Inorg. Chem. **2008**, *47*, 481–486

Inorganic Chemistry

Article

Strongly Luminescent Palladium(0) and Platinum(0) Diphosphine Complexes

Taro Tsubomura,* Yasuhiro Ito, Satoshi Inoue, Yu Tanaka, Kenji Matsumoto, and Toshiaki Tsukuda

Department of Materials and Life Science, Seikei University, Kichijoji-Kitamachi,
Musashino, Tokyo 180-8633, Japan

Received March 12, 2007

The synthesis, structure, and photoluminescence of palladium(0) and platinum(0) complexes containing biarydiphosphines, biphep (biphep = 2,2′-bis(diphenylphosphino)-1,1′-biphenyl) and binap (binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) have been studied. X-ray structure analysis of [Pt(biphep)$_2$] revealed the distorted-tetrahedral geometry of the complex. The photophysical properties of the three complexes [Pd(biphep)$_2$], [Pt(biphep)$_2$], and [Pd(binap)$_2$] were investigated and compared with that of the previously reported [Pt(binap)$_2$] complex. The [Pd(biphep)$_2$] complex shows the strongest luminescence with a high quantum yield (38%) and a long lifetime (3.2 μs) in a toluene solution at room temperature. The luminescence should be due to metal-to-ligand charge transfer excited states. At room temperature, radiative rate constants of the four complexes show similar values. The difference in the luminescent properties should reflect the different nonradiative rate constants of the complexes. The temperature-dependence of the luminescence spectra and lifetime of the complexes were also discussed.

Introduction

Luminescent metal complexes have experienced a remarkable development since the demonstration of the advantage of triplet emitter over singlet emitter for organic light-emitting diode devices by Thompson et al.[1]

A large number of iridium(III)[2] and platinum(II)[3] complexes that serve as highly luminescent materials have been reported. On the other hand, the study of luminescent palladium complexes is rare;[4] the low energy level of d−d excited states is believed to be the reason for the nonluminescent nature of the Pd(II) complexes compared with the Pt(II) complexes. Recently, a significant research effort has focused on the photophysics of d^{10} metal complexes[5] such as gold(I)[6] and copper(I)[7] complexes. A few platinum(0) and palladium(0) complexes have been known as luminescent in fluid solutions, but the photophysical study on the Pd(0) species is limited.[8,9] Our group reported that [Pt(binap)$_2$] (binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) shows relatively strong luminescence (Φ = 12%) and a long lifetime (τ = 1.3 μs) in solution.[10] The unusual photophysical properties of the complex were thoroughly studied, and the luminescence was shown to be emitted mainly from a thermally populated singlet metal-to-ligand charge transfer (MLCT) state rather than the triplet MLCT state.[10] Addition-

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* To whom correspondence should be addressed. E-mail: tsubomura@st.seikei.ac.jp.

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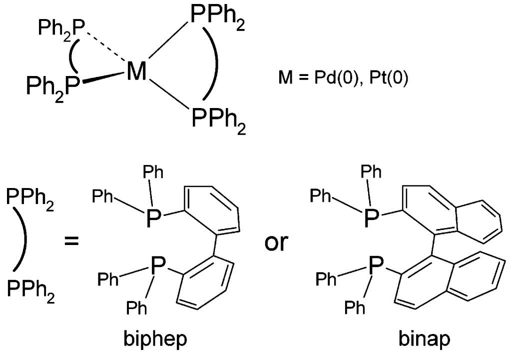
10.1021/ic700475z CCC: $40.75

Chart 1. Schematic Drawings of the Complexes and the Ligands



ally, we reported the energy transfer process from the ^{3}MLCT state to oxygen and the generation of singlet oxygen.[11] Recently, we found that some structurally related palladium(0) complexes show very strong luminescence in solution at room temperature. In this work, the photophysics of a series of the palladium(0) and platinum(0) complexes (Chart 1) is investigated in detail. The photophysics and its temperature-dependence on the complexes are discussed.

