**1**)	422 (9300), 368 (14000), 308 (17300)
Pt(bthpy)$_2$ (**2**)	454 (9000), 364 (17200), 342 sh (18700), 318 (24500), 278 (23600)
Pt(thq)$_2$ (**3**)	466 (4400), 384 (14000), 348 sh (9900), 314 (22000), 292 sh (17300)
Pd(bhq)$_2$ (**4**)	392 (6600), 374 (6700), 336 sh (10000)
Pd(phpy)$_2$ (**5**)	348 (9000), 304 sh (15000), 274 (35000)
Pd(thpy)$_2$ (**6**)	380 (9400), 318 (24500), 292 (31000)
Pd(bthpy)$_2$ (**7**)	408 (10000), 340 sh (17000), 330 sh (19000), 310 (19000), 394 (25000)
Pd(thpy)(phpy) (**8**)	394 sh (5500), 360 (8200), 316 sh (18800), 294 sh (26300)
Pd(thpy)(bhq)	372 sh (9000), 316 sh (22900), 296 (27900), 240 sh (44900), 233 (46900)
Pd(bhq)(phpy) (**10**)	396 sh (4400), 376 sh (6100), 332 sh (11700), 298 sh (21000), 276 (26500)

Table 3. Solvatochromy (nm) of Homoleptic Platinum(II) Complexes in Different Solvents

solvent	Pt(bhq)$_2$ (**1**)		Pt(bthpy)$_2$ (**2**)		Pt(thq)$_2$ (**3**)	
EtOH	360	416	360 sh	452	380	464
acetonitrile	362	418	342 sh	436	378	462
CH_2Cl_2	368	422	364 sh	454	384	466
toluene	374	432	368 sh	462	390	474
mesitylene	376	434	372 sh	464	392	474

tion is assigned to a metal to ligand charge transfer (MLCT) transition into the lowest unoccupied π^* orbital of the ligand. The absorption wavelengths increase from 422 nm (CH_2Cl_2) for Pt(bhq)$_2$ (**1**) to 466 nm for Pt(thq)$_2$ (**3**). The solvatochromy (Table 3) was measured and found to be similar in all cases to that observed for other Pt($C\frown N$)$_2$ complexes.[16a] From ethanol to mesitylene, there are appreciable spectral changes ($\Delta \sim 15$ nm). These differences are mainly due to solvent shifts of the intramolecular electronic transitions. Some contribution from charge transfer to solvent bands is also plausible.[14]

The spectra of the palladium compounds are given in Figure 5, while Table 2 lists their absorption wavelengths and extinction coefficients. The low energy bands are generally in the UV, except for Pd(bthpy)$_2$ (**7**), where it is shifted to 408 nm. The shift toward higher energies is in agreement with the higher oxidation potential Pd(II) $\rightarrow$ Pd(III), as compared to the analogous transitions in the platinum(II) complexes. In the heteroleptic palladium complexes (Table 2), there is always one relatively broad band in the low energy region, probably due to the superposition of the individual MLCT transitions of the two different ligands.

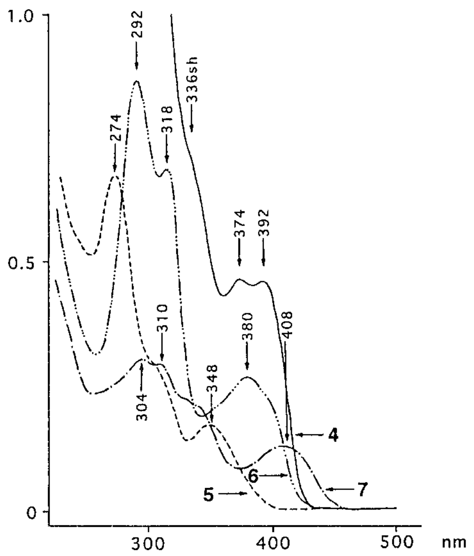


Figure 5. Absorption spectra in CH_2Cl_2 of Pd(bhq)$_2$ (**4**), Pd(phpy)$_2$ (**5**), Pd(thpy)$_2$ (**6**), and Pd(bthpy)$_2$ (**7**).

