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Functionalized 2-Pyridyl-Substituted Metallo-1,2-enedithiolates. Synthesis, Characterization, and Photophysical Properties of (dppe)M$\{S_2C_2$(2-pyridine(ium))(CH_2CH_2OR'')$\}$ and (dppe)M[$\{S_2C_2$(CH_2CH_2-*N*-2-pyridinium)$\}$]$^+$ (R″ = H, Acetyl, Lauroyl; M = Pd, Pt; dppe = 1,2-Bis(diphenylphosphino)ethane)

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The complexes (dppe)M$\{S_2C_2$(2-pyridine)($CH_2CH_2OC(O)CH_3$)$\}$ (dppe = 1,2-bis(diphenylphosphino)ethane; M = Pd, Pt) were prepared from 1-(2-pyridyl)-4-acetoxy-2-bromobutan-1-one and the corresponding (dppe)M$(SH)_2$ complexes. The acetyl group was removed from the metal complexes to yield the corresponding alcohols, (dppe)M$\{S_2C_2$(2-pyridine)(CH_2CH_2OH)$\}$. The lauroyl derivatives (dppe)M$\{S_2C_2$(2-pyridine)($CH_2CH_2OC(O)(CH_2)_{10}CH_3$)$\}$ were prepared by esterifying the alcohols with lauroyl chloride. The alkylated pyridinium complexes [(dppe)M$\{S_2C_2$(CH_2CH_2-*N*-2-pyridinium)$\}$]$^+$ were generated by the addition of either *p*-toluenesulfonyl chloride or bis(triazole) *o*-chloroaryl phosphate to (dppe)M$\{S_2C_2$(2-pyridine)(CH_2CH_2OH)$\}$. [(dppe)Pd$\{S_2C_2$(CH_2CH_2-*N*-2-pyridinium)$\}$][BPh_4] crystallizes in the $P\bar{1}$ space group with $a = 9.1924(2)$ Å, $b = 16.0191(2)$ Å, $c = 17.4368(3)$ Å, $\alpha = 106.292(2)°$, $\beta = 96.235°$, and $\gamma = 95.183(2)°$. The molecule is best described as a square planar palladium complex with a planar metallo-1,2-enedithiolate which is coplanar with the alkylated pyridinium. The pyridinium-substituted platinum 1,2-enedithiolate complexes have a 1,2-enedithiolate to heterocycle π^* charge-transfer transition (ILCT) that is the lowest lying band. Like [(dppe)Pt$\{S_2C_2$(2-pyridinium)(H)$\}$]$^+$, [(dppe)Pt$\{S_2C_2$(CH_2CH_2-*N*-2-pyridinium)$\}$]$^+$ is luminescent in room-temperature solution with two emissive states assigned to the ILCT* singlet and triplet. The lifetime of the ^{1}ILCT* is 0.2 ns, $^1\phi = 0.002$, while the lifetime of the ^{3}ILCT is 8.3 μs, $^3\phi = 0.01$ (DMSO). While [(dppe)Pt$\{S_2C_2$(CH_2CH_2-*N*-2-pyridinium)$\}$]$^+$ is emissive, the [(dppe)Pt$\{S_2C_2$(2-pyridinium)(CH_2CH_2OR'')$\}$]$^+$ complexes are weak emitters at best in solution with triplet quantum yields of <0.0001 (DMSO). These photophysical studies suggest that the heterocycle and the 1,2-enedithiolate must be coplanar in the ILCT excited states for the complexes to be emissive in room-temperature solution.

Introduction

Transition metal complexes that are luminescent in room-temperature solution have been used in a variety of chemical and biochemical applications.[1−14] Many of these applications require that the metal lumiphore be functionalized so that it can be appended to a molecule or macromolecule of interest or activated by chemical reaction. Such functionalized lumiphores have been used in electron-transfer studies,[1−4] in the design of new biosensors,[5−12] and in the formulation of emissive paints.[13,14]

While platinum 1,2-enedithiolates have emerged as a new class of luminescent molecules,[15−27] most of the synthetic

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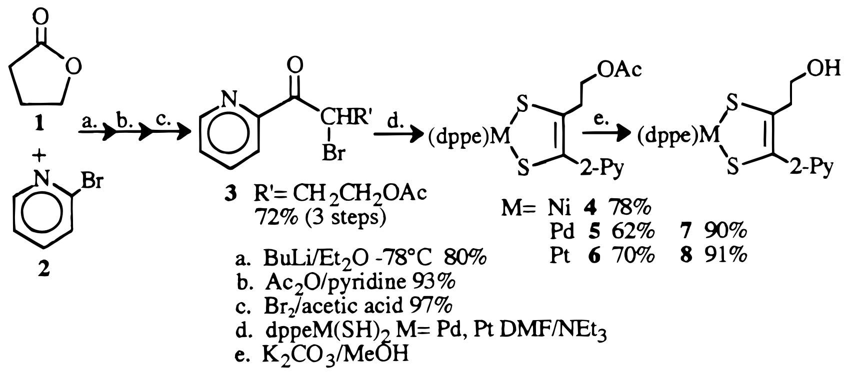
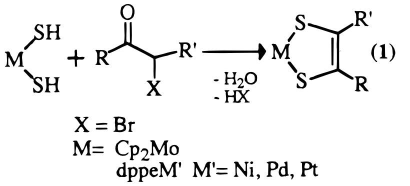
Scheme 1

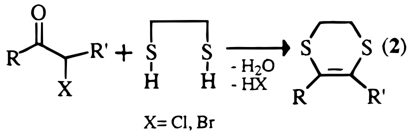


methods for these complexes have not allowed functionalization of the lumiphores. In this paper, we report the synthesis of (dppe)M{S_2C_2(2-pyridine)(CH_2CH_2OH)} (M = Pd, Pt; dppe = 1,2-bis(diphenylphosphino)ethane). These 1,2-enedithiolate complexes are readily functionalized and can be used to generate $[(dppe)M\{S_2C_2(CH_2CH_2\text{-}N\text{-}2\text{-pyridinium})\}]^+$. A comparison of the photophysical properties of $[(dppe)Pt\{S_2C_2(2\text{-pyridinium})(CH_2CH_2OR'')\}]^+$ (R″ = H, acetyl, lauroyl) with those of $[(dppe)Pt\{S_2C_2(CH_2CH_2\text{-}N\text{-}2\text{-pyridinium})\}]^+$ and $[(dppe)Pt\{S_2C_2(2\text{-pyridinium})(H)\}]^+$ provides evidence that the intraligand charge transfer (ILCT*) excited states have considerable 1,2-enedithiolate to heterocycle π^* charge transfer character and that the emissive excited states likely possess a coplanar 1,2-enedithiolate and heterocycle.