Results and Discussion

Synthesis and Crystal Structure of the Complexes. [Pd(binap)$_2$][12] was prepared from [Pd(P(o-tol)$_3$)$_2$] (P(o-tol)$_3$ = tris(o-tolyl)phosphine) by the method of Alcazar-Roman et al. The solid samples of the complexes can be handled under air, although the Pd(0) complexes show some degradation of colors if stored in air. [Pd(biphep)$_2$] was synthesized by a similar method (biphep = 2,2′-bis(diphenylphosphino)-1,1′-biphenyl). [Pt(binap)$_2$] and [Pt(biphep)$_2$] were prepared from the corresponding [PtCl$_2$(diphosphine)] complexes. Both [Pd(biphep)$_2$] and [Pt(biphep)$_2$] give a single ^{31}P NMR signal in C_6D_6 at room temperature although the NMR spectrum of the Pt complex contains ^{195}Pt satellites. The Pt−P coupling constant for [Pt(biphep)$_2$] (3570 Hz) is comparable to that for [Pt(binap)$_2$] (3740 Hz).

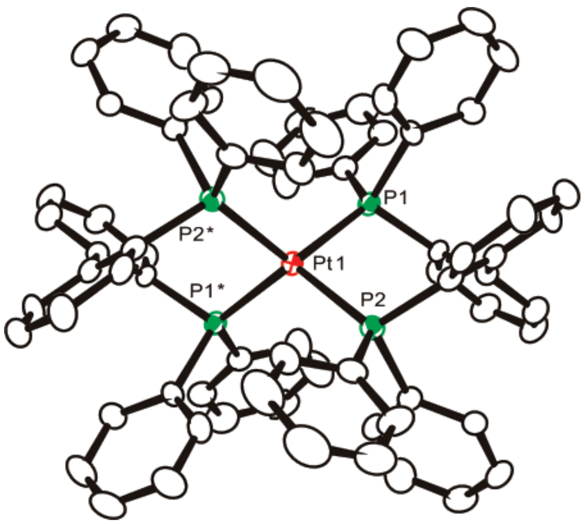


Figure 1. ORTEP drawing of [Pt(biphep)$_2$] viewed along the C_2 axis. The Pt1 atom is located on the C_2 axis. Atoms with an asterisk are the symmetrically located atoms. Important bond lengths (Å) and angles (deg): Pt1−P1, 2.325(3); Pt1−P2, 2.327(3); P1−Pt1−P2, 94.1(1); P1−Pt1−P1*, 120.8(1); P1−Pt1−P2*, 114.8(1); P2−Pt1−P2*, 120.4(2).

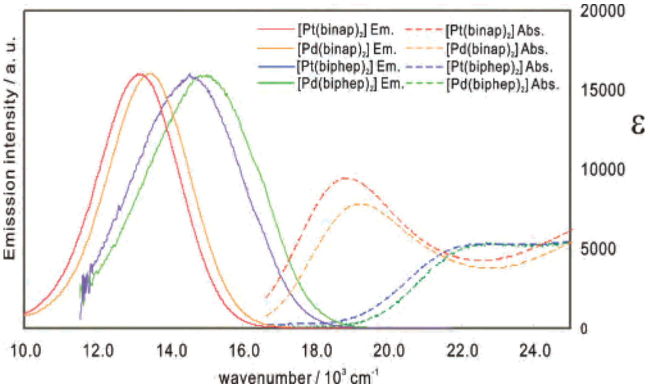


Figure 2. Absorption and the corrected luminescence spectra of the complexes (1×10^{-5} M, toluene, room temperature).