Table 4. Selected Distances (Å) and Angles (deg) in *cis*-Bis(benzo[*h*]quinoline) platinum(II), Pt(bhq)$_2$ (**1**)

Pt−N(1)	2.153(8)	Pt−N(2)	2.149(9)
Pt−C(11)	1.999(12)	Pt−C(24)	1.976(9)
N(1)−C(13)	1.339(14)	N(2)−C(26)	1.361(12)
C(11)−C(12)	1.414(15)	C(24)−C(25)	1.420(17)
C(12)−C(13)	1.420(13)	C(25)−C(26)	1.448(14)
N(1)−Pt−N(2)	102.8(3)	C(11)−Pt−C(24)	98.0(4)
N(1)−Pt−C(11)	79.4(4)	N(2)−Pt−C(24)	80.1(4)
N(1)−Pt−C(24)	174.9(4)	N(2)−Pt−C(11)	175.4(3)
PT−N(1)−C(1)	129.7(8)	Pt−N(2)−C(14)	130.1(8)
Pt−N(1)−C(13)	111.8(6)	Pt−N(2)−C(26)	112.0(6)
Pt−C(11)−C(10)	130.9(9)	Pt−C(24)−C(23)	131.1(9)
Pt−C(11)−C(12)	114.4(7)	Pt−C(24)−C(25)	114.6(7)
C(11)−C(12)−C(13)	116.5(10)	C(24)−C(25)−C(26)	116.5(9)
N(1)−C(13)−C(12)	116.7(8)	N(2)−C(26)−C(25)	115.0(10)

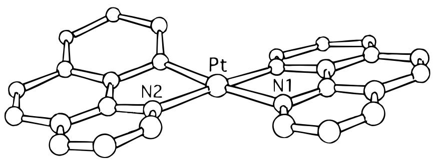
Table 5. Selected Distances (Å) and Angles (deg) in *cis*-Bis[2-(2′-thienyl)quinoline]platinum(II), Pt(thq)$_2$ (**3**)[a]

Pt−N(1)	2.156(2)	C(2)−C(14)	1.430(4)
Pt−C(11)	1.984(3)	C(11)−C(14)	1.389(4)
N(1)−C(2)	1.352(3)		
N(1)−Pt−C(11)	79.9(1)	Pt−N(1)−C(2)	112.5(2)
N(1)−Pt−N(1^{i})	105.3(1)	Pt−C(11)−C(14)	112.0(2)
N(1)−Pt−C(11^{i})	163.8(1)	N(1)−C(2)−C(14)	112.9(2)
C(11)−Pt−C(11^{i})	99.5(1)	C(2)−C(14)−C(11)	120.1(2)

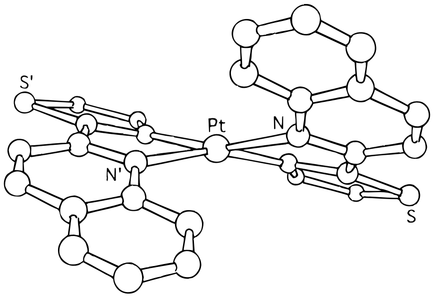
[a] Symmetry operations: (i) $x - y$, $-y$, $1.33333 - z$.

Crystal and Molecular Structure. Selected bond distances and angles in the two complexes **1** and **3** are given in Tables 4 and 5. The Pt−N and Pt−C distances in Pt(bhq)$_2$ (**1**) and Pt(thq)$_2$ (**3**) are very similar to those observed in related complexes.[16a,f,g]

Complexes **1** and **3** are *cis*-configured. For Pt(bhq)$_2$ (**1**), the *cis* configuration is clearly deduced from the metal to ligand bond lengths. The Pt−N distances are 2.153(8) and 2.149(9) Å, whereas the Pt−C distances are 1.999(12) and 1.976(9) Å. In Pt(thq)$_2$ (**3**), the same distances are 2.156(2) and 1.984(3) Å, respectively. Figure 6 illustrates the nonplanarity of complexes **1** and **3**. Pt(bhq)$_2$ (**1**) is much less distorted from planarity than Pt(thq)$_2$ (**3**). The benzo[*h*]quinoline ligand in **1**, involving atom N(2), is less planar than that involving atom N(1). The benzo moiety, involving atom C(24), is inclined by



Pt(bhq)$_2$ (**1**)



Pt(thq)$_2$ (**3**)

Figure 6. Front view of Pt(bhq)$_2$ (**1**) and Pt(thq)$_2$ (**3**).

16.2° to the pyridine moiety while in the second ligand the same dihedral angle is only 11.6°.

In Pt(thq)$_2$ (**3**), the molecule has crystallographic C_2 symmetry and is chiral. The space group $P3_221$ indicates a spontaneous splitting of the racemate on crystallization. The thioquinoline ligand is highly strained with the best plane through the thiophene ring inclined by 23.7° to the best plane through the phenyl moiety of the quinoline group. The latter is inclined to the best plane through the pyridine moiety by 6.8°. The mutual steric influence of the hydrogen atoms on C(8) and C(8′) [H(8)···H(8′) = 1.864 Å], causes the ligands to distort in a unilateral anti-twist fashion. The distortion from ideal square planar geometry in Pt(thq)$_2$ (**3**) is quite substantial, like it is in *cis*-bis(2,6-diphenylpyridine)platinum(II),[16f] which was the first "square planar" coordination species showing this type of chirality.