Results and Discussion

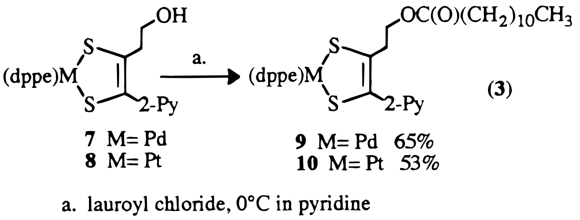
In previous studies,[25,28] a new synthetic route to metallo-1,2-enedithiolates (eq 1), patterned after the synthesis of organic 1,4-dithiins (eq 2)[29−31] was applied to the synthesis of a range of (dppe)M{S_2C_2(R)(R′)} (dppe = 1,2-bis(diphenylphosphino)ethane; M = Ni, Pd, Pt) derivatives. In these previous studies, the R group was varied to included a number of heterocycles but R′ was limited to either H or Me. As shown in Scheme 1, this method has now been extended to 1,2-enedithiolate complexes containing R′ = CH_2CH_2OH, a group that is readily functionalized. The α-substituted ketone required for this method is generated in three steps from γ-butyrolactone and 2-bromopyridine. 1-(2-Pyridyl)-4-acetoxy-2-bromobutan-1-one, **3**, reacts with (dppe)M$(SH)_2$, where M = Ni, Pd, and Pt, to generate, upon neutralization, complexes **4**−**6.** The terminal alcohol of the Pd and Pt complexes was deprotected using standard conditions to generate complexes **7** and **8**. While only the synthesis of the 2-pyridyl-substituted 1,2-enedithiolate ligands is described, this method is versatile being limited only by the ability to prepare a lithio aryl or lithio heterocyclic reagent. Since a range of substituted γ-butyrolactones and δ-valerolactones are either commercially available or readily prepared,[32,33] it should be possible to vary both 1,2-enedithiolate appended groups by adapting this method.





Complex **4** was prepared only to aid in the assignment of the electronic transitions of these complexes and was not studied further. It is anticipated that the nickel analogues of **7** and **8** could be prepared by methods similar to those described for the corresponding Pd and Pt complexes.

Complexes **7** and **8** can be esterified with acid chlorides or anhydrides, as shown in eq 3 for the synthesis of the lauroyl derivatives **9** and **10**.



The alkylated pyridinium complexes **15** and **16** (Scheme 2) were prepared by either the addition of *p*-toluenesulfonyl chloride or bis(triazole) *o*-chloroaryl phosphate to **7** and **8**. These reactions presumably proceed through intermediates which contain an appended tosylate (**11** and **12**) and phosphate (**13** and **14**), respectively, and which undergo attack from the appended 2-pyridine resulting in the generation of **15** and **16** (Scheme 2). Complexes **15** and **16** were isolated as the tetraphenylborate salts upon the addition of $NaBPh_4$ to methanol solutions of the metal complexes.

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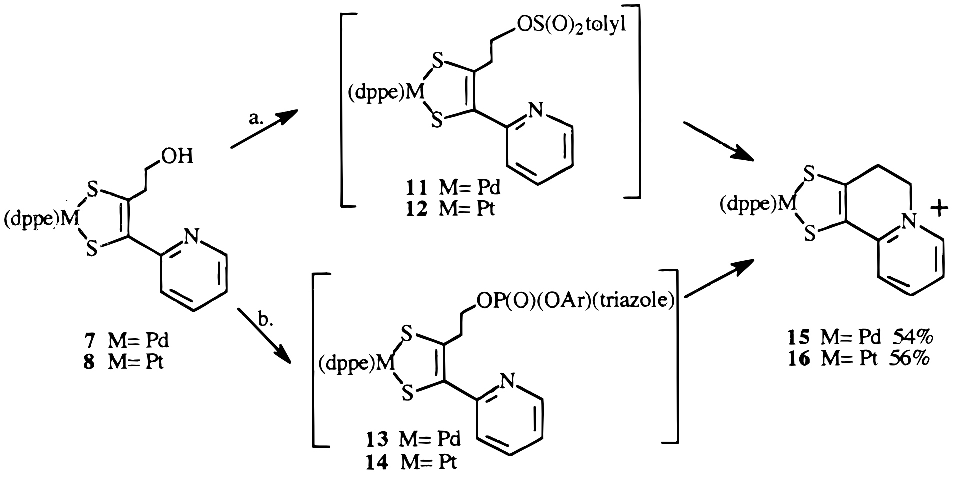
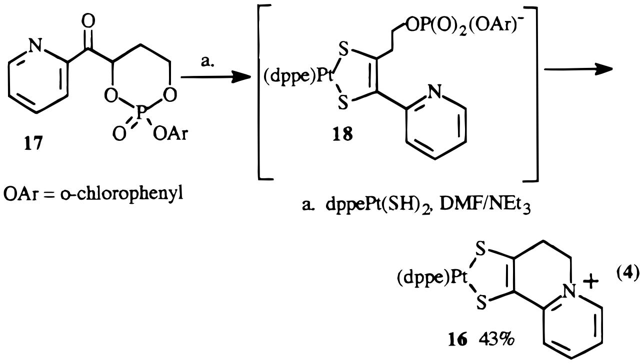
Scheme 2



a. p-toluenesulfonyl chloride 0°C in pyridine
b. (O)P(OAr)(triazole)$_2$ in dioxane 5°C
OAr= o-chlorophenyl

Complex **16** was also prepared from the reaction of the α-phosphorylated ketone **17** with (dppe)Pt(SH)$_2$ and likely proceeds through intermediate **18** (eq 4).[34]



X-ray Crystallography Results for Complex 15 as the [BPh$_4$]$^-$ Salt. Complex **15** was the subject of a single-crystal X-ray study, the results of which are presented in Table 1 and shown in Figure 1. The solid-state structure of **15** is similar to those of other group VIII metallo-1,2-enedithiolate complexes.[15,25,35-40] The S(1)−Pd−S(2) angle of 89.49(6)°, the P(1)−Pd−P(2) angle of 84.67(7)°, and the coplanarity of Pd, S(1), S(2), P(1), and P(2) (the mean deviation from the plane of the five atoms is 0.0584 Å) are all expected for a bis(phosphine) Pd(II) complex. The Pd−S bond lengths are 2.297(2) and 2.303(2) Å and are best described as single bonds, while the C(1)−C(9) bond at 1.372(9) Å is best described as a double bond. The metallo-1,2-enedithiolate is a planar five-membered ring with no atom deviating from the least-squares plane by more than 0.026 Å. The sum of the bond angles about N(1) is 359.9(6)°, suggesting that the heterocyclic ring is aromatic.

