

**Figure 2.** Spectroelectrochemical data for  $(\text{Cp})_2\text{Ti}(\text{bpy})$  in THF, TBAP ( $T = 0$ ; initial complex (---),  $T = 20$  s (---),  $T = 1$  min (—)): (a) spectral range of 220–320 nm, reduction at  $E = -1.10$  V; (b) spectral range of 220–320 nm, oxidation at  $E = 1.10$  V. Potentials are vs a Pt-wire pseudo reference electrode.

to 0.10 V, regeneration of  $(\text{Cp})_2\text{Ti}(\text{bpy})$  is observed, consistent with reversible electrochemical behavior.

Figure 2b shows the spectral changes that occur upon oxidation of  $(\text{Cp})_2\text{Ti}(\text{bpy})$  at 1.10 V. The absorbance above 295 nm decreases, while the absorption band at 282 nm increases with an isosbestic point at 295 nm. In addition, the bands at 238 and 243 nm show a slight increase in intensity. Re-reduction at 0.10 V does not produce any significant changes, and hence,  $(\text{Cp})_2\text{Ti}(\text{bpy})$  does not reform. This demonstrates that the oxidation is irreversible on longer time scales.

Although several metal–bipyridine complexes are known to exhibit multiple, reversible, one-electron-transfer steps,<sup>13,14</sup> the stability of  $(\text{Cp})_2\text{Ti}(\text{bpy})$  toward the addition or abstraction of electrons is surprising given the reactive nature of this species.<sup>2,6</sup> In addition, the potential for wave 1 is low, considering that  $(\text{Cp})_2\text{TiCl}_2$  is reduced at  $E_{1/2} = -0.81$  V vs SCE under identical conditions.<sup>15</sup> The spectral data do not allow distinction between a metal or ligand

center for the first reduction,<sup>12</sup> and MO calculations suggest such a distinction is not relevant.<sup>6</sup>

The spectral data for the first oxidation are complicated by the subsequent chemical reaction(s). A reasonable interpretation is that free bipyridine is generated, since the bands at 238, 243, and 282 nm all increase in intensity and bipyridine has absorption bands at 280 and 235 nm. Although the monocation is not stable under our conditions, it is interesting to note that isolation of  $[(\text{Cp})_2\text{Ti}(\text{bpy})]\text{PF}_6$  has been achieved<sup>7</sup> by addition of bpy to the Ti(III) complex  $[(\text{Cp})_2\text{TiCl}_2]$ . Further work in our laboratories aimed at elucidating the electron-transfer properties of related low-valent early-transition-metal organometallic complexes is in progress.

### $(\sigma\text{-Alkoxy carbonyl})(\sigma\text{-vinyl})\text{bis}(\text{triphenylphosphine})\text{-platinum(II)}$ Complexes, Possible Models for the Metal-Catalyzed Carbalkoxylation of Electrophilic Substrates

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**Summary:** Reaction of sodium alkoxides in the corresponding alcohol solvents with  $(\sigma\text{-vinyl})\text{Pt}^{\text{II}}$  carbonyl complexes, produced by the nucleophilic substitution of the corresponding labile triflate complexes with carbon monoxide, affords *trans*-( $\sigma\text{-alkoxy carbonyl})(\sigma\text{-vinyl})\text{Pt}^{\text{II}}$  complexes in good yield. Key spectral features and a single-crystal X-ray structure determination are described for these novel complexes. Heating between 60 and 80 °C in a variety of solvents results in acrylate esters via reductive elimination.

The palladium-catalyzed carbalkoxylation of a variety of electrophilic substrates, such as alkyl, aryl, and vinyl halides and triflates, to esters has become an important method for the synthesis of this valuable class of organic compounds,<sup>1</sup> with increasing recent attention given to the reaction of triflates.<sup>2</sup> In principle this reaction may proceed by two main mechanisms.<sup>3</sup> The first is CO in-

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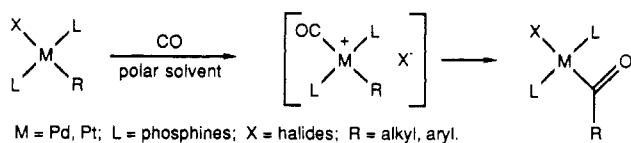
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(15) The first reduction of  $(\text{Cp})_2\text{Ti}(\text{bpy})$  is approximately 200 mV positive of  $(\text{Cp})_2\text{TiCl}_2$  when the differences between the reference electrodes are considered.