The X-ray crystal structure analysis of the crystals of [Pt(biphep)$_2$] shows that the complex has a distorted-tetrahedral structure as shown in Figure 1. The corresponding palladium complex [Pd(biphep)$_2$] has been revealed to have a similar structure, although the crystallographic data is poor.[13] We have not succeeded in the crystallization of [Pd(binap)$_2$], but the crystal structure of [Pd(tol-binap)$_2$] was already reported,[12] where tol-binap = 2,2′-bis(di-p-tolylphosphino)-1,1′-binaphthyl. The two coordination structures of [Pt(biphep)$_2$] and [Pt(binap)$_2$][14] resemble each other; for example, the average Pt−P bond lengths are equal (2.33 Å) within error limits. The structures of all complexes discussed here are similar around the metal centers, although the palladium complexes tend to have slight longer metal−phosphorous bond lengths (2.38−2.40 Å). The geometrical data are shown in Table S1 in the Supporting Information. One notable difference between the biphep and binap complexes is in the dihedral angles between the two aryl groups in the biaryl moieties; the averaged angles are 66° for [Pt(biphep)$_2$] and [Pd(biphep)$_2$], 71° for [Pt(binap)$_2$], and 72° for [Pd(tol-binap)$_2$]. The result suggests that the binap ligand may favor a large dihedral angle, which should be due to the steric demand within the ligand. To confirm the hypothesis, we examined the reported structures of the biphep and binap complexes in the CCDC crystallographic database.[15] We found 25 structures of transition-metal complexes containing one or more biphep ligands. Biphep derivatives (e.g., 3,3′-dimethyl-biphep) were not included in the list because the substituents may significantly affect the geometries of the complexes. The average of the dihedral angles P−C−C−P, which represent the twist angle of the biphenyl groups, in the 25 structures is 67.4 (4.2)°. The standard deviation is shown in parentheses. On the other hand, the average angle

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Table 1. Absorption and Emission Maxima, Lifetimes (τ), Emission Quantum Yields (Φ), and Apparent Radiative and Nonradiative Rate Constants (k_r and k_{nr}) of the Pt(0) and Pd(0) Complexes in Degassed Toluene Solution at 25 °C

complex	absorption ν_{max} 10^3 cm^{-1}	emission ν_{max} 10^3 cm^{-1}	τ 10^{-6} s	Φ	k_r[b] 10^5 s^{-1}	k_{nr}[b] 10^5 s^{-1}	ref
[Pd(binap)$_2$]	19.2	13.4	2.6	0.32	1.2	2.6	this work
[Pt(binap)$_2$]	18.9	13.1	1.25	0.12	0.99	6.8	[a]
[Pd(biphep)$_2$]	22.9	15.0	3.2	0.38	1.2	1.9	this work
[Pt(biphep)$_2$]	22.7	14.5	2.4	0.27	1.1	3.0	this work

[a] Ref 10. [b] The "apparent" rate constants are calculated as $k_r = \Phi/\tau$, $k_{nr} = (1 - \Phi)/\tau$.

of the 169 structures of the binap complexes is 72.4 (4.6)°. These values agree well with the angles found in our complexes. Since steric bulkiness on the biaryl group should favor the dihedral angle of 90°, the smaller dihedral angle of the biphep ligand appears to be proof of the flexibility of the ligand.

Absorption and Emission Spectra. These complexes have absorption bands in the visible region ($18-24 \times 10^3$ cm^{-1}). The photophysical data are listed in Table 1. We already clarified that the absorption band in the visible region of the [Pt(binap)$_2$] complex is due to the ^{1}MLCT transition.[10] The bands of the present complexes can be also assigned to ^{1}MLCT. The band of each biphep complex shows a blue shift by ca. 3700 cm^{-1} relative to those of the corresponding binap complexes, which should reflect the shrinkage of the π-conjugated groups in the biaryl moieties. Furthermore, the band maxima of the two palladium complexes are located at 200−300 cm^{-1} higher energy compared with those of the corresponding platinum complexes.

Figure 2 shows the luminescence spectra of the complexes measured in degassed toluene solution. The two palladium complexes and [Pt(biphep)$_2$] show strong luminescence in degassed toluene solution. All the luminescence is effectively quenched by oxygen. The highest quantum yield reaches 38%, and the lifetimes of the excited states are in the range 2.6−3.2 μs for the palladium complexes. The luminescence band of each Pt complex shows a slight red shift compared with the corresponding Pd complexes. Furthermore, both the biphep complexes have higher-energy luminescence bands than the binap complexes. In recent years, some metal complexes containing binap and related ligands were reported to luminesce.[16] However, the luminescence of the Pd(0) and Pt(0) biaryl complexes shown in this work is characterized as very intense emission with a long lifetime in solution. The long lifetime of the excited states should show the participation of the triplet MLCT states in the emissive excited states.

Emission was also observed for the solid samples. The emission maxima for [Pd(binap)$_2$], [Pt(biphep)$_2$], and [Pd(biphep)$_2$] are 13.9×10^3, 16.5×10^3, and 15.6×10^3 cm^{-1}, respectively. The values measured in toluene solution show red shifts of 500−1500 cm^{-1} when compared with the values observed for the solid sample.

