

Cyclopalladated Complexes of Perylene Imine: Formation of Acetato-Bridged Dinuclear Complexes with 6,6- and 5,6-Membered Metallacycles

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Perylene-3-carbaldehyde (1) was condensed with 4-ethylaniline to give 3-perilenylmetilen-4'-ethylaniline (2). The metalation reaction of 2 with palladium acetate, in toluene at 60 °C, produced a mixture of palladium complexes where the two major components, 3 and 4, have been characterized as acetatebridged dimers. Complex 3 is made of two identical six-membered *endo* cyclometalated Pd(C^N) moieties, in which the palladium is bound to the *peri* site with *anti* arrangement. Compound 4 is the first example combining six- and five-membered metallacycles in a dinuclear compound and adopts an unusual *syn* arrangement of metal ligands. The X-ray structures of 3 and 4 show $\pi - \pi$ stacking of perylenyl rings, intermolecular for 3 and intramolecular for 4. The intramolecular $\pi - \pi$ stacking in 4 has a detrimental effect on luminescence. The imine 2 and all the palladium complexes exhibit fluorescence associated with the perylene fragment, with emission quantum yields, in solution at room temperature, in the range 0.04–0.13 (and emission lifetimes ~5 ns). The similarity of the luminescence spectral pattern of the imine and their metalated complexes to that of perylene, although red-shifted, strongly suggests a perylene-dominated intraligand $\pi - \pi^*$ emissive state, metal-perturbed by interaction of the palladium fragment.

Introduction

Cyclopalladated compounds, particularly those involving benzene derivatives, have been widely studied for their application in synthesis, catalysis, photochemistry, metallomesogen chemistry, asymmetric synthesis, resolution of racemic ligands, and other fields.^{1,2} The cyclometalation of N-donor ligands involving fused ring has been less explored and poses the question of regioselectivity of the orthometalation, due to the presence of nonequivalent metalation positions. There are a few reports on ligands based on two or three fused rings with one or two nonequivalent metalation sites, leading to fiveor six-membered metallacycles,3 but not on higher polyaromatic systems, such as perylene, which are of interest for their remarkable electro-optical properties.^{4–6} Perylene derivatives have been used in photovoltaic cells,⁷ xerography,⁸ optical switches,⁹ organic electronic devices such as organic light-emitting diodes (OLED),¹⁰ laser dyes,¹¹ and fluorescent collectors,¹² as tracers in fluorescence analytical assays,¹³ for charge transport in Langmuir-Blodgett films,14 for liquid crystals with special spectral properties,15 as fluorescent labeling reagents, or as fluorescent chemosensors,¹⁶ and recently, providing highly fluorescent J-aggregates.¹⁷

Complexes have been reported where the metal center is coordinated to a ligand that contains the perylene core¹⁸ or is π -bonded to the perylene core.¹⁹ In contrast, perylene-containing transition metal compounds with a direct σ -bond of the metal to the aromatic perylene core have been little studied. We have recently published platinum organometallic complexes of

perylene and perylene monoimide, with Pt σ -bonded directly to the perylene core,²⁰ and have found that the coordination of Pt has only a moderate quenching effect on the fluorescence

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attaching directly metal centers to aromatic cores of organic chromospheres is usually very detrimental for fluorescence.^{21,22} Only two Pd complexes have been reported, by the Rybtchinski group, obtained by oxidative addition to Pd(0). These contain Pd directly attached to the 1,7 aromatic positions of a perylene diimide.²³ The cyclopalladation reaction should offer a good opportunity to extend this family of derivatives.¹ Thus, exploring the functionalization of perylene by cyclometalation looks interesting. Although luminiscent cyclopalladated complexes are rare and, with very few exceptions,²⁴ emit only at low temperatures and with low efficiency,²⁵ the area has not yet been sufficiently explored.

The presence of the metal and their ancillary ligands in the perylene system should, additionally, offer an easy way to modify the optoelectronic properties of the material and could offer an efficient tool to create new structural and functional motifs, significantly widening the diversity of photofunctional systems available.