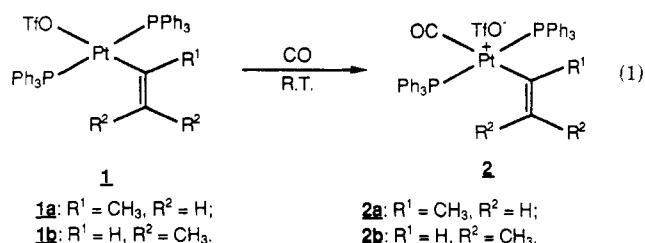
Scheme I



sertion into the Pd-C bond and formation of an acyl-palladium complex,<sup>1c,4</sup> which upon base-assisted alcoholysis yields the product ester.<sup>1c,3</sup> The second involves an alkoxycarbonyl intermediate,<sup>1f,k,5</sup> generated either by CO insertion into the M-O bond<sup>5a-c</sup> or by the nucleophilic attack of an alkoxide anion at the coordinated CO.<sup>3c,5d</sup> The product ester is then formed by reductive elimination. The first mechanism has been extensively studied with alkyl and aryl halides,<sup>1c,3,4</sup> and some aryl and alkylacylpalladium and alkylacylplatinum complexes have been isolated and characterized.<sup>4</sup> In contrast, vinylacylpalladium or vinylacylplatinum complexes have not been reported.<sup>6</sup> Moreover, the mechanism of carbalkoxylation of triflates as substrates has not been investigated, and there is no previous information on the accessibility of a carbonyl-organopalladium triflate complex and its subsequent reaction with alkoxide anion to form an alkoxycarbonyl species,<sup>3c</sup> in particular, an (alkoxycarbonyl)organopalladium complex.<sup>3b,d</sup> The analogous ionic carbonyl complexes have also been proposed, but not well established, as intermediates in the carbonyl insertion reaction of halide complexes (Scheme I).<sup>4c,e</sup> Recently, it was reported that platinum complexes can also catalyze the carbalkoxylation of organic halides under conditions similar to those for the palladium catalysts.<sup>7</sup> Initiated by our interest in the cross coupling reactions of platinum complexes as models of the analogous palladium systems,<sup>8</sup> we wish to report the ready synthesis and spectral characterization of stable *trans*-( $\sigma$ -alkoxycarbonyl)( $\sigma$ -vinyl)platinum(II) complexes. These vinylic complexes are unique since they might be models for the analogous palladium complexes, which have not been isolated and characterized but only postulated as intermediates in the palladium-catalyzed carbalkoxylation reaction.<sup>2d,e,3b-d</sup> Similar compounds with saturated organic ligands are known;<sup>5a-c</sup> however, in the case of *trans*-Pd(PMe<sub>3</sub>)<sub>2</sub>(PhCH<sub>2</sub>)(COOMe), obtained by reaction of Pd(PMe<sub>3</sub>)<sub>2</sub>(PhCH<sub>2</sub>)Cl with ClHgCOOCH<sub>3</sub>, the reductive-elimination reaction was completely inhibited due to the presence of the small and more basic PMe<sub>3</sub>.<sup>3b,d</sup>

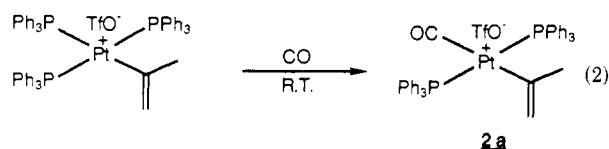
Carbonyl complexes **2a**<sup>9</sup> and **2b**<sup>10</sup> can be obtained by the

nucleophilic substitution of the labile triflate complexes **1a**<sup>8</sup> and **1b** with CO, respectively (eq 1). Specifically,

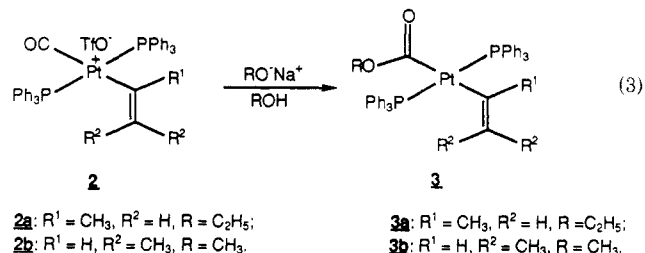


reaction of **1a** with 1 atm of CO in CH<sub>2</sub>Cl<sub>2</sub> at room temperature gives the cationic, *trans* carbonyl complex **2a** in 65% isolated yield. Similarly, reaction of **1b** with CO in toluene at room temperature affords complex **2b** in 50% isolated yield.