As shown in Figure 2, these complexes show large Stokes shifts, especially in solution. (1) A larger distortion in the excited states toward planar structure and (2) the attack of solvent molecule and formation of exciplexes may account for the red shift in solution.[7a] One can see a significant difference in the magnitude of the Stokes shift (5800 cm^{-1} for the binap complexes and 7900−7200 cm^{-1} for the biphep complexes) which is independent of the metal species. The biphep ligand is known to be more flexible than the binap ligand, which is shown by the fact that binap can be optically resolved but biphep cannot. The structural studies have also shown the flexibility of the biphep ligand in comparison with that of the binap ligand (vide supra). A larger distortion in the biphep complexes in the excited states may be a reason for the larger Stokes shift in the biphep complexes. However, different participation of the solvent molecules on the binap and biphep complexes is another possibility.

As shown in Table 1, we can see that the apparent radiative rate constants k_r are similar in the four complexes at room temperature, and the difference in the quantum yields of the complexes is due to the variation of the nonradiative processes. For both the binap and biphep complexes, the platinum complexes have higher k_{nr} values than the corresponding palladium complexes. Moreover, [Pd(biphep)$_2$] and [Pt(biphep)$_2$] show smaller k_{nr} values than the corresponding binap complexes, respectively. The higher quantum yield and smaller k_{nr} values for the biphep complexes relative to those of the binap complexes may be rationalized by the energy-gap law.[17] The variation of k_{nr} values will again be discussed.

Solvent-dependence on the photophysical parameters of the complexes has been observed (see Table S3, Supporting Information). The solvent-dependence on the absorption maxima is small. On the other hand, a red shift of the emission maxima was observed in polar solvent. This result and the large solvent dependence on k_{nr} suggests the attack of the solvent to the excited states of the complexes. It should be noted that no significant differences are observed for the solvent effect between the platinum and palladium complexes.

Temperature-Dependence of the Spectra. Recently, it was shown that the major part of the luminescence intensity of the [Pt(binap)$_2$] complex comes from the thermally populated singlet MLCT excited state, not from the triplet state.[10] Similar conclusion that room-temperature emission is mainly "delayed fluorescence" was proposed by McMillin et al. for some Cu(I) systems[18] and recently reexamined by

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(16) (a) Pawlowski, V.; Kunkely, H.; Vogler, A. *Inorg. Chim. Acta* **1994**, *357*, 1309. (b) Pawlowski, V.; Kunkely, H.; Lennartz, C.; Böhn, K.; Vogler, A. *Eur. J. Inorg. Chem.* **2004**, 4242. (c) Kunkely, H.; Vogler, A. *Inorg. Chem. Commun.* **1999**, *2*, 533.

(17) Nonradiative rate constants of the $T_1 \rightarrow S_0$ process often show an exponential energy-gap dependence; $k_{nr} = a \exp(-c\Delta E)$. See ref 21.

(18) Kirchhoff, J. R.; Gamache, R. E.; Blaskie, M. W.; Paggio, A. D.; Lengel, R. K.; McMillin, D. R. *Inorg. Chem.* **1983**, *22*, 2380.