Results and Discussion

A general problem in the study of perylene derivatives is the poor solubility of the compounds. To circumvent this problem, we devised imine (2), with an ethyl group in the anilinic part, accessible from perylene through perylene-3-carbaldehyde (1). This ethyl group and the ancillary ligands in the metalated compounds should enhance the solubility of the compounds.

From imine **2** a five-membered ring with the metal σ -bonded to the perylene core in an *ortho*-(C2) position, or a six-membered ring with the metal bonded to the *peri*-(C4) position, can be expected depending on the metalation position (Figure 1), as found in structurally similar naphthyl, phenanthryl, and an-thracenyl derivatives.³ Five-membered chelate ring formation is generally favored over six-membered rings, but this seems a rather loose rule.¹

Synthesis of the Compounds. The conversion of perylene to imine was achieved in two steps. The starting perylene was formylated in the 3 position,²⁶ and the perylene-3-carbalde-hyde (1) was condensed with 4-ethylaniline, in toluene at room

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Figure 1. Metalation sites for the 3-substituted perylene.

Scheme 1



temperature, to give 2 in good yield (Scheme 1). In the NMR spectrum of 2, the signal of the imine proton (HC=N) appears at rather low-field shift (9.08 ppm), showing the deshielding induced by the perylenyl group. The orthopalladation reaction of 2 with palladium acetate, in toluene at 60 °C for 2 h, produced a deep purple suspension consisting of a mixture of palladium complexes (Scheme 1). The two major components, 3 and 4, could be separated in toluene (see Experimental Section) and are acetate-bridged dimers. Complex 3, more soluble in toluene, is made of two identical six-membered endo cyclometalated $Pd(C^N)$ moieties, in which the palladium is bound to the peri site. Compound 4 is a mixture of two isomers (syn and anti) of a structure containing one six-membered and one five-membered endo metallacycle. The separation of the two isomers of **4** by recrystallization or chromatography techniques was not possible.

The source of isomerism in these dinuclear complexes is the fact that acetato bridges force the molecule into nonplanar open-book (or butterfly) structures with syn or anti arrangements depending on the arrangement of the imine moieties in the dimer (Figure 2). The ¹H NMR spectra of the crude product initially isolated confirmed the presence of a single isomer of 3, the anti isomer, and two isomers of 4 in approximately 4:1 syn:anti ratio (see Figure 3). As expected, the spectrum of 3 displays one singlet for the two acetate groups at 1.35 ppm and one ethyl group, whereas for 4 two signals for the acetates (1:1) and two ethyl groups (1:1) are observed for each of the two isomers. Therefore there are two singlets at 2.39 and 1.30 ppm corresponding to the two acetates of the 4-syn isomer and two singlets at 1.68 and 1.52 ppm belonging to the acetate group of the 4-anti isomer. The very different chemical shift of the two acetate groups in 4-syn is due to the anisotropic shielding induced on one of them by the close EtC₆H₄ groups



Figure 2. Possible isomers (enantiomers are not shown) depending on the combination of ring size and coordination isomerism. The number of members of the cyclometalated rings is indicated inside each ring.

of the imine (see Figure 4). The structures of **3**-*anti* and **4**-*syn* were further supported by X-ray diffraction studies (see later).

The formation of 3 or 4 is irreversible, and the isomers are inert toward isomerization. Thus, heating 3 in toluene solution does not produce any 4. However, some control of the direction of metalation can be achieved changing the reaction conditions, as shown in synthetic experiments checked by NMR. Thus, in THF at 30 °C for 48 h the molar ratio obtained is $3:4 \approx 1:1$, and in THF at 50 °C for 24 h, 4 is obtained quite preferently (molar ratio $3:4 \approx 1:10$). In both solvents the metalation to six-membered cycles is more favorable, although in the latter conditions the difference is small.²⁷ It is remarkable that all the five-membered moieties formed in the metalation are found in the form of 6,5-dimers (besides 6,6-dimers accounting for the excess of six-membered moieties in the product), while no 5,5-dimers are observed. This suggests that the combination $2 \times (6,5)$ in a dimer is far more favorable than the nonobserved (5.5) plus the corresponding (6.6).

X-ray Diffraction Crystal Structures. X-ray quality crystals could be obtained for the dimers. Their molecular structures were determined by single-crystal X-ray diffraction methods and are shown in Figure 5. Selected bond lengths and angles are collected in Table 1.