Both carbonyl complexes may be recrystallized from CH<sub>2</sub>Cl<sub>2</sub>-toluene solutions to give colorless microcrystals. Compound **2a** can also be obtained by the ligand substitution reaction of cationic ( $\sigma$ -CH<sub>2</sub>=C(CH<sub>3</sub>))(PPh<sub>3</sub>)<sub>3</sub>Pt<sup>+</sup>TfO<sup>-</sup> with CO (eq 2).<sup>9</sup>



Addition of excess sodium ethoxide to the suspension of carbonyl complex **2a** in absolute ethanol gives, after 2 h of stirring and workup, ethoxycarbonyl complex **3a** in 76% isolated yield (eq 3). Likewise, addition of excess



sodium methoxide to the methanol solution of complex **2b** immediately results in methoxycarbonyl complex **3b** in 69% isolated yield.

Both complexes **3a** and **3b** are stable, colorless microcrystalline solids that have been fully characterized on the basis of multinuclear NMR (Table I), IR, and FAB MS spectroscopy and elemental analysis<sup>11</sup> and, in the case of **3a**, confirmed by single-crystal X-ray diffraction.

The spectral data clearly establish the complexes to have a *trans* stereochemistry. The <sup>31</sup>P NMR resonances are singlets with <sup>195</sup>Pt satellites, and the <sup>13</sup>C NMR resonances at about 205 ppm are characteristic of the carbonyl carbon of the  $\sigma$ -bonded alkoxycarbonyl ligands. The IR spectra have a strong absorption at about 1625 cm<sup>-1</sup> due to the C=O stretch.

The single-crystal molecular structure of **3a** is illustrated

(11) Compound **3a**: mp 150–151 °C dec; IR (KBr) 3053 m, 2970 m, 2909 m, 1966 w, 1888 w, 1811 w, 1627 s, 1482 s, 1435 s, 1379 w, 1312 w, 1186 m, 1157 w, 1096 s, 1031 s, 856 m, 745 s, 694 s, 632 m cm<sup>-1</sup>; FAB MS *m/e* 788 (3%), 762 (18%), 761 (100%), 760 (90%), 759 (28%), 721 (15%), 720 (22%), 719 (85%), 718 (60%), 717 (78%), 457 (18%), 456 (65%), 455 (28%), 154 (86%). Anal. Calcd: C, 60.50; H, 4.84. Found: C, 60.41; H, 4.85. Compound **3b**: mp 158–159 °C dec; IR (KBr) 3055 m, 2896 m, 2836 w, 1965 w, 1900 w, 1823 w, 1625 s, 1482 m, 1434 s, 1359 w, 1312 w, 1271 w, 1185 m, 1097 s, 1024 s, 927 m, 745 s, 693 s, 628 m cm<sup>-1</sup>; FAB MS *m/e* 802 (3%), 777 (13%), 774 (60%), 721 (22%), 720 (39%), 719 (76%), 717 (42%), 459 (20%), 458 (15%), 457 (83%), 456 (85%), 455 (89%), 454 (21%), 453 (18%), 183 (100%). Anal. Calcd: C, 60.50; H, 4.84. Found: C, 60.41; H, 4.82.

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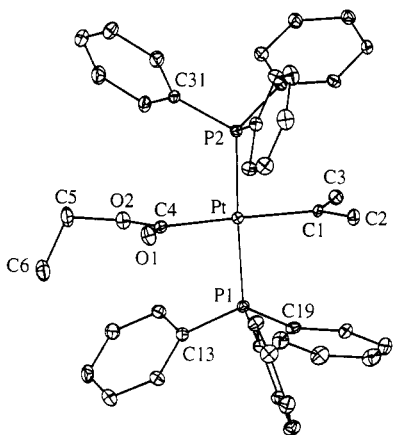
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(10) Compound **2b**: mp 143–144 °C dec; IR (KBr) 3058 m, 2899 w, 2089 s, 1614 w, 1482 m, 1436 s, 1264 s, 1223 m, 1150 s, 1099 s, 1031 s, 998 m, 752 m, 693 s, 637 s cm<sup>-1</sup>; FAB MS *m/e* 802 (5%), 776 (92%), 774 (100%), 773 (70%), 720 (61%), 717 (61%), 457 (28%), 456 (70%), 455 (65%). Anal. Calcd: C, 53.00; H, 3.92. Found: C, 53.07; H, 3.96.