Table 1. Crystallograpic Data for **15**

formula	$C_{59}H_{52}BNP_2PdS_2$
fw	1018.29
space group	$P\bar{1}$
a (Å)	9.1924(2)
b (Å)	16.0181(2)
c (Å)	17.4368(3)
α (deg)	106.292(2)
β (deg)	96.235(2)
γ (deg)	95.183(2)
V (Å^3)	2430.09(7)
Z	2
crystal color, habit	red plate
D_{calc} (g/cm^{-3})	1.392
μ(Mo Kα) (cm^{-1})	5.75
T (°C)	−55(2)
diffractometer	Siemens P4/CCD
radiation	Mo Kα (λ = 0.710 73 Å)
$R(F)$ [$I > 2\sigma(I)$], %[a]	6.42
$R_w(F)$ [$I > 2\sigma(I)$], %[a]	11.80

[a] Quantity minimized: $R_w(F^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$. $R = \sum\Delta/\sum(F_o)$, $\Delta = |F_o - F_c|$.

UV−Visible Spectra. In accord with our previous studies of (dppe)M{S$_2$C$_2$(Het)(H)} (M = Ni, Pd, Pt; Het = 2-, 3-, and 4-pyridine(ium), 2-pyrazine(ium), 2-quinoxaline(ium)), all of the complexes prepared in this study have a visible band assigned to an intraligand charge-transfer transition (ILCT) with considerable 1,2-enedithiolate to heterocycle π* charge-transfer character.[25−27] For the cationic complexes reported, the transition is found between 430 and 500 nm, where it can be readily studied. The ILCT assignment is based on (1) the similarity in energy of the bands for the corresponding Ni, Pd, and Pt complexes (Table 2), (2) the solvent dependence of the energy of these bands, and (3) the red shift of these bands upon protonation or alkylation. The similarity in the energy of the transition for the corresponding Ni, Pd, and Pt complexes rules out assignment of this transition to a metal to ligand charge transfer (MLCT), ligand to metal charge transfer (LMCT), or d to d transition (Figure 2).[25,41,42] The energy of these bands in

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Table 2. UV−Visible Data for Complexes **4**−**10** (Neutral and Protonated), **15**, and **16** Recorded in CH_2Cl_2

complex	M	R, R′	λ_{max} (ϵ)^a pyridine	λ_{max} (ϵ)^a pyridinium
4	Ni	2-py, CH_2CH_2OAc	357 (4300), 580 (90)	365 (4400), 456 (3350), 580 (90)
5	Pd	2-py, CH_2CH_2OAc	348 (5600), 525 (530)	347 (5700), 448 (2850), 511 (2370)
6	Pt	2-py, CH_2CH_2OAc	334 (4300), 415 (410)	332 (8000), 471 (2800)
7	Pd	2-py, CH_2CH_2OH	334 (8400), 520 (440)	346 (6900), 435 (3500), 508 (2000)
8	Pt	2-py, CH_2CH_2OH	350 (6000), 410 (580)	334 (4300), 455 (1800)
9	Pd	2-py, $(CH_2)_2O$-lauroyl	348 (5500), 506 (540)	345 (6900), 449 (4000), 510 (2050)
10	Pt	2-py, $(CH_2)_2O$-lauroyl	342 (5200), 415 (490)	333 (6100), 470 (2700)
15	Pd	CH_2CH_2-*N*-2-pyridinium		329 (11 700), 489 (2700)^b
16	Pt	CH_2CH_2-*N*-2-pyridinium		344 (12 400), 496 (3200)

[a] λ_{max} in nanometers (ϵ is the molar absorptivity). [b] In CH_2Cl_2, the ILCT and LMCT overlap; in CH_3CN, these bands are observed at 463 and 512 nm.

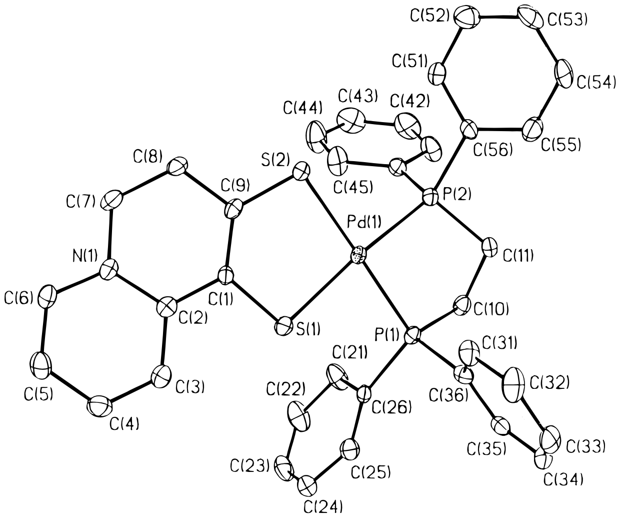

Figure 1. ORTEP drawing of **15** with the thermal ellipsoids drawn at 50% probablility. Selected bond lengths (Å) and angles (deg): Pd−S(1), 2.297(2); Pd−S(2), 2.303(2); S(1)−C(1), 1.748(6); S(2)−C(9), 1.709(7); C(1)−C(9), 1.372(9); C(1)−C(2), 1.434(9); S(1)−Pd−S(2), 89.49(6); Pd−S(1)−C(1), 102.6(7); Pd−S(2)−C(9), 102.5(2); S(1)−C(1)−C(9), 121.4(5); C(9)−C(1)−C(2), 121.6(6).