For complex 3 the crystal structure shows two six-membered endo palladacycles (Figure 2). Reports of other X-ray structures with six-membered palladacycles are scarce: a few complexes derived from Schiff bases, with the ligand coordinated through a CH_2 (sp³) carbon, and only one complex that contains a metalated aromatic (sp^2) carbon atom, found in an endocyclic six-membered cyclopalladated imine derived from anthracene.¹ In the structure reported here, the dimeric molecules pack in pairs via $\pi - \pi$ stacking of two perylene rings, making nonequivalent the two Pd atoms of each dimer. The plane-to-plane stacking distance is 3.511 A. The coordination around Pd(1) and around Pd(2) is essentially planar, as also are the $\pi - \pi$ stacked perylenes, but both are not coplanar. Both palladacycles adopt an envelope-like conformation. Five of the six ring atoms are almost coplanar, while the Pd atom is situated out of the plane (0.3955 Å for Pd(1) and 0.5709 Å for Pd(2)).

⁽²⁷⁾ The proportion of 6- and 5-metallacycles formed would afford approximate metalation rates of 9:1 in toluene at 60 °C and 6:5 in THF at 50 °C.



Figure 3. ¹H NMR spectra (aliphatic zone) of 3 (top) and 4 (bottom).

In contrast, there is a much bigger distortion in the two perylene fragments not involved in stacking, so that the perylene is far from planar, particularly in the "naphthalene" moiety bonded to Pd(1). A more detailed quantitative description is given in the Supporting Information.

For compound 4-syn the X-ray structure unambiguously confirms two unusual features. First of all, the molecule contains two dissimilar $Pd(C^N)$ moleties corresponding to both possibilities of metalation: a perylene imine metalated at

the *ortho*-C(2) to yield a five-membered *endo* metallacycle and another metalated at the *peri*-C(4) position, giving a sixmembered *endo* metallacycle. Moreover, the two imines adopt a *syn* arrangement.²⁸ The Pd(2) atom, with a five-membered metallacycle, shows a slightly distorted square-planar geometry (the maximum deviation is represented by the angle C(32)–Pd-(2)–N(2) of 81.1° and the angle N(2)–Pd(2)–O(4) of 97.06°) and is approximately coplanar with the perylene fragment (dihedral angle between them, 3.06°). The other palladium atom, Pd(1), is bound to C(7) (the *peri* position perylene fragment), to N(1) of the imine group, and to O(1) and O(3) of two different acetate groups. The coordination around the Pd(1) is essentially planar, and the coordination angles are close to the 90°. The conformation of the six-membered metallacycle

⁽²⁸⁾ To the best of our knowledge, only one example has been reported of a *syn* disposition of the metalated imine ligands: Fernández, A.; Vázquez-García, V.; Fernández, J. J.; López-Torres, M.; Suárez, A.; Castro-Juiz, S.; Vila, J. M. *Eur. J. Inorg. Chem.* **2002**, 2389.



Figure 4. Anisotropic shielding of one of two acetate groups in 4-syn by the close EtC₆H₄ groups of the imine.



Figure 5. ORTEPs of the crystal structures of 3-*anti* and 4-*syn*. The ellipsoids are shown at 30% probability (H atoms are omitted for clarity).

is as expected for a six-membered ring (see above). The Pd atom is situated 0.6741 Å out of the plane C(1)–C(6)–C(7)–C-(21)–N(1). In spite of these differences, the two perylene fragments display fairly good π – π stacking. The angle between the planes is 1.6°, and the average stacking separation is 3.48 Å (Figure 7).