Table I. NMR Data for Complexes 2b and 3<sup>a</sup>

compd	<sup>1</sup> H NMR	<sup>31</sup> P NMR <sup>b</sup>	<sup>13</sup> C NMR
2b	0.59 (t, <sup>5</sup> J <sub>PH</sub> = 1.8, 3 H)	16.8 (s, <sup>1</sup> J <sub>PtP</sub> = 2666)	26.4 (s, <sup>3</sup> J <sub>PtC</sub> = 47.8)
	1.02 (td, <sup>5</sup> J <sub>PH</sub> = 3.1, <sup>4</sup> J <sub>HH</sub> = 1.2, 3 H)		28.7 (s, <sup>3</sup> J <sub>PtC</sub> = 62.5)
	5.80 (t, <sup>3</sup> J <sub>PH</sub> = 4.9, 1 H)		121.5 (q, <sup>1</sup> J <sub>FC</sub> = 321.5) <sup>c</sup>
	7.5–7.7 (aromatics)		128.0 (t, <sup>1</sup> J <sub>PC</sub> = 30.8, <sup>2</sup> J <sub>PtC</sub> = 30.5)
			129.6 (t, <sup>3</sup> J <sub>PC</sub> = 5.6)
			131.3 (t, <sup>2</sup> J <sub>PC</sub> = 11.5) <sup>d</sup>
			132.8 (s)
			134.7 (t, <sup>2</sup> J <sub>PC</sub> = 6.2)
			141.2 (t, <sup>3</sup> J <sub>PC</sub> = 5.0) <sup>e</sup>
			179.6 (t, <sup>2</sup> J <sub>FC</sub> = 8.0) <sup>f</sup>
3a	0.44 (t, <sup>3</sup> J <sub>HH</sub> = 7.1, 3 H)	18.0 (s, <sup>1</sup> J <sub>PtP</sub> = 3243)	14.1 (s)
	0.85 (s, <sup>3</sup> J <sub>PtH</sub> = 21.1, 3 H)		30.7 (s, <sup>2</sup> J <sub>PtC</sub> = 21.3)
	2.76 (q, <sup>3</sup> J <sub>HH</sub> = 7.1, 2 H)		56.2 (s, <sup>3</sup> J <sub>PtC</sub> = 18.8)
	4.31 (dt, <sup>2</sup> J <sub>HH</sub> = 3.8, <sup>4</sup> J <sub>PH</sub> = 1.2, <sup>3</sup> J <sub>PtH</sub> = 27.8, 1 H)		119.5 (t, <sup>3</sup> J <sub>PC</sub> = 3.8) <sup>e</sup>
	5.30 (dt, <sup>2</sup> J <sub>HH</sub> = 3.8, <sup>4</sup> J <sub>PH</sub> = 1.4, <sup>3</sup> J <sub>PtH</sub> = 59.8, 1 H)		127.5 (t, <sup>3</sup> J <sub>PC</sub> = 5.3)
	7.3 (m, 18 H)		129.9 (s)
	7.7 (m, 12 H)		131.6 (t, <sup>1</sup> J <sub>PC</sub> = 28.0, <sup>2</sup> J <sub>PtC</sub> = 32.0)
			134.8 (t, <sup>2</sup> J <sub>PC</sub> = 6.1)
	161.7 (t, <sup>2</sup> J <sub>PC</sub> = 11.6) <sup>d</sup>		
	205.0 (t, <sup>2</sup> J <sub>PC</sub> = 12.6) <sup>g</sup>		
3b	0.48 (br s, 3 H)	19.1 (s, <sup>1</sup> J <sub>PtP</sub> = 3157)	24.7 (s, <sup>3</sup> J <sub>PtC</sub> = 40.5)
	0.98 (br d, <sup>4</sup> J <sub>HH</sub> = 1.0 Hz, 3 H)		29.9 (s, <sup>3</sup> J <sub>PtC</sub> = 46.8)
	2.45 (s, 3 H)		47.7 (s, <sup>3</sup> J <sub>PtC</sub> = 20.1)
	5.77 (br s, 1 H)		127.4 (t, <sup>3</sup> J <sub>FC</sub> = 5.2)
	7.3 (m, 18 H)		129.7 (s)
	7.6 (m, 12 H)		132.1 (t, <sup>1</sup> J <sub>PC</sub> = 28.1, <sup>2</sup> J <sub>PtC</sub> = 32.7)
			134.7 (t, <sup>2</sup> J <sub>PC</sub> = 6.1)
			136.6 (br s) <sup>e</sup>
			137.9 (t, <sup>2</sup> J <sub>PC</sub> = 12.9) <sup>d</sup>
			206.8 (t, <sup>2</sup> J <sub>PC</sub> = 12.1) <sup>g</sup>