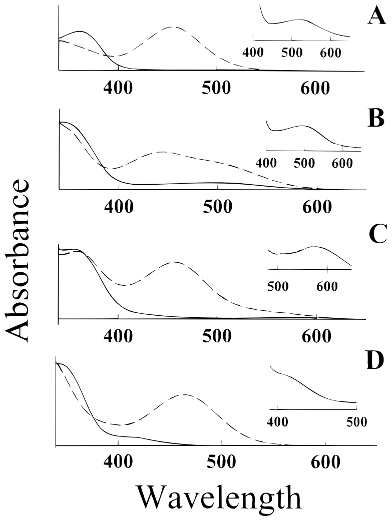

Figure 2. UV−vis absorption spectra in CH_2Cl_2. Part A: solid line, (dppe)Pd{S_2C_2(2-pyridine)(H)}; dashed line, [(dppe)Pd{S_2C_2(2-pyridinium)(H)}]$^+$. Part B: solid line, (dppe)Pd{S_2C_2(2-pyridine)(CH_2CH_2-OAc)}; dashed line, [(dppe)Pd{S_2C_2(2-pyridinium)(CH_2CH_2OAc)]$^+$. Part C: solid line, (dppe)Ni{S_2C_2(2-pyridine)(CH_2CH_2OAc)}; dashed line, [(dppe)Ni{S_2C_2(2-pyridinium)(CH_2CH_2OAc)}]$^+$. Part D: solid line, (dppe)Pt{S_2C_2(2-pyridine)(CH_2CH_2OAc)}; dashed line, [(dppe)-Pt{S_2C_2(2-pyridinium)(CH_2CH_2OAc)}]$^+$. Insets in parts A−D are expansions of the regions of the visible spectra assigned to the d to d and LMCT bands.

the cationic complexes increases by ≈2000 cm^{-1} when the solvent is changed from CH_2Cl_2 to DMSO. The solvent dependence is consistent with a charge-transfer transition where the excited state is less polar than the ground state. In the protonated or alkylated complexes, the ILCT would diffuse the positive charge imparted to the heterocycle by protonation or alkylation and the excited state would be less polar than the ground state. While the energy of the ILCT transition is solvent dependent, this dependence does not correlate with the solvent polarity parameters E^*_{MLCT} and π^*,[43] an observation consistent with our previous findings for ILCT transitions in related complexes.[25−28] The red shift of this band upon protonation or alkylation is consistent with lowering the reduction potential of the appended heterocycle which bears the accepting orbital in the electronic transition.[25]

While the pyridinium-substituted Ni and Pt complexes prepared in this study have visible spectra similar to those of the (dppe)M{S_2C_2(2-pyridinium)(H)} complexes (see Figure 2),[25,26] the palladium complexes have an additional visible band (Figure 2) which has been assigned to a LMCT transition. This assignment is consistent with an electron-releasing R′ group, decreasing the energy of the transition. It is also consistent with the transition being lower in energy in the Pd complexes than in the corresponding Ni and Pt complexes.[25,41,42] The LMCT transitions in the palladium complexes **5**, **7**, and **9**, the corresponding protonated complexes, and **15** overlap with the d to d transition which in (dppe)Pd{S_2C_2(2-pyridine(ium))(H)} is found at 520 nm ($\epsilon_{d-d} = 80-90$). The LMCT transition in the Ni and Pt complexes is likely found at higher energy with the π to π^* transitions.

While all of the complexes have an ILCT transition, it is the lowest energy band in only the cationic platinum complexes. From previous studies, complexes with lowest lying ILCT transitions can be emissive at room temperature in solution, and as such the emissive properties of the protonated forms of **6**, **8**, and **10**, as well as **16**, were investigated.

Emission Spectra. Like [(dppe)Pt{S_2C_2(2-pyridinium)(H)}]$^+$, [(dppe)Pt{S_2C_2(CH_2CH_2-*N*-2-pyridinium)}]$^+$, **16**, is luminescent in room-temperature solution with two emissive states (Figure 3). As in our previous studies, the emissive states have been assigned to an ^{1}ILCT* and an ^{3}ILCT*.[26,27] The lifetime of the ^{1}ILCT* is 0.2 ns, $^1\phi = 0.002$, while the lifetime of the ^{3}ILCT is 8.3 μs, $^3\phi = 0.01$ (DMSO).[26] Given the ^{3}ILCT* lifetimes, this excited state is rapidly quenched by exposure to dioxygen, and as such the measured ^{3}ILCT* lifetime in aerated DMSO is 560 ns (Table 3).

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Table 3. Solvent Dependence of the Luminescence Maxima, Quantum Yields, and Lifetimes of **16**

solvent	$^1\phi$	$^3\phi$	$^1\lambda_{max}$ (nm)	$^3\lambda_{max}$ (nm)	$^{air}\tau^a$ (ns)	$^{Ar}\tau^a$ (ns)
DMSO	0.002	0.01	677	732	0.2 (77%)	0.2 (less than 20%)
					560 (23%)	8300[b] (greater than 80%)
DMF	0.003	0.008	678	739	0.1 (80%)	0.1 (23%)
					270 (20%)	6500 (77%)
CH_2Cl_2	0.0009	0.004	703	739	0.2 (85%)	0.2 (39%)
					240 (15%)	6800 (61%)

[a] Lifetimes; the values in parentheses are the contributions of the species to the overall emission. [b] Determined by transient absorption spectroscopy.

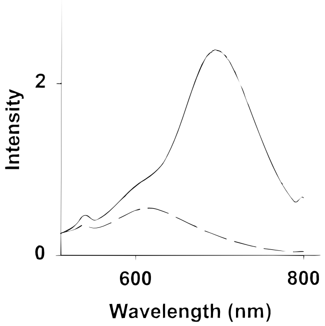
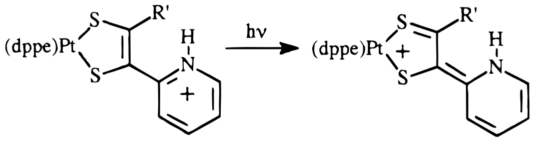


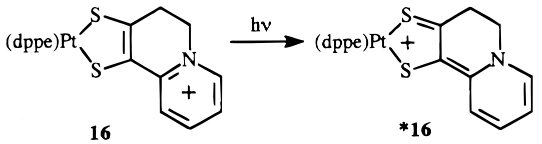
Figure 3. Emission spectra of **16** in DMSO at 298 K prior to instrument correction: solid line, air free; dashed line, in air.