As for other features found in the structures of 3 and 4, they are quite normal. The Pd-Pd distances are 2.923 Å in 3 and 2.907 Å in 4, both within the range observed in similar structures containing bridging acetate groups. The Pd-O bond lengths to the acetate groups are in the range

 Table 1. Selected Interatomic Distances (Å) and Angles (deg) for the Complexes 3-anti and 4-syn

	1 2			
	3-anti	4 -syn		
Pd(1)-C(7)	1.980(6)	1.972(6)		
Pd(1) - N(1)	1.997(4)	1.985(5)		
Pd(1) - O(1)	2.068(4)	2.048(4)		
Pd(1) - O(3)	2.144(4)	2.152(4)		
Pd(2) - C(32)		1.962(5)		
Pd(2) - C(37)	1.964(6)			
Pd(2) - N(2)	2.003(5)	2.031(5)		
Pd(2) - O(2)	2.060(4)	2.055(4)		
Pd(2) - O(4)	2.143(4)	2.123(4)		
Pd(1) - Pd(2)	2.923	2.907		
C(7) - Pd(1) - N(1)	91.4(2)	91.0(2)		
C(7) - Pd(1) - O(1)	92.34(19)	91.19(19)		
N(1) - Pd(1) - O(1)	174.77(17)	174.68(17)		
C(7) - Pd(1) - O(3)	177.44(19)	174.89(18)		
N(1) - Pd(1) - O(3)	90.81(17)	91.26(18)		
O(1) - Pd(1) - O(3)	85.41(16)	86.98(17)		
C(32) - Pd(2) - N(2)		81.1(2)		
C(37) - Pd(2) - N(2)	91.6(2)			
C(32) - Pd(2) - O(2)		92.8(2)		
C(37) - Pd(2) - O(2)	90.5(2)			
N(2) - Pd(2) - O(2)	177.44(18)	172.84		
C(32) - Pd(2) - O(4)		176.32(19)		
C(37) - Pd(2) - O(4)	175.9(2)			
N(2) - Pd(2) - O(4)	92.40(17)	97.06(18)		
O(2) - Pd(2) - O(4)	85.47(16)	88.77(17)		







Figure 7. Intramolecular π -stacking of the perylene groups in **4**-*syn*.

2.048–2.068 Å for bonds *trans* to N and in the range 2.123–2.152 Å for bonds *trans* to C, as expected from their dissimilar *trans* influences.

The fact that complex 4-syn is the first example of a sixand five-membered metallacycle in a dinuclear compound, and combining this with an unusual syn arrangement of metal ligands, suggests that this might not be by chance. It

Table 2. UV–Visible Absorption and Emission Data for Perylene-3-carbaldehyde (1), the Imine 2, and Their Palladium Complexes 3 and 4, in Chloroform at 298 K

compd	λ (nm) (10 ⁻³ ε)/dm ³ mol ⁻¹ cm ⁻¹	λ_{ex} /nm	$\lambda_{\rm em}/{\rm nm}$	Φ^a	$ au^b/\mathrm{ns}$
1	240 (26), 263 (30.6), 425 (15), 449 (24), 476 (26.4)	467	516, 553	0.53	
2	243 (34.5), 263 (51.6), 425 (17), 449 (33.8), 477 (33.8)	447	510	0.13	5.29
3	241 (65.2), 276 (39.1), 359 (16.6), 487 (21,1), 519 (34.3), 553 (34.9)	516, 551	588, 634	0.09	0.87 (94.9) 3.37 (5.1)
4	243 (62.6), 361 (14.4), 492 (26.6), 522 (38.4), 557 (31.6)	526, 542	586, 634	0.04	0.95 (78.9) 8.31 (21.1)

^a Quantum yield. ^b Fluorescence lifetimes. Decays were biexponential; numbers in parentheses indicate the relative amplitude of components.



Figure 8. Absorption spectra, recorded in CHCl₃ solution $(\sim 10^{-5} \text{ M})$ at room temperature, for perylene-3-carbaldehyde (1) and imine 2 and their dinuclear palladium complexes 3 and 4.

looks that the combination of the slight flexibility of the sixmembered metallacycle with the rigidity of the five-membered metallacycle strongly favors a good a $\pi - \pi$ stacking with additional stabilization of the molecule, which in part compensates the usual preference for the *anti* arrangement found in the other products of the reaction. Thus, for the 6,6 complexes only the *anti* arrangement is observed; for the 6,5 complexes, both *syn* and *anti* are formed, but the *syn* is the major isomer (4:1).