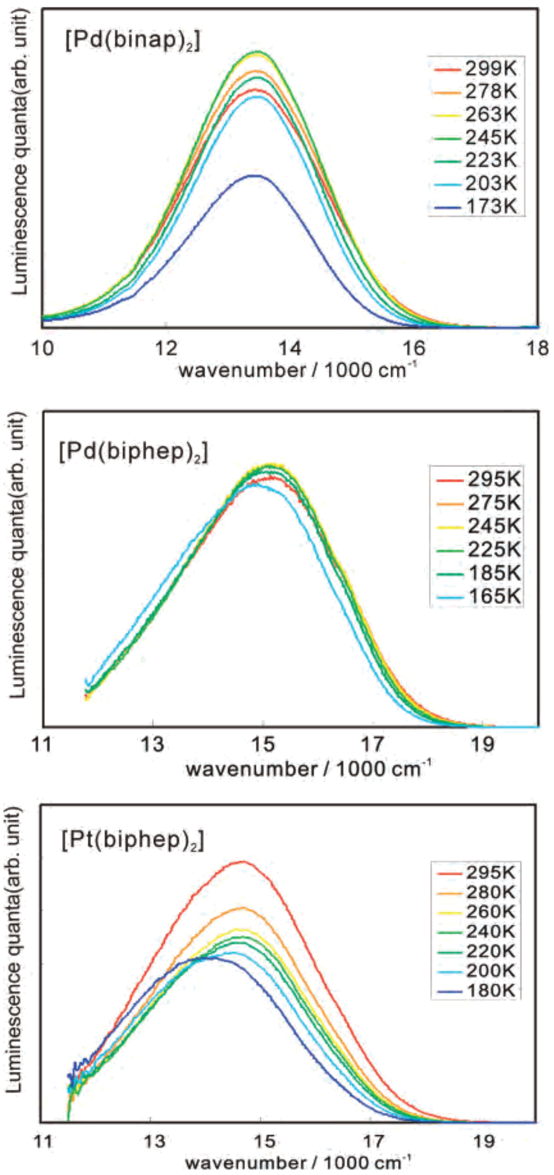
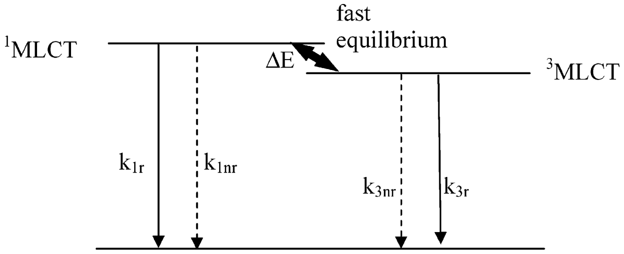


Figure 3. Temperature-dependence of the corrected luminescence spectra of the three complexes. These data were measured in degassed toluene solution.

Nozaki et al.[19] The characteristic was shown by the fact that (1) the intensity of the luminescence becomes lower as the temperature goes down and (2) the luminescence lifetime increases with lowering the temperature. A slight red shift of the emission bands has been observed in some complexes including [Pt(binap)$_2$]. These spectral features can be understood if the emitters have thermally equilibrated two emissive states and the radiative rate constant of the upper level is much higher than that of the lower state. Thus, the apparent rate constants calculated from the lifetime and quantum yield values do not directly describe the emissive properties of the excited-triplet states.

As shown in Figure 3, the complexes studied show different temperature-dependence of the emission spectra. The temperature-dependence of the luminescence of [Pt(biphep)$_2$] is similar to that of [Pt(binap)$_2$];[10] the intensity of the luminescence decreases on lowering the temperature and a slight red shift of the spectra is observed just above the freezing point. However, different dependencies were observed for the palladium complexes. For [Pd(binap)$_2$], the intensity of the luminescence initially increases on lowering the temperature from 300 K. However, the intensity again decrease as the temperature goes down below 250 K. A small red shift of the spectra is observed at low temperature. For [Pd(biphep)$_2$], the spectra show only a slight change with the change of the temperature, but the tendency of the temperature-dependence is similar to that of [Pd(binap)$_2$].

Chart 2 Energy Diagram of Two-Emitting-State Model



The lifetimes of the excited states increase on lowering the temperature for all of the complexes, as shown in Figure S2 (Supporting Information). Each decay curve can be fitted with a single exponential curve in all the temperature ranges studied.

In the previous study of [Pt(binap)$_2$],[10] analysis of the temperature change in the radiative rate constants afforded the parameters for the two-states model including radiative rate constants of singlet and triplet excited states and the energy gap between the two states (Chart 2). In this model, the ratio of the populations of the two states, K, is denoted by the following equation:[10]

$$K = \frac{1}{3}\exp\left(-\frac{\Delta E}{RT}\right)$$

In the present work, we tried to interpret the complex temperature-dependence by examining the temperature-dependence of the apparent radiative and nonradiative rate constants of the luminescence.