<sup>a</sup>Spectra of 2b were recorded in CD<sub>2</sub>Cl<sub>2</sub>; spectra of 3 were recorded in CDCl<sub>3</sub>; shifts are in ppm, and *J* values are in Hz. <sup>b</sup>To external H<sub>3</sub>PO<sub>4</sub> (85%). <sup>c</sup>Carbon of triflate anion. <sup>d</sup>α-carbon of vinyl. <sup>e</sup>β-carbon of vinyl. <sup>f</sup>Terminal carbonyl carbon. <sup>g</sup>Carbonyl carbon of alkoxycarbonyl.

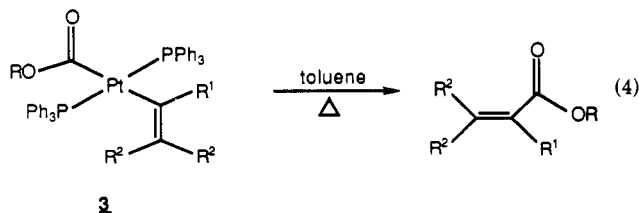


**Figure 1.** ORTEP representation of 3a. Selected bond distances (Å): Pt–P1 = 2.292 (1); Pt–P2 = 2.299 (1); Pt–C1 = 2.071 (6); Pt–C4 = 2.092 (6); C1–C2 = 1.306 (9); C1–C3 = 1.54 (1); C4–O1 = 1.205 (8); C4–O2 = 1.378 (8); C5–O2 = 1.480 (8). Selected bond angles (deg): P2–Pt–C1 = 89.3 (2); C1–Pt–P1 = 89.0 (2); P1–Pt–C4 = 91.3 (2); C4–Pt–P2 = 89.8 (2); Pt–C1–C2 = 121.9 (6); Pt–C1–C3 = 118.9 (5); C2–C1–C3 = 119.2 (6); Pt–C4–O1 = 123.4 (5); Pt–C4–O2 = 114.7 (5); O1–C4–O2 = 121.9 (6); C4–O2–C5 = 116.3 (5); P1–Pt–P2 = 174.94 (6); C1–Pt–C4 = 172.9 (3).

in Figure 1.<sup>12</sup> The geometry is very close to square planar with all four bond angles about the Pt center at 90 ± 1°. The vinyl carbon–Pt bond length of 2.071 (6) Å is normal for platinum–vinyl carbon bonds, as is the ethoxycarbonyl carbon–Pt bond length of 2.092 (6) Å. The ethoxycarbonyl

and vinyl moieties are coplanar but nearly perpendicular with an angle of 85.8° to the coordination plane. These features are similar to those in compatible alkoxycarbonyl complexes.<sup>13</sup>

These reactions not only provide the first systematic synthesis of (alkoxycarbonyl)(vinyl)platinum complexes<sup>14</sup> but also demonstrate a possible pathway for the Pd-catalyzed carbalkoxylation of organic triflates. The σ-vinyl group is introduced via oxidative addition of the vinyl triflate and the alkoxycarbonyl group by the nucleophilic attack of alkoxide anion at the CO ligand of the carbonyl vinyl complex, which is in turn formed via nucleophilic substitution of the labile triflate by carbon monoxide. These complexes, now available in a systematic fashion, are excellent models for the palladium-catalyzed carbalkoxylation as stable analogues to the reactive palladium species. Like the palladium species, the platinum complexes in this study readily undergo cross coupling upon heating at as low as 60 °C in many solvents such as toluene, chlorobenzene, nitrobenzene, etc., to yield substituted acrylic esters (eq 4). Further work is in progress, and the



3a: R<sup>1</sup> = CH<sub>3</sub>, R<sup>2</sup> = H, R = C<sub>2</sub>H<sub>5</sub>;

3b: R<sup>1</sup> = H, R<sup>2</sup> = CH<sub>3</sub>, R = CH<sub>3</sub>.