Photophysical Studies. a. UV–Vis Absorption Spectra. The UV–vis absorption and emission spectra of the aldehyde, imine, and palladium(II) complexes of dilute solutions in chloroform ($c \approx 10^{-5}$ M) are summarized in Table 2. On the other hand, the absorption spectra of **3** and **4** are compared with those of perylene-3-carbaldehyde (1) and perylene imine (2) in Figure 2. By similarity to the absorption bands of the free imine ligand, the high-energy absorption bands at 250–300 nm are tentatively assigned to the intraligand transitions. In the palladium complexes the low-energy bands exhibit red shifts most likely associated with the disturbance of the π - π * transitions by the metal and appear at about 540 nm.

The UV-vis spectra of perylene-3-carbaldehyde (1) and imine 2 (Figure 8) are very similar, with two intense absorptions assigned to perylene $\pi - \pi^*$ transitions, namely, a first band in the ultraviolet in the range 230–320 nm with two maxima at 240 and 263 nm and a second band in the visible region in the range 380–530 nm with one shoulder and two peaks at 425, 449, and 476 nm, respectively. These lowest energy bands have similar band shapes that resemble the spectrum of perylene (a vibronic structure with a vibrational spacing of ~1300 cm⁻¹ due to the stretching frequency of the C=C bond of the aromatic systems), with a moderate red shift of ca. 1800 cm⁻¹ relative to perylene.

Similar absorption patterns are observed in the dinuclear complexes 3 and 4, supporting that the perylene imine chromophore is largely responsible for the structured $\pi - \pi^*$ transitions between 435–590 nm. The lowest energy bands are significantly red-shifted about 2900 cm⁻¹ relative to those of



Figure 9. Emission spectra recorded in $CHCl_3$ solution (10^{-5} M) at room temperature.

the free imine, showing that when palladium is σ -bonded to the perylene fragment, a noticeable perturbation in the electronic spectrum of the perylene imine occurs, due to the interaction between the Pd orbitals and the perylene π -system. It is noticeable that the relative peak intensity of the dinuclear complex **4** is different from that of complex **3**. The absorption maximum of **4** is at 522 nm, which is blue-shifted relative to that of **3** (absorption maximum at 553 nm). This intensity change can be attributed to the formation of a face-to-face stacked perylene fragment.²⁹ Another difference observed upon complexation is the appearance of weak absorptions in the range 335–380 nm, with extinction coefficients of 14.4 × 10^3 M^{-1} (for **4**) and $16.6 \times 10^3 \text{ M}^{-1}$ (for **3**), tentatively assigned to intraligand $\pi - \pi^*$ transitions.

Moreover, the lowest energy bands of **3** are only slightly sensitive to solvent polarity, as they are red-shifted by less than 200 cm⁻¹ upon changing the solvent from toluene to chloroform (see Figure S3 in the Supporting Information). This behavior suggests that these bands are most probably linked to electronic $\pi - \pi^*$ transitions within the ligand, rather than to charge transfers.

b. Luminescence Spectra. The luminescence spectra of the perylene-3-carbaldehyde (1), perylene imine (2), and the palladium complexes at room temperature in chloroform are listed in Table 2. All complexes exhibit luminescence in solution (which is unusual for Pd complexes) and display emission bands with scarcely defined vibronic structures in the range 550–700 nm (see Figure 9), which can be correlated to those well-defined for perylene at about 425–525 nm and also scarcely defined for 1 and 2 at about 450–625 nm. The structurally similar luminescence spectra of all these cyclometalated complexes strongly suggest a ligand-dominated emissive state, which can be assigned as intraligand $\pi - \pi^*$ transitions disturbed by the metal. On the basis of similar Stokes shifts from absorption to emission for 2 and for the

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complexes (less than 1000 cm^{-1}), the luminescence observed can be assigned to $\pi - \pi^*$ fluorescence, which is supported by the fact that the emission properties remain unchanged in the presence of air, and further confirmed by their emission lifetimes (in the range 0.8–9 ns; see Table 2).

Study of Quantum Yields. The emission quantum yields, Φ , for 1–4, measured in dichloromethane at room temperature, are in the range 0.04–0.53 (Table 2). The fluorescence quantum yields of 1 and 2 were determined relative to perylene in methanol ($\Phi_{fl} = 0.92$), using an excitation wavelength 434 nm. The palladated complexes were determined using cresyl violet in methanol ($\Phi_{fl} = 0.54$), with an excitation wavelength of 540 nm.