Temperature-Dependence in k_r. At room temperature, apparent k_r values ($=QE/\tau$) of all four complexes are similar, as already stated above. Decreases of the k_r value at lower temperature were observed for all complexes (see Figure S3, Supporting Information). The energy gap ΔE between the singlet and the triplet states and radiative rate constants of the two states can be principally obtained by nonlinear least-square analyses of the temperature-dependence of the k_r

$$\frac{QE}{\tau} = \frac{k_{1r}K + k_{3r}}{1 + K}$$

data.[10] The data are shown in the Supporting Information (Table S2). The result shows that ΔE values of the four complexes are within the range of 900−1400 cm^{-1}. This means that K, the population of the upper singlet state, is 0.4−0.04%, even at 298 K. However, due to the high k_{r1}/k_{r3} ratio (over 10^4), most of the emission intensity should come from the thermally equilibrated upper singlet state. If we

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assume a population of 0.1% and a k_{r1}/k_{r3} ratio of 10^4, simple calculation shows that 90% of the intensity of the emission originates from the upper singlet state. Unfortunately, because of the limitations of the temperature range and the errors in the experimental data, noticeable errors are included in the k_{r1} and k_{r3} values.[20]

Temperature-Dependence in k_{nr}. As stated before, the difference in k_{nr} values almost determines the luminescence quantum yield of the complexes at room temperature. The temperature-dependence of k_{nr} values of [Pt(biphep)$_2$] resembles that of [Pt(binap)$_2$]. As for the palladium complexes, large temperature-dependence is observed compared with that of the platinum complexes (see Figure S3, Supporting Information). For the platinum complexes, the decrease in k_{nr} on lowering the temperature is gentler than that in k_r; thus, the quantum yields of the luminescence essentially decrease at low temperature.[10] On the other hand, in the case of [Pd(biphep)$_2$], the k_r and k_{nr} curves closely resemble each other, so the quantum yield does not change with temperature. The temperature-dependent k_{nr} data of [Pt(binap)$_2$] were fit with

$$\frac{1 - QE}{\tau} = \mathrm{k}_{nr1} \exp(-\Delta E'/RT) + k_{nr2}$$

an Arrhenius-type rate equation. In the treatment, k_{nr1} denotes the lifetime of the higher-lying state which gives rise to deactivation, and k_{nr2} is the intrinsic lifetime of the emitting ^{3}MLCT. The temperature-dependence of the apparent k_{nr} data (Figure S3, Supporting Information) clearly shows that k_{nr2}, which is equal to the low-temperature limiting value of the apparent k_{nr} value, is small for the palladium complexes as compared with that of the platinum complexes. What is the reason for the difference in the rate of the nonradiative deactivation between the two metal species? We have shown that the geometry found in the two complexes, [Pt(biphep)$_2$] and [Pd(biphep)$_2$], is similar, as clarified by X-ray analysis, and furthermore, the solvent effect on the photophysical parameters of the platinum and palladium complexes seem to be similar. Harvey and Gray also observed a great difference in the excited-state lifetime of the two binuclear platinum(0) and palladium(0) complexes.[9a] The lifetime of the former is far smaller than that of the latter complex. They concluded that the difference in the spin−orbit coupling may be the reason for this result. It has been shown that spin−orbit coupling must be included in the evaluation of nonradiative rates for the relaxation between states of different multiplicity.[21] Since there is a large difference in the spin−orbit coupling constants for the platinum atom (4400 cm^{-1}) and palladium atom (1500 cm^{-1}), spin−orbit coupling should be one of the essential reasons for the great difference in the nonradiative rates of relaxation of the platinum and palladium complexes.

Conclusion. We found high-intensity luminescence of the biaryldiphosphine complexes of Pd(0) and Pt(0) metals. Many researchers may consider this result strange, because many platinum complexes luminesce but palladium complexes do not, especially at room temperature. This should be true for divalent platinum and palladium complexes, because low-lying d−d states effectively quench the CT excitation energies of the palladium complexes. However, the result for platinum(0) and palladium(0) complexes is opposite that of the divalent complexes. It has been reported that some platinum(0) complexes show luminescence with a very short lifetime due to large k_{nr} values. For example, [Pd(PPh$_3$)$_3$] has lifetime of 3.6 μs in solution at room temperature, but [Pt(PPh$_3$)$_3$] has a lifetime of 0.7 μs.[8] The variation of the photophysical properties of the complexes described in the present work should be mainly ascribed to the variation of nonradiative processes. Large spin−orbit coupling in the platinum complexes may be the reason for the large nonradiative deactivation. The palladium(0)−phosphine complexes have long been known as precursors of many homogeneous catalysts, but the interesting photophysical properties of the complexes have not been explored so far. In this study, we shed light on additional promising applications of the palladium complexes as luminescent materials.