In the molecular packing of **1**, the Pt(bhq)$_2$ molecules, related by a center of symmetry, form dimeric units. A similar arrangement has been observed in Pt(phpy)$_2$, where the Pt···Pt distances were found to be 3.53 Å.[16a] However in **1**, the Pt···Pt distances of 4.30 Å are much larger, implying almost negligible interaction between the two metallic centers. In the crystal structure of **3**, the Pt(bhq)$_2$ molecules stack in the *c* direction about a right-handed screw axis, with a rotation of 120° and a translation of $^2/_3$ of *c*, that is 13.44 Å.

^{1}H NMR. Since all bis-homoleptic complexes of platinum(II) and palladium(II) possess a C_2 symmetry in solution, only one series of signals are observed for the two ligands. This is not the case for the bis-heteroleptic complexes, whose spectra show distinct signals for the two different ligands. For each ligand, the disappearance of the corresponding signal shows that a complexation occured at the expected position. The ^{1}H NMR chemical shifts values of the protons in the *ortho* positions to the M−C and M−N bonds are listed in Table 6. All H−C9, H−C3′, and H−C4′ signals are shifted downfield in comparison with the free ligand, indicating a π retrodonation between the metal and the carbons of the thienyl or the phenyl rings. This back-donation of electrons is also observed between the metal and the nitrogens of the pyridine rings in the case of Pt(phpy)$_2$, Pt(thpy)$_2$, and Pt(bthpy)$_2$. On the contrary, the signal for the protons in the *ortho* position of the metal−nitrogen bonds is shifted upfield in the case of Pt(bhq)$_2$, Pd(bhq)$_2$, Pd(phpy)$_2$, Pd(thpy)$_2$, and Pd(bthpy)$_2$, indicating that the pyridine rings act, this time, as σ donors rather than as π acceptors.

Table 6. ^{1}H NMR (CDCl$_3$) Chemical Shift Values (ppm) of Platinum(II) and Palladium(II) Complexes and the Related Free Ligands

	H−C2	H−C6	H−C9	H−C3′	H−C4′
H-bhq	9.29		7.70		
Pt(bhq)$_2$	9.19		8.52		
Pd(bhq)$_2$	9.12		8.47		
H-phpy		8.69		7.49	
Pt(phpy)$_2$[a,b]		8.79		8.08	
Pd(phpy)$_2$		8.59		8.08	
H-thpy		8.56			7.11
Pt(thpy)$_2$		8.61			7.69
Pd(thpy)$_2$		8.48			7.65
H-bthpy		8.64			
Pt(bthpy)$_2$[a]		8.77			
Pd(bthpy)$_2$		8.57			
H-thq					7.13
Pt(thq)$_2$[a]					7.81

[a] Solvent CD$_2$Cl$_2$. [b] Reference 32.

Solution Equilibria. The preparation of the mixed complex Pd(thpy)(phpy) described above, prompted us to compare the NMR spectra of this complex in chloroform solution and the mixtures of the two homoleptic species Pd(thpy)$_2$ and Pd(phpy)$_2$. It was found that neither solution is stable over an extended period of time. The two homoleptic complexes slowly form the heteroleptic species and vice versa.

$$\mathrm{Pd(thpy)_2 + Pd(phpy)_2 \rightleftharpoons 2Pd(thpy)(phpy)}$$

Equilibrium can be reached from both sides and was established within ca. 50 hours at room temperature. The equilibrium constant (measured at 20 °C, K = [Pd(thpy)(phpy)]^2/[Pd(thpy)$_2$][Pd(phpy)$_2$]) is approximately 1.8. This value, which is lower than the statistical equilibrium constant, indicates that the homoleptic complexes are thermodynamically slightly prefered.

Some mechanistic insight was obtained by examining the possibility of the following reaction:

$$\mathrm{Pd(C^\frown N)_2 + H\text{-}(C'^\frown N') \rightarrow Pd(C^\frown N)(C'^\frown N') + H\text{-}(C^\frown N)}$$

Mixed complexes were not formed in this way, excluding the possibility of a "free ligand" pathway for the exchange reaction. Furthermore the exchange is independent of solvent purity (CDCl$_3$), since highly purified chloroform gave the same results. However, the exchange is considerably slowed down in CH$_2$Cl$_2$. The exchange takes place between Pd(bhq)$_2$ and Pd(phpy)$_2$ as well as Pd(thpy)$_2$, but with a considerabely slower rate. Equilibrium is not reached within the time in which the compounds can be considered to be stable in CDCl$_3$.

The most probable explanation of this exchange is the direct bimolecular reaction involving a dimer transition state as intermediate, which can be either a bridged σ-bonded species or an associate with π−π interactions.

Acknowledgment. This work was supported by the Swiss National Science Foundation.

Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for Pt(bhq)$_2$ (**1**) and for Pt(thq)$_2$ (**3**) (11 pages).

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