The fluorescence quantum yields of the perylene-3-carbaldehyde (1)(0.53) is smaller than that of pervlene and similar to 3-aminoperylene.³⁰ The fluorescence intensity of the imine 2 is significantly lower (0.13) than the emission of the perylene moiety, probably because the fluorescence of the perylene moiety is quenched by a photoinduced intramolecular electron transfer (PET) process.³¹ For the cyclopalladated complexes **3** and 4 the emission quantum yield is somewhat lower than for the imine precursor, but still on the same order of magnitude, which for Pd complexes is notably high. The Pd quenching effect is lower than usual probably because the interaction of Pd with the pervlene is mainly a σ interaction involving the 4d_z orbital of Pd, with very little π component. Due to the high stabilization of the d orbitals at the end of the transition metal series,³² the π back-bonding component of this bond, which should involve donation from the π orbitals of Pd to the π^* orbitals of the aryl, is expected to be small. The same effect has been observed in related Pd²³ and Pt systems.²⁰

The difference between the emission quantum yields for **3** $(\phi_{\rm fluo} = 0.09)$ and **4** $(\phi_{\rm fluo} = 0.04)$ is remarkable and can be related to their structure, since the two aromatic rings of perylene in **4** have an intramolecular $\pi - \pi$ stacking interaction between them, which induces a loss of luminescence intensity,^{28b-c} not observed in **3**, where the *anti* arrangement of the imines prevents that interaction.

Conclusions

The metalation of 3-perilenylmetilen-4'-ethylaniline with palladium acetate shows preference for the *peri* position with respect to the imine group, giving six-membered metallacycles, but metalation at the *ortho* position, giving five-membered metallacycles, also occurs. The combination of 5,5-metallacycles into dimers is not observed: all the five-membered moieties make part of the 6,5-dimers, suggesting that this combination in the dimer is energetically favored. The structure of the major isomer of 4, 4-*syn*, compared to that of 3, suggests that the combination 6,5 into acetato-bridged dimers might increase the intramolecular $\pi - \pi$ interactions and also reduce slightly the Pd-Pd distance. In contrast with the majority of palladium complexes reported so far, which usually emit only at low temperatures, complexes 3 and 4

exhibit fluorescence associated with the perylene system in solution at room temperature. The intramolecular $\pi - \pi$ interactions observed for 4-syn, which persist in solution, explain the difference between the absorption spectra of 3 and 4 and the lower emission quantum yields for 4.

Experimental Section

Materials and General Methods. All reactions were carried out under dry nitrogen. The solvents were purified according to standard procedures. C, H, N analyses were carried out on a Perkin-Elmer 2400 microanalyzer. IR spectra (cm⁻¹) were re-corded on a Perkin-Elmer FT-1720X spectrometer. ¹H NMR spectra were recorded on Bruker AC 300 or Bruker 400 MHz spectrophotometers in CDCl₃, with chemical shifts referred to TMS. UV-vis absorption spectra were obtained on a Shimadzu UV-1603 spectrophotometer, in chloroform solution (1 \times 10^{-5} M). Luminescence data were recorded on a Perkin-Elmer LS-luminescence spectrometer, in CHCl₃ (1 × 10^{-5} M). Luminescence quantum yields were obtained at room temperature using the optically dilute method (A < 0.1) in degassed dichloromethane (quantum yield standards were perylene in methanol $(\Phi_{\rm fl} = 0.92)^{33}$ and violet of cresyl violet in ethanol $(\Phi_{\rm fl} = 0.54)^{34}$ and using an excitation wavelength of 434 and 540 nm, respectively, in dichloromethane). The emission lifetime measurements were carried out with a Lifespec-red picosecond fluorescence lifetime spectrometer from Edinburgh Instruments. As excitation sources two diode lasers, with 405 and 470 nm nominal wavelengths, were used. The first wavelength (405 nm) has a pulse width of 88.5 ps, with a typical average power of 0.40 mW. The second wavelength (470 nm) has a pulse width of 97.2 ps, and its typical average power is 0.15 mW. The pulse period is 1 μ s, and the pulse repetition frequency is 10 MHz. The monochromator slit is 2 nm. The instrument response measure at hwhm (half-width at half-maximum) was below 350 ps. The technique used is "time-correlated single-photon counting" (TCSPC).