Experimental Section

Synthesis of the Complexes. Metal sources and phosphines were obtained from Tanaka Kikinzoku Kogyo, Ltd. and Strem Chemicals, respectively. The syntheses of the bis(diphosphine)complexes should be done under argon atmosphere, although the obtained crystals of the zerovalent complexes can be handled in air. [Pd(P(*o*-tol)$_3$)$_2$] was prepared by the reported procedure.[22]

[Pd(binap)$_2$] was prepared according to the Alcazar-Roman method.[12]

[Pd(biphep)$_2$] was prepared by a similar method, as follows. Benzene (3 mL) was added to a mixture of [Pd(P(*o*-tol)$_3$)$_2$] (0.14 mmol) and biphep (0.28 mmol) and stirred until the complex dissolved. The mixture was filtered under argon, and *n*-heptane was added slowly and then kept in a refrigerator. Orange crystals (0.12 g) were afforded after several days. Yield, 72%. Anal. Calcd. for $C_{72}H_{56}P_4Pd(C_6H_6)_3$: C, 78.00; H, 5.38. Found: C, 77.66; H, 5.39. ^{31}P NMR (160 MHz, C_6D_6): $\delta = 20.3$.

[Pt(biphep)$_2$] was synthesized from [PtCl$_2$(biphep)], which was prepared from [PtCl$_2$(C$_6$H$_5$CN)$_2$] as follows. Portions of 0.25 mmol of [PtCl$_2$(C$_6$H$_5$CN)$_2$] and 0.25 mmol of biphep were dissolved in 50 mL of benzene and stirred at 70 °C for 1 h. After cooling, the solution was concentrated to 10 mL and was allowed to stand for 24 h at 5 °C. White powders of [PtCl$_2$(biphep)] deposited (77% yield) were collected by filtration. To a THF solution (22.5 mL) containing both the dichloride complex (0.13 mmol) and biphep (0.13 mmol) was added dropwise an aqueous solution (5 mL) of NaBH$_4$ (0.39 mmol) under argon atmosphere. The solution was dried in vacuo. Toluene (20 mL) was added to the residue, and the insoluble solid was separated by filtration. Heptane (20 mL) was added to the toluene solution, and the solution was allowed to stand for a week at 5 °C. [Pt(biphep)$_2$] was obtained as orange crystals. Yield, 48%. Anal. Calcd. for $C_{72}H_{56}P_4Pt$: C, 69.73; H, 4.55. ^{31}P NMR (160 MHz, C_6D_6): $\delta = 13.2$ ($J_{PtP} = 3570$ Hz).

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(20) In the least-squares calculation, results are seemingly accurate with small standard deviations, but different weight function gave different results, especially for k_{1r} and k_{3r}. Thus, the actual errors should be considerably larger than the calculated standard deviations. Therefore, we discuss ΔE values only in this section.

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Crystallographic Study of [Pt(biphep)$_2$]. The orange crystal was glued on the tip of a glass fiber with epoxy resin and mounted on a four-circle automated diffractometer (AFC-5S of Rigaku, Ltd.). The detailed data collection parameters and the crystal data were listed in a CIF file. The positions of the heavy atom were determined by a direct method using the *SIR92* program.[23] The structure was expanded and refined by the *SHELX97* software.[24] Two kinds of toluene molecules of solvate were found in an asymmetric unit. For one toluene molecule, the parameters of the carbon atoms of the toluene molecules were refined with the multiplicities of each atom set to unity. One more toluene molecule was found on a crystallographic two-fold axis. The multiplicities of the carbon atoms of the toluene molecule were set to 1 or 0.5 so that a disordered pair of the molecule was located on the position. Some C−C distances of the toluene molecules were restrained to 1.36 Å.