While [(dppe)Pt{S_2C_2(CH_2CH_2-*N*-2-pyridinium)}]$^+$ and [(dppe)Pt{S_2C_2(2-pyridinium)(H)}]$^+$ have similar excited-state properties, all of the [(dppe)Pt{S_2C_2(2-pyridinium)(CH_2CH_2-OR″)}]$^+$ complexes are weak emitters at best with $^3\phi < 0.0001$ in DMSO. While the rapid nonradiative decay in [(dppe)Pt-{S_2C_2(2-pyridinium)(CH_2CH_2OR″)}]$^+$ could be due to high-frequency N−H modes, this seems unlikely given that [(dppe)-Pt{S_2C_2(2-pyridinium)(H)}]$^+$ is emissive. Furthermore, similar quenching of both the singlet and triplet emissions by methyl substitution in the complexes (dppe)Pt{S_2C_2(2-quinoxaline)(R′)} (R′ = H, Me)[27] was observed, suggesting that steric bulk of R′ is a controlling factor for room-temperature emission.[27]

The difference in the quantum yields of [(dppe)Pt{S_2C_2(CH_2-CH_2-*N*-2-pyridinium)}]$^+$ and [(dppe)Pt{S_2C_2(2-pyridinium)-(H)}]$^+$ from that of [(dppe)Pt{S_2C_2(2-pyridinium)(CH_2CH_2-OR″)}]$^+$ supports an ILCT* excited state where the charge transfer formally oxidizes a 1,2-enedithiolate sulfur and reduces the pyridinium nitrogen. This leads to an exocyclic double bond between the dithiolate and the heterocycle in the excited state as shown in eqs 5 and 6. Such a configuration requires a coplanar 1,2-enedithiolate and heterocycle. This criterion is forced upon *16 by the ground-state structure (see Figure 1). However, in the protonated complexes (eq 5) the ability of the 1,2-enedithiolate and heterocycle to be coplanar is controlled by the bulk of the R′ group. It would appear that the CH_2CH_2-OR″ groups are sufficiently bulky as to not allow the 1,2-enedithiolate and pyridinium to be coplanar. This destabilizes the charge-transfer state and leads to rapid nonradiative decay.



(5)



16 *16

(6)

In principle, the ILCT* excited states are similar to twisted internal charge-transfer (TICT) excited states. In the TICT excited states emission occurs when the charge separation is stabilized by twisting the molecule by 90°.[10,44] In these ILCT* excited states, emission occurs when maximum positive charge is localized on the 1,2-enedithiolate sulfurs, which requires a coplanar 1,2-enedithiolate and heterocycle.

Conclusion. In this study we have further developed a versatile new method to functionalized metallo-1,2-enedithiolates. This method was applied to the preparation of (dppe)M-{S_2C_2(2-pyridine)(CH_2CH_2OR″)} where M = Ni, Pd, or Pt and R″ = H, acetyl, or lauroyl. The further development of this method will make it possible to append metallo-1,2-enedithiolates to a range of other molecules by functionalizing the CH_2-CH_2OH group. By tosylation or phosphorylation of (dppe)M-{S_2C_2(2-pyridine)(CH_2CH_2OH)}, the [(dppe)M{S_2C_2(CH_2CH_2-*N*-2-pyridinium)}]$^+$ complexes can be obtained. The conversion of the nonemissive (dppe)Pt{S_2C_2(2-pyridine)(CH_2CH_2OH)} to the luminescent [(dppe)Pt{S_2C_2(CH_2CH_2-*N*-2-pyridinium)}]$^+$ could serve as a probe for molecules which functionalize alcohols. As such, (dppe)Pt{S_2C_2(2-pyridine)(CH_2CH_2OH)} is being studied as a possible probe for the detection of activated phosphates.[45]

The Ni and Pd complexes as well as the neutral Pt complexes have low-lying d to d transitions that lead to rapid decay of the excited states by nonradiative processes. Upon protonation (or alkylation as in **16**), the Pt complexes have a 1,2-enedithiolate π to heterocycle π^* intraligand charge-transfer transition (ILCT) as their lowest lying band, an observation consistent with our previous findings.[25−27] The difference in the quantum yields of [(dppe)Pt{S_2C_2(CH_2CH_2-*N*-2-pyridinium)}]$^+$ and [(dppe)Pt-{S_2C_2(2-pyridinium)(H)}]$^+$ from that of [(dppe)Pt{S_2C_2(2-pyridinium)(CH_2CH_2OR″)}]$^+$ provided insight into the nature of the ILCT excited states. These findings strongly support a planar ILCT* excited state where a 1,2-enedithiolate sulfur is formally oxidized and the pyridinium nitrogen reduced.

While [(dppe)Pt{S_2C_2(2-pyridinium)(CH_2CH_2OR″)}]$^+$ are weak emitters in solution, they are currently being studied in rigid media and under pressure, where free volumes are decreased and the heterocycle and 1,2-enedithiolate are more likely to be coplanar and hence the molecules emissive.[46,47]

Experimental Section

Physical Measurements. NMR spectra were acquired with a Bruker AF 200, AM 400, DRX 400, or DRX 500. IR spectra were collected with either a Perkin-Elmer 1600 or a Nicolet 5 DXL FT-IR spectrom-

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eter. UV−visible spectra were recorded on either a Perkin-Elmer Lambda 2S or a Hewlet Packard 8452A spectrometer. EI and FAB mass spectral data were collected on a Magnetic Sector VG 7070E.

Luminescence Measurements. Room-temperature excitation and emission spectra were acquired with an SLM AB2 fluorescence spectrometer. Emission spectra were corrected for instrumental response using factors supplied by the manufacturer. Oxygen-free luminescence measurements were made on 10^{-5} M solutions of all complexes that were deoxygenated by three freeze−pump−thaw N_2-backfill cycles in a fluorescence cell equipped with a reservoir and a Teflon valve. Quantum yields, ϕ, were calculated relative to Zn(tpp) $\{\phi_{std} = 0.04\}$ (tpp = tetraphenylporphyrinato)[48] in air and under Ar.

Luminescent lifetimes at various quencher concentrations were acquired with an ISS K2 digital frequency-domain spectrofluorometer. Singlet and triplet lifetimes were determined using an ISS K2 digital frequency-domain spectrofluorometer. The excitation source was a 300 W xenon lamp and the band-pass of the excitation monochromator was 16 nm. Sample and reference solutions were contained in 1 cm quartz cells at room temperature. A scattering solution of glycogen in Milli-Q water was used as the reference. For some low-intensity samples, a neutral density filter was used to reduce the intensity of the reference scatter. Single-channel detection at 90° was employed, with long-pass filters used to block the excitation line and Raman scatter from the sample. The frequency range used for the experiments was 0.4−340 MHz. Lifetimes were determined from the frequency dependence of the signal phase shifts and demodulation, relative to the reference, using the ISS least-squares analysis software. The minimization procedure assumed discrete lifetimes. The procedure provided lifetimes, fractional photon contributions, and χ^2 for the least-squares fit. The χ^2 values for the data reported are between 20 and 30. From the least-squares fit matrix analysis, the errors associated with the measurement of the singlet emission of **16** were <0.03 ns while those of the triplet emission were <1100 ns.