Preparation of Perylene-3-carbaldehyde (1). This compound was synthesized by following the procedure reported before.²⁶ UV–vis (CHCl₃) λ_{max} (nm) (10⁻³ ε)/(M⁻¹ cm⁻¹) = 240 (26), 263 (30.6), 449 (24), 476 (26.4). Fluorescence emission (CHCl₃, λ_{exc} = 467 nm) λ_{em} = 516 nm, 553 nm.

Preparation of 3-Perilenylmetilen-4'-ethylaniline (2). To a mixture of perylene-3-carbaldehyde (1) (0.439 g, 1.56 mmol) in toluene (70 mL) under a nitrogen atmosphere were added 4-ethylaniline (0.23 mL, 1.85 mmol), zeoliths, and a small crystal of monohydrated p-toluensulfonic acid. The orange mixture was stirred in the dark at room temperature overnight, then filtered through a Kieselguhr filter, and orange crystals were obtained by cooling the toluene solution (0.400 g, 67%) at -20 °C. Anal. Calcd for C₂₉H₂₁N (383.49): C, 90.82; H, 5.51; N 3.65. Found: C, 90.50; H, 5.45; N, 3.55. ¹H NMR (300.13 MHz, CDCl₃): δ 9.08 (s, 1H, HC=N, 8.90 (d, J = 8.3 Hz, 1H), 8.31-8.25 (m, 4H), 8.12 (d, J =7.9 Hz, 1H), 7.74 (t, J = 8.3 Hz, 2H), 7.64 (t, J = 7.9 Hz, 1H), 7.53 $(t, J = 8.3 \text{ Hz}, 2\text{H}), 7.28 \text{ (s, AA'BB' system, 4H, C}_{6}H_{4}), 2.72 \text{ (q, })$ J = 7.9 Hz, 2H, CH_2CH_3), 1.30 (t, J = 7.9 Hz, 3H, CH_2CH_3). UV-vis (CHCl₃) λ_{max} (nm) (10⁻³ ε)/ (M⁻¹ cm⁻¹) = 243 (34.5), 263 (51.6), 449 (33.8), 477 (33.8). Fluorescence emission (CHCl₃, $\lambda_{\rm exc} = 447 \text{ nm}$) $\lambda_{\rm em} = 510 \text{ nm}$.

Preparation of 3 and 4. A mixture of 2(0.370 g, 0.96 mmol) and Pd₃(OAc)₆ (0.196 g, 0.87 mmol) in toluene (20 mL) was stirred under a nitrogen atmosphere at 60 °C for 2 h. The reaction mixture was cooled to room temperature, and the two compounds could be separated (3 is in the solution and 4 is insoluble).

The purple filtrate solution was evaporated, and the final residue was washed with diethyl ether ($4 \times 10 \text{ mL}$) and acetone

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 $(2 \times 5 \text{ mL})$. The residue was dried under vacuum to obtain compound **3** as a dark purple solid (0.197 g, 41%). Anal. Calcd for C₆₂H₄₈N₂O₄Pd₂ (1097.91): C, 67.71; H, 4.58; N 2.55. Found: C, 67.07; H, 4.10; N 2.48. ¹H NMR (400 MHz, CDCl₃): δ 8.45 (d, J = 7.9 Hz, 2H), 8.33–8.26 (m, 4H), 7.99 (d, J = 8.3 Hz, 2H), 7.90, 6.75 (AA'BB' system, J = 8.1 Hz, 8H), 7.78 (d, J = 7.9 Hz, 2H), 7.65 (m, 4H), 7.07–7.03 (m, 6H), 6.67 (d, J = 7.9 Hz, 2H), 2.60 (q, J = 7.5 Hz, 4H, CH₂CH₃), 1.35 (s, 6H, CH₃), 1.20 (t, J = 7.5 Hz, 6H, CH₂CH₃). Fluorescence emission (CHCl₃, $\lambda_{\text{exc}} = 516, 551 \text{ nm} \lambda_{\text{em}} = 588 \text{ nm}, 634 \text{ nm}.$ UV–vis (CHCl₃) λ_{max} (nm) (10⁻³ ε)/(M⁻¹ cm⁻¹) = 241 (65.2), 276 (39.1), 359 (16.6), 519 (34.3), 553 (34.9).