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(12) Crystal data for 3a: PtP<sub>2</sub>O<sub>2</sub>C<sub>45</sub>H<sub>40</sub>; colorless; crystal dimensions 0.31 × 0.27 × 0.21 mm; triclinic; *P*1̄; *a* = 9.696 (2) Å, *b* = 11.910 (3) Å, *c* = 16.069 (3) Å, α = 94.83 (2)°, β = 100.03 (2)°, γ = 91.64 (2)°, *V* = 1819 Å<sup>3</sup>, *z* = 2.0; no decay correction applied; μ = 40.156 cm<sup>-1</sup>; Mo Kα radiation at ambient temperature (16 ± 1 °C); 2θ limit 2.5–48.0°; reflections collected, 5745 unique, 4634 with *I* > 3σ(*I*); *R* = 0.0401, *R*<sub>w</sub> = 0.0540, GOF = 3.12.

detailed mechanistic studies will be the subject of future reports.

**Acknowledgment.** Financial support by the NSF (Grant No. CHE 8802622) and the loan of Pt by Johnson

Matthey are gratefully acknowledged.

**Supplementary Material Available:** Experimental details of the X-ray diffraction study of complex **3a**, including tables of crystallographic data, atomic positional and thermal parameters, and selected intramolecular distances and angles (18 pages). Ordering information is given on any current masthead page.

## Additions and Corrections

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Leo A. Paquette,\* Kevin J. Moriarty, and Robin D. Rogers: (1*R*)-(-)-Nopol as the Source of an Optically Pure Fused Cyclopentadienyl Ligand. Stereochemical Course of Complexation to Cyclopentadienyltitanium and -zirconium Dichloride Fragments. **1989**, 8, 1506.

The absolute configuration depicted for the structure of **10** in Figure 1 is incorrect. The correct assignment is properly given in the line drawing of **10** on page 1509. Refinement of the correct configuration has been carried out. The new atomic coordinates, bond distances and angles, and the final *R* values represent an inversion of all previous coordinates through 0, 0, 0. The new *R* values are *R* = 0.029, *R*<sub>w</sub> = 0.029, and *R*<sub>inverse</sub> = 0.030; the GOF is 1.34. The bond distances and angles were refined to values within 0.5σ of those published. These parameters with a revised ORTEP drawing have been deposited as supplementary material.

**Supplementary Material Available:** Listings of bond lengths and angles, final fractional coordinates, and thermal parameters and an ORTEP drawing (6 pages); a table of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

Ruth A. Bartlett, H. V. Rasika Dias, Marilyn M. Olmstead, Philip P. Power,\* and Kenneth J. Weese: Synthesis of the Monomeric HBTrip<sub>2</sub> (Trip = 2,4,6-*i*-Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) and the X-ray Crystal Structures of [HBMes<sub>2</sub>]<sub>2</sub> (Mes = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) and HBTrip<sub>2</sub>. **1990**, 9, 146.

On page 147, in the paragraph dealing with HBTrip<sub>2</sub> (**1**) in the Experimental Section, the following data should be added at the end. IR: ν(B-H) = 2465 cm<sup>-1</sup>.

We also wish to point out that the monomeric nature of **1** was established as well by Pelter and co-workers (see ref 14).

P. Espinet,\* E. Lalinde, M. Marcos, J. Perez, and J. L. Serrano\*: Liquid Crystals Based on Ortho-Palladated Azines: Nonplanar Mesogens. **1990**, 9, 555.

In the Experimental Section, on page 559, the first sentence in the paragraph on Pd<sub>2</sub>(μ-Br)<sub>2</sub>L<sub>2</sub> should read "A suspension of II...". On page 560, the first sentence in the paragraph on Pd<sub>2</sub>(μ-SCN)<sub>2</sub>L<sub>2</sub> should read "A suspension of II...".