Crystallographic parameters for [Pt(biphep)$_2$]·$(C_6H_5CH_3)_3$: $C_{93}H_{80}P_4$Pt, $M = 1516.6$, monoclinic, $a = 19.818(8)$ Å, $b = 14.219(3)$ Å, $c = 26.677(2)$ Å, $\beta = 97.87(2)°$, $V = 7446(3)$ Å^3, space group $C2/c$, $Z = 4$, $T = 293$ K, $\mu = 2.02$ mm^{-1}, reflections collected 9146, unique 7561; final $R_1(F) = 0.078$ ($I > 2\sigma(I)$), $R_2(F^2) = 0.162$ (all).

Spectroscopy All spectroscopic measurements were carried out using strictly degassed solutions by repeated freeze−pump−thaw procedures. The spectroscopic properties of [Pd(binap)$_2$] were studied by the methods described in the recent paper.[10] In short, the luminescence spectra of the complex up to 1000 nm were measured with a polychromator equipped with a CCD detector.

The spectroscopic properties of [Pd(biphep)$_2$] and [Pt(biphep)$_2$] complexes were measured as follows. The UV−vis absorption spectra and the luminescence spectra were recorded on a Shimadzu UV-2100 spectrometer and a Shimadzu RF-5000 spectrofluorometer, respectively. In the spectrofluorometer, a red-enhanced-type photomultiplier tube (Hamamatsu R3896) was used. The concentrations of the complexes were adjusted as the absorbance of the solutions at the excitation wavelength was set to around 0.1. The temperature was kept constant by means of circulating thermostatted water for the measurements at around room temperature. For the low-temperature measurements, a custom-made LN$_2$ cryostat manufactured by Jecc-Torisha Co., Ltd., and a temperature controller (Scientific Instruments, Model 9700) were used. The correction factors for the sensitivity of wavelength-dependence of the spectrometer were determined bycomparison of the reported spectral curves of 4-dimethylamino-4′-nitrostilbene and 3-(dimethylamino)-nitrobenzene with our recorded spectra.[25] The quantum yields of [Pd(biphep)$_2$] and [Pt(biphep)$_2$] complexes were calculated by the following equation:[26]

$$\Phi = \Phi^*\left(\frac{n}{n^*}\right)^2\left(\frac{S}{S^*}\right)\left(\frac{I^*}{I}\right)\left(\frac{1 - 10^{-A^*}}{1 - 10^{-A}}\right)$$

where n is refractive index of the solvent, S is the area of the corrected emission spectra (quanta per wavenumber vs wavenumber), I is the intensity of light at the excitation wavelength, and A is the absorbance at the excitation wavelength. The asterisk refers to the standard sample. At low temperature, a slight narrowing of the absorption band widths and an increase in the absorption maxima were observed, and then they were corrected for the determination of the quantum yields. Rhodamine 101 was used for the standard of the quantum yield ($\Phi = 0.92$).[27] The wavelengths of excitation were as follows: 440 nm for Pd(biphep)$_2$ and Pt(biphep)$_2$ and 525 nm for rhodamine 101. The intensity ratio of the excitation, I^*/I, was determined using a quantum counter of a rhodamine 101 solution (5 g/L) dissolved in ethanol. Luminescence decay curves were measured on a laboratory-made apparatus; the sample was excited using a nitrogen laser (USHO AN-200), and the emission light was focused into a Jovin-Ybon H-20 monochromator equipped with a photomultiplier (Hamamatsu R-955). The output of the photomultiplier was digitized by a Iwatsu-Lecroy DS-4262 digital oscilloscope and then downloaded to a PC. NMR spectra were measured on a JEOL Λ-400 spectrometer using H_3PO_4 solution as an external reference.

Acknowledgment. We are grateful to Prof. Koichi Nozaki of the University of Toyama for measuring the luminescence spectra of [Pd(binap)$_2$]. We thank the Ministry of Education, Culture, Sports, Science and Technology (MEXT) for their financial support of this research through the High-Tech Research Center Project and Grant-in-Aid for Scientific Research.

Supporting Information Available: Crystallographic data of [Pt(biphep)$_2$] and [Pd(biphep)$_2$]; geometrical parameters of the complexes; temperature-dependence of the photophysical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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