The precipitate was collected by filtration, washed with toluene $(2 \times 3 \text{ mL})$, and dried under vacuum to obtain compound **4** as a mixture of isomers *syn/anti* with ratio 4:1 (0.150 g, 31%). Anal. Calcd for C₆₂H₄₈N₂O₄Pd₂ (1097.91): C, 67.71; H, 4.58; N, 2.55. Found: C, 67.43; H, 4.40; N, 2.35. ¹H NMR (400 MHz, CDCl₃) *syn* + *anti* isomers: δ 8.5–8.2 m, 8.0–7.3 m 7.1–6.3 m. (The aromatic signals for **4** are too complex to be reported in detail. This part of the spectrum is given in the SI, as Figure S1.)

syn isomer: $\delta 2.85$ (q, J = 7.5 Hz, 2 H, CH₂CH₃), 2.58 (q, J = 7.8 Hz, 2H, CH₂CH₃), 2.39 (s, 3H, CH₃), 1.44 (t, J = 7.5 Hz, 3H, CH₂CH₃), 1.30 (s, 3H, CH₃), 1.18 (t, J = 7.5 Hz, 3H, CH₂CH₃); anti isomer: $\delta 2.60$ (q, J = 7.5 Hz, 2H, CH₂CH₃), 2.50 (q, J = 7.8 Hz, 2H, CH₂CH₃), 1.68 (s, 3H, CH₃), 1.52 (s, 3H, CH₃), 1.21 (t, J = 7.6 Hz, 3H, CH₂CH₃), 1.11 (t, J = 7.6 Hz, 3H, CH₂CH₃), 1.11 (t, J = 7.6 Hz, 3H, CH₂CH₃), 2.50 (q. J = 7.8 Hz, 2H, CH₂CH₃), 1.68 (s, 3H, CH₃), 1.52 (s, 3H, CH₃), 1.21 (t, J = 7.6 Hz, 3H, CH₂CH₃), 1.11 (t, J = 7.6 Hz, 3H, CH₂CH₃), UV-vis (CHCl₃) λ_{max} (nm) (10⁻³ ε)/(M⁻¹ cm⁻¹) = 243 (62.6), 361 (14.4), 522 (38.4), 553 (30.1). Fluorescence emission (CHCl₃, $\lambda_{exc} = 516$, 551 nm): $\lambda_{em} = 588$ nm, 634 nm.

X-ray Crystal Structure Analysis. Single crystals of 3.2THF suitable for X-ray diffraction studies were obtained from slow

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diffusion of hexane into a THF solution of the crude products at room temperature. Crystals from 4 were grown from slow diffusion of Et₂O into a dichloromethane solution of the product at -20 °C. Data were taken on a Bruker AXS SMART 1000 CCD diffractometer, using ϕ and ω scans, Mo K α radiation (λ = 0.71073 Å), a graphite monochromator, and T = 298 K. Raw frame data were integrated with the SAINT³⁵ program. Structures were solved by direct methods with SHELXTL³⁶ Semiempirical absorption correction was made with SADABS.³⁷ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms, with a common thermal parameter. All calculations were made with SHELXTL. In the structures of compounds 3 and 4 there is an incipient disorder in the ethyl groups of the imine ligands that could not be satisfactory modeled. Compound 3 crystallized with two molecules of disordered THF. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications with the following deposition numbers: CCDC 797245 and 797246 for complexes 3 and 4, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif. A table with the X-ray structure data is provided in the SI.

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Supporting Information Available: ¹H NMR spectra (aromatic zone) of **3** and **4**, Table S1 with X-ray structure data, a more detailed quantitative description of the crystal structures of **3** and **4**, absorption spectra of **3** in different solvents, and emission spectra of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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