Materials. (dppe)M(Cl)$_2$ and (dppe)M(SH)$_2$ (M = Ni, Pd, Pt; dppe = 1,2-bis(diphenylphosphino)ethane),[49−51] 1-(2-pyridyl)-4-acetoxybutan-1-one,[52] and 2-chlorophenyl bis(triazole) phosphate[53] were prepared according to the literature procedures. All reactions were performed under an atmosphere of nitrogen using standard Schlenk line techniques. Workups were performed in air unless stated otherwise. Dichloromethane, acetonitrile, and pentane were dried over calcium hydride and distilled under nitrogen. Diethyl ether, tetrahydrofuran, and dioxane were dried over Na/benzophenone and distilled under nitrogen. Triethylamine was dried over potassium hydroxide and vacuum-distilled. DMF, γ-butyrolactone, 2-bromopyridine, and *n*-butyllithium were used as received from Acros Chemical. Neutral activated alumina, 80−325 mesh, was purchased from EM Science, Cherry Hill, NJ, and treated with 6% H_2O by weight to generate the Brockmann activity 3 material used throughout this study.

Syntheses. (a) 2-PyCOCH(Br)CH$_2$CH$_2$OAc, 3. A solution of bromine (914 mg, 5.72 mmol) in acetic acid (2 mL) was added to 1-(2-pyridyl)-4-acetoxybutan-1-one (1.02 g, 4.92 mmol). The mixture was heated at 80 °C for 10 min and then cooled to 25 °C. The mixture was diluted with H_2O and extracted with CH_2Cl_2 (3 × 10 mL). The extract was collected and evaporated to dryness in vacuo to yield **3** in 97% yield as a brown oil (1.36 g, 4.76 mmol). ^1H NMR ($CDCl_3$): δ 8.62 (m, 1H, C_5H_4N), 8.00 (m, 1H, C_5H_4N), 7.81 (m, 1H, C_5H_4N), 7.45 (m, 1H, C_5H_4N), 5.98 (t, 1H, CHBr, J_{H-H} = 6 Hz), 4.23 (t, 2H, CH_2O, J_{H-H} = 6 Hz), 2.39 (second-order t, 2H, CH_2, line spacing = 6 Hz), 1.94 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 193.5 (2-pyCO), 170.6 (OCO), 148.9, 137.1, 127.6, 123.2 (C_5H_4N), 61.7 (CHBr), 42.8 (CH_2), 32.1 (CH_2O), 20.7 (CH_3). IR (thin film, cm^{-1}): 3055 (w), 2961 (w), 1746 (s), 1697 (s), 1583 (m), 1346 (m), 1362 (m), 1318 (m), 1243 (s), 1043 (m), 995 (m). Mass spectrum (EI): *m/z* 287 (M^+).

(b) (dppe)Ni{S$_2$C$_2$(2-pyridine)(CH$_2$CH$_2$OAc)}, 4. To a DMF (5 mL) solution of (dppe)Ni(SH)$_2$ (100 mg, 0.191 mmol) was added 1-(2-pyridyl)-2-bromo-4-acetoxybutan-1-one (132 mg, 0.463 mmol). The orange solution was stirred for 2 h and became purple. The DMF was removed in vacuo, and the solid was chromatographed on a 1 × 20 cm alumina column where the product was eluted with CH_2Cl_2. The eluate was evaporated to dryness to give **4** as a green crystalline solid in 78% yield (108 mg, 0.152 mmol). ^1H NMR ($CDCl_3$): δ 8.52 (m, 1H, C_5H_4N,), 7.78−7.70 (m, 8H, PC_6H_5 and 1H, C_5H_4N), 7.54−7.42 (m, 12H, PC_6H_5 and 1H, C_5H_4N), 7.02 (m, 1H, C_5H_4N), 4.22 (t, 2H, CH_2O, J_{H-H} = 7 Hz), 3.01 (t, 2H, CH_2, J_{H-H} = 7 Hz), 2.35 (m, 4H, PC_2H_2), 1.84 (s, 3H, CH_3). ^{31}P NMR (DMSO): δ 58.6 (br s). IR (thin film, cm^{-1}): 3210 (w), 3052 (w), 2962 (w), 1732 (s), 1582 (s), 1435 (m), 1260 (m), 1099 (s), 1027 (m). High-resolution mass spectrum (FAB), *m/z*: calcd, 710.101 62 for $C_{37}H_{35}O_2NP_2S_2{}^{58}Ni$; found, 710.101 72.

(c) (dppe)Pd{S$_2$C$_2$(2-pyridine)(CH$_2$CH$_2$OAc)}, 5. This compound was prepared and isolated as described for complex **4** using (dppe)-Pd(SH)$_2$ (250 mg, 0.438 mmol) and 1-(2-pyridyl)-2-bromo-4-acetoxy-butan-1-one (132 mg, 0.438 mmol). Complex **5** was isolated as a yellow crystalline solid in in 62% yield (206 mg, 0.271 mmol). ^1H NMR ($CDCl_3$): δ 8.49 (m, 1H, C_5H_4N,), 7.79−7.77 (m, 8H, PC_6H_5, and 1H, C_5H_4N), 7.55−7.23 (m, 12H, PC_6H_5, and 1H, C_5H_4N), 6.99 (m, 1H, C_5H_4N), 4.25 (t, 2H, CH_2O, J_{H-H} = 7 Hz), 2.89 (t, 2H, CH_2, J_{H-H} = 7 Hz), 2.47 (m, 4H, PC_2H_2), 1.86 (s, 3H, CH_3). ^{31}P NMR (DMSO): δ 51.7 (br q, second-order spectrum with line spacings of 41 and 4 Hz). IR (thin film, cm^{-1}): 3210 (w), 3052 (w), 2899 (w), 2846 (w), 1734 (s), 1588 (s), 1537 (m), 1464 (w), 1423 (s), 1264 (m), 1102 (s). High-resolution mass spectrum (FAB), *m/z*: calcd, 759.062 32 for $C_{37}H_{35}O_2NP_2S_2{}^{108}Pd$; found, 759.059 45.

(d) (dppe)Pt{S$_2$C$_2$(2-pyridine)(CH$_2$CH$_2$OCOCH$_3$)}, 6. This compound was prepared and isolated as described for complex **4** using (dppe)Pt(SH)$_2$ (250 mg, 0.379 mmol) and 1-(2-pyridyl)-2-bromo-4-acetoxy-butan-1-one (114 mg, 0.417 mmol). Complex **6** was isolated as a yellow crystalline solid in in 70% yield (266 mg, 0.265 mmol). ^1H NMR ($CDCl_3$): δ 8.45 (m, 1H, C_5H_4N), 7.98−7.75 (m, 8H, PC_6H_5, and 1H, C_5H_4N), 7.48 (m, 1H, C_5H_4N,), 7.43−7.24 (m, 12H, PC_6H_5), 6.96 (m, 1H, C_5H_4N), 4.28 (t, 2H, CH_2O, J_{H-H} = 7 Hz), 3.02 (t, 2H, CH_2, J_{H-H} = 7 Hz), 2.43 (m, 4H, PC_2H_2), 1.85 (s, 3H, CH_3). ^{31}P NMR (DMSO): δ 45.8 (d with Pt satellites, J_{P-P} = 12 Hz; J_{Pt-P} = 2748 Hz), 45.5 (d with Pt satellites, J_{P-P} = 12 Hz; J_{Pt-P} = 2748 Hz). IR (thin film, cm^{-1}): 3052 (w), 2961 (w), 1732 (s), 1676 (w), 1582 (m), 1463 (w), 1437 (s), 1244 (s), 1104 (m). High-resolution mass spectrum (FAB), *m/z*: calcd, 847.123 41 for $C_{37}H_{35}O_2NP_2S_2{}^{196}Pt$; found, 847.121 76.

(e) (dppe)Pd{S$_2$C$_2$(2-pyridine)(CH$_2$CH$_2$OH)}, 7. To a solution of 0.1 M K_2CO_3 in MeOH was added complex **5** (141 mg, 0.185 mmol). The solution was stirred at 25 °C for 1 h, and the resulting mixture was concentrated in vacuo. The resulting solid was dissolved in CH_2Cl_2, and the solution was washed with H_2O and concentrated in vacuo to yield complex **7** in 90% yield (120 mg, 0.167 mmol). ^1H NMR ($CDCl_3$): δ 8.33 (m, 1H, C_5H_4N), 7.79−7.74 (m, 8H, PC_6H_5, and 1H, C_5H_4N), 7.54−7.25 (m, 12H, PC_6H_5, and 1H, C_5H_4N), 6.96 (m, 1H, C_5H_4N), 3.94 (t, 2H, CH_2O, J_{H-H} = 5 Hz), 2.89 (br t, 2H, CH_2, J_{H-H} = 5 Hz), 2.45 (m, 4H, PC_2H_2). ^{31}P NMR (DMSO): δ 51.6 (br q, second-order spectrum with major line spacings of 41 and 4 Hz). IR (thin film, cm^{-1}): 3052 (m), 2964 (w) 1742 (s), 1673 (s), 1582 (s), 1538 (m), 1486 (m), 1435 (s), 1247 (s), 1104 (s). High-resolution mass spectrum (FAB), *m/z*: calcd, 716.043 95 for $C_{35}H_{32}ONP_2S_2{}^{108}Pd$; found, 716.043 59.

(f) (dppe)Pt{S$_2$C$_2$(2-pyridine)(CH$_2$CH$_2$OH)}, 8. This compound was prepared and isolated as described for complex **7**, using **6** (160 mg, 0.189 mmol). Complex **8** was isolated as a yellow solid in 91% yield (138 mg, 0.172 mmol). ^1H NMR ($CDCl_3$): δ 8.34 (m, 1H, C_5H_4N), 7.82−7.75 (m, 8H, PC_6H_5, and 1H, C_5H_4N), 7.53−7.41 (m, 12H, PC_6H_5, and 1H, C_5H_4N), 7.02 (m, 1H, C_5H_4N), 3.94 (t, 2H, CH_2O, J_{H-H} = 5 Hz), 2.90 (br t, 2H, CH_2, J_{H-H} = 5 Hz), 2.68 (broad singlet, 1H, OH), 2.50 (m, 4H, PC_2H_2). ^{31}P NMR (DMSO): δ 45.5 (d with Pt satellites, J_{P-P} = 13 Hz; J_{Pt-P} = 2722 Hz), 45.4 (d with Pt satellites, J_{P-P} = 13 Hz; J_{Pt-P} = 2722 Hz). IR (thin film, cm^{-1}): 3210 (w),

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3053 (w), 2959 (w), 2851 (w), 1587 (s), 1542 (w), 1464 (w), 1435 (s), 1237 (m), 1104 (s). High-resolution mass spectrum (FAB), *m*/*z*: calcd, 804.104 98 for $C_{35}H_{32}ONP_2S_2{}^{196}Pt$; found, 804.107 85.

(g) (dppe)Pd$\{S_2C_2$(2-pyridine)$(CH_2CH_2OCO(CH_2)_{10}CH_3)\}$, 9. To a solution of complex **7** (100 mg, 0.140 mmol) in pyridine (10 mL) was added lauroyl chloride (34 μL, 0.150 mmol), and the solution was stirred for 2 h. The pyridine was removed in vacuo, and the resulting solid was chromatographed on a 1 × 20 cm alumina column where the product was eluted with CH_2Cl_2. The eluate was evaporated to dryness to give **9** as a red solid in 65% yield (81 mg, 0.090 mmol). ^{1}H NMR ($CDCl_3$): δ 8.65 (m, 1H, C_5H_4N), 7.86−7.73 (m, 8H, PC_6H_5, and 1H C_5H_4N), 7.46−7.40 (m, 12H, PC_6H_5, and 2H C_5H_4N), 4.21 (t, 2H, CH_2O, $J_{H-H} = 7$ Hz), 2.90 (m, 2H, CH_2), 2.53 (m, 4H, PC_2H_2), 2.31 (t, 2H, $OCOCH_2$, $J_{H-H} = 7$ Hz), 1.43 (t, 2H, CH_2CH_3, $J_{H-H} = 7$ Hz), 1.18 (m, 16H, CH_2), 0.84 (t, 3H, CH_3, $J_{H-H} = 7$ Hz). ^{31}P ($CDCl_3$): δ 45.6 (br q, second-order spectrum with major line spacings of 44 and 5 Hz). IR (thin film, cm^{-1}): 3054 (w), 2926 (m), 2853 (w), 1719 (s), 1576 (m), 1539 (s), 1458 (m), 1436 (s), 1262 (w), 1187 (w), 1104 (s). High-resolution mass spectrum (FAB), *m*/*z*: calcd, 897.218 44 for $C_{47}H_{55}O_2NP_2S_2{}^{106}Pd$; found, 897.218 47.

(h) (dppe)Pt$\{S_2C_2$(2-pyridine)$(CH_2CH_2OCO(CH_2)_{10}CH_3)\}$, 10. This compound was prepared and isolated as described for complex **9** using complex **8** (66 mg, 0.082 mmol) and lauroyl chloride (19 μL, 0.081 mmol). Complex **10** was isolated in 53% yield as a yellow solid (43 mg, 0.435 mmol). ^{1}H NMR ($CDCl_3$): δ 8.49 (m, 1H, C_5H_4N), 7.84−7.76 (m, 8H, PC_6H_5, and 1H C_5H_4N), 7.53−7.36 (m, 12H, PC_6H_5, and 2H, C_5H_4N), 4.29 (t, 2H, CH_2O, $J_{H-H} = 7$ Hz), 3.02 (t, 2H, CH_2, $J_{H-H} = 7$ Hz), 2.52 (m, 4H, PC_2H_2), 2.43 (t, 2H, $OCOCH_2$, $J_{H-H} = 7$ Hz), 1.51 (t, 2H, CH_2CH_3, $J_{H-H} = 7$ Hz), 1.2 (m, 16H, CH_2), 0.85 (t, 3H, CH_3, $J_{H-H} = 7$ Hz). ^{31}P NMR (DMSO): δ 46.5 (d with Pt satellites, $J_{P-P} = 13$ Hz; $J_{Pt-P} = 2769$ Hz), 46.4 (d with Pt satellites, $J_{P-P} = 13$ Hz; $J_{Pt-P} = 2769$ Hz). IR (thin film, cm^{-1}): 3052 (w), 2960 (w), 2926 (m), 2854 (w), 1732 (s), 1582 (m), 1462 (w), 1435 (s), 1262 (m), 1103 (m), 1208 (w). High-resolution mass spectrum (FAB), *m*/*z*: calcd, 986.281 53 for $C_{47}H_{55}O_2NP_2S_2{}^{195}Pt$; found, 986.279 72.

(i) [(dppe)Pd$\{S_2C_2(CH_2CH_2$-*N*-2-pyridinium)$\}$][BPh$_4$], 15. Complex **7** (32 mg, 0.040 mmol) was dissolved in dry pyridine (10 mL), and the solution was cooled to −10 °C. To this solution was added *p*-toluenesulfonyl chloride (15 mg, 0.080 mmol). The reaction mixture was allowed to warm to room temperature over 1 h, and the reaction was quenched by the addition of 1 mL of water. The pyridine solution was subsequently removed in vacuo. The resulting solid was dissolved in 5 mL of MeOH to which 1 mL of a $NaBPh_4$-saturated MeOH solution was added. Complex **15** was isolated by filtration as a red solid in 54% yield (24 mg, 0.021 mmol) and was washed with 3 × 5 mL of MeOH. ^{1}H NMR (DMSO): δ 8.59 (m, 1H, C_5H_4N), 8.52 (m, 1H, C_5H_4N), 7.83−7.71 (m, 8H, PC_6H_5, and 1H, C_5H_4N), 7.57−7.46 (m, 12H, PC_6H_5, and 1H, C_5H_4N), 7.21−7.12 (m, 9H, $B(C_6H_5)_4$), 6.95−6.87 (m, 9H, $B(C_6H_5)_4$), 6.80−6.73 (m, 2H, $B(C_6H_5)_4$), 4.57 (m, 2H, CH_2), 2.90 (m, 2H, CH_2), 2.76 (m, 4H, PC_2H_2). ^{31}P NMR (DMSO): δ 45.7 (q, second-order spectrum with major line spacings of 39 and 44 Hz). IR (thin film, cm^{-1}): 3054 (w), 2958 (w), 1619 (s), 1493 (s), 1435 (s), 1262 (m), 1103 (m). High-resolution mass spectrum (FAB), *m*/*z*: calcd, 698.046 39 for $C_{35}H_{32}NP_2S_2{}^{106}Pd$; found, 698.048 65.

(j) [(dppe)Pt$\{S_2C_2(CH_2CH_2$-*N*-2-pyridinium)$\}$][BPh$_4$], 16. This compound was prepared and isolated as described for complex **15** using complex **8** (0.200 mg, 0.228 mmol) and *p*-toluenesulfonyl chloride (0.87 mg, 0.456 mmol). Complex **16** was isolated in 56% yield (152 mg, 0.127 mmol) as an orange solid. ^{1}H NMR ($CDCl_3$): δ 8.49 (m, 1H, C_5H_4N), 7.62−7.58 (m, 8H, PC_6H_5, and 1H C_5H_4N), 7.45−7.37 (m, 12H, PC_6H_5, and 1H, C_5H_4N), 7.13−7.09 (m, 9H, $B(C_6H_5)_4$), 7.00 (m, 1H, C_5H_4N), 6.87−6.80 (m, 9H, $B(C_6H_5)_4$), 6.69−6.62 (m, 2H, $B(C_6H_5)_4$), 3.93 (t, 2H, CH_2, $J_{H-H} = 7$ Hz), 2.60 (t, 2H, CH_2, $J_{H-H} = 7$ Hz), 2.38 (m, 4H, PC_2H_2). ^{31}P NMR (DMSO): δ 47.3 (d with Pt satellites, $J_{P-P} = 13$ Hz; $J_{Pt-P} = 2790$ Hz), 47.2 (d with Pt satellites, $J_{P-P} = 13$ Hz; $J_{Pt-P} = 2790$ Hz). IR (thin film, cm^{-1}): 3054 (w), 2960 (w), 1620 (s), 1494 (s), 1435 (s), 1264 (m), 1104 (m). High-resolution mass spectrum (FAB), *m*/*z*: calcd, 787.117 60 for $C_{35}H_{32}NP_2S_2{}^{195}Pt$; found, 787.109 92.

Crystallographic Structural Determination. The single-crystal X-ray diffraction experiment was performed on a Siemens P4/CCD diffractometer. The systematic absences in the diffraction data were consistent for space groups *P*1 and $P\bar{1}$. The *E* statistics strongly suggested the centrosymmetric space group $P\bar{1}$, which yielded chemically reasonable and computationally stable results of refinement. The structure was solved using direct methods, completed by subsequent difference Fourier synthesis, and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in the SHELXTL (version 5.03) program library (G. Sheldrick, Siemens XRD, Madison, WI).

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for complex **15** is available on the Internet only. Access information is given on any current masthead page.

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