Low-Lying Singlet and Triplet Electronic Excited States of Binuclear (d^{10}–d^{10}) Palladium(0) and Platinum(0) Complexes

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Abstract: The UV–visible absorption, emission, and excitation spectra and the emission lifetimes of $M(PPh_3)_3$ and $M_2(dppm)_3$ (M = Pd, Pt; dppm = bis(diphenylphosphino)methane) in 2-methyltetrahydrofuran solution at room temperature and 77 K have been investigated. Electronic absorption and emission bands attributable to $p\sigma \leftarrow d$ transitions are observed in the 400–900-nm region in the d^{10}–d^{10} binuclear complexes; the M_2 emissive state is $^3A_2''(d\sigma^*)(p\sigma)$. Resonance Raman spectra associated with excitation in the $M_2(dppm)_3$ $p\sigma \leftarrow d\sigma^*$ singlet absorption band have been measured: peaks attributable to M–M stretching vibrations are at 120.0 ($k = 0.45$; M = Pd) and 102.5 cm^{-1} ($k = 0.60$ mdyn Å^{-1}; M = Pt), thereby confirming the presence of weak M–M bonding interactions. When an empirical distance/force constant equation is used, the Pd–Pd distance in $Pd_2(dppm)_3$ is estimated to be 3.043 Å.

The spectroscopic properties and photochemical reactivities of d^8–d^8 complexes have been extensively investigated.[1-3] Related d^{10}–d^{10} species[4] have not attracted as much attention, but the luminescence behavior of $Pd_2(dppm)_3$ (dppm bis(diphenylphosphino)methane) and $Pd_2(dpam)_3$ (dpam = bis(diphenylarsino)methane) has been reported.[5] The d^{10}–d^{10} systems exhibit long-lived luminescences and are very reactive in solution with small molecules.[4c,5] The aim of this work is to elucidate the electronic structures of the lowest singlet and triplet excited states of d^{10}–d^{10} Pd_2 and Pt_2 species.

Experimental Section

Materials. K_2PtCl_4, K_2PdCl_4 (Aldrich), PPh_3, and dppm (Strem) were used without further purification. $M(PPh_3)_3$ and $M_2(dppm)_3$ complexes were synthesized according to standard procedures[4c,6,7] and were purified by triple recrystallization in benzene/ethanol or benzene/propanol. Purity was checked by elemental analysis and ^{31}P and ^1H NMR spectroscopy (500 MHz; 1000 scans). All complexes are air-sensitive; they were stored in an oxygen-free drybox when not in use. The $M(PPh_3)_3$ complexes also are light-sensitive in the solid state; they were stored in the dark.[8] Ethanol, propanol, and 2-MeTHF (Aldrich) were purified according to standard procedures.[9,10] Benzene (B&J) was used without further purification. Syntheses were performed in a nitrogen-flush box, and spectroscopic measurements were made after freeze–pump–thaw degassing the solutions.

Table I. Spectroscopic and Emission Lifetime Data for $M(PPh_3)_3$ and $M_2(dppm)_3$

A. Spectroscopic Energies[a]

	$^1(p\sigma \leftarrow d\sigma^*)$	$3(p\sigma \leftarrow d\delta^*)$	$3(p\sigma \leftarrow d\sigma^*)$	emission
$Pd_2(dppm)_3$	22 700	20 000	17 400	14 400
	(33 800)	(2 500)	(530)	
$Pt_2(dppm)_3$	20 500	18 900	16 900	~12 700
	(27 400)	(5 100)	(1 200)	

B. Emission Lifetimes[b,c]

	τ_e, μs (λ_{max}, nm)	τ_e, μs (λ_{max}, nm)
$Pd(PPh_3)_3$	6.61 ± 0.02 (635)	98 ± 1 (590)
$Pd_2(dppm)_3$	5.93 ± 0.01 (710)	107 ± 1 (685)
$Pt(PPh_3)_3$	0.69 ± 0.01 (705)	24.9 ± 0.1 (645)
$Pt_2(dppm)_3$	<0.02 (790)	10.6 ± 0.2 (790)

C. Raman Data[d]

	ν_{M-M}, cm^{-1}	k, mdyn Å^{-1}	M–M, Å
$Pd_2(dppm)_3$	120 ± 0.5	0.45	3.043
$Pt_2(dppm)_3$	102 ± 0.5	0.60	3.024[e]

[a] In cm^{-1} at 77 K (ϵ in M^{-1} cm^{-1}). [b] Measured at λ_{max}. [c] Experimental error is based on the largest difference between the lowest and highest measured lifetimes at different concentrations. [d] Solid-state data at room temperature. [e] 3.025 Å from a structure determination.[14]

Measurements. The UV–visible spectra were recorded on a Cary 17 spectrometer. The emission and excitation spectra were obtained with a Perkin-Elmer MPF-66 spectrofluorometer. The emission lifetimes were measured on a Quanta Ray Nd-YAG (8-ns fwhm; 355- and 532-nm excitation) laser system.[11] The solid-state resonance Raman spectra were recorded on an I.S.A. micro-Raman Jobin Yvon U1000 spectrometer, with the 454.5- and 514.5-nm lines of an argon ion laser.

Results and Discussion

The room-temperature and 77 K UV–visible absorption spectra of $M(PPh_3)_3$ and $M_2(dppm)_3$ (M = Pd,Pt) in 2-MeTHF are shown

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(1) (a) Marshall, J. L.; Stiegman, A. E.; Gray, H. B. In *Excited States and Reactive Intermediates: Photochemistry, Photophysics, and Electrochemistry*; Lever, Ed.; A.B.P. ACS Symposium Series 307; American Chemical Society: Washington, DC, 1986; p 166. (b) Che, C.-M.; Lee, W. M. *J. Chem. Soc., Chem. Commun.* **1986**, 512. (c) Roundhill, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 4354. (d) Peterson, J. R.; Kalyanasundaram K. *J. Phys. Chem.* **1985**, *89*, 2486. (e) Che, C.-M.; Butler, L. G.; Grunthaner, P.; Gray, H. B. *Inorg. Chem.* **1985**, *24*, 4662. (f) Kim, J.; Fan, F. F.; Bard, A. J.; Che, C.-M.; Gray, H. B. *Chem .Phys. Lett.* **1985**, *121*, 543. (g) Rice, S. F.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 4571. (h) Che, C.-M.; Butler, L. G.; Gray, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 7796. (i) Fordyce, W. A.; Crosby, G. A. *J. Am. Chem. Soc.* **1982**, *103*, 7061.

(2) (a) Rice, S. F.; Milder, S. J.; Gray, H. B.; Goldbeck, R. A.; Kliger, D. S. *Coord. Chem. Rev.* **1982**, *43*, 349 and references therein. (b) Gray, H. B.; Maverick, A. W. *Science (Washington, D.C.)* **1981**, *214*, 1201. (c) Eidem, P. K.; Maverick, A. W.; Gray, H. B. *Inorg. Chim. Acta* **1981**, *50*, 59. (d) Mann, K. R.; DiPierro, M. J.; Gill, T. P. *J. Am. Chem. Soc.* **1980**, *102*, 3965.

(3) (a) Marshall, J. L.; Stobart, S. R.; Gray, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 3027. (b) Winkler, J. R.; Marshall, J. L.; Netzel, T. L.; Gray, H. B. *J. Am. Chem. Soc.* **1986**, *108*, 2263.

(4) (a) DeLaet, D. L.; Fanwick, P. E.; Kubiak, C. P. *Organometallics* **1986**, *5*, 1807. (b) Stern, E. W.; Maples, P. K. *J. Catal.* **1972**, *27*, 120. (c) Grossel, M. C.; Brown, M. P.; Nelson, C. D.; Yavari, A.; Kalles, E.; Moulding, R. P.; Seddon, K. R. *J. Organomet. Chem.* **1982**, *232*, C13. (d) Yoshida, T.; Tulip, T. H.; Ibers, J. A.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 2063. (e) Karch, H. H.; Schubert, U. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 186. (f) Briant, C. E.; Hall, K. P.; Mingos, D. M. P. *J. Organomet. Chem.* **1982**, *229*, C5 and references therein.

(5) Caspar, J. V. *J. Am. Chem. Soc.* **1985**, *107*, 6718.

(6) The reduction of $M(PPh_3)_2Cl_2$ by $NaBH_4$ in the presence of dppm[4c] gives strongly emissive $M(PPh_3)_3$ as a residual impurity: $M(dppm)Cl_2$ is preferred as a starting material for the preparation of $M_2(dppm)_3$.

(7) Ittel, S. D. *Inorg. Synth.* **1976**, *17*, 117. For $Pd(PPh_3)_3$, the impurity is $Pd(PPh_3)_4$, which is readily detected by its strong green luminescence (instead of orange).

(8) Both $Pd(PPh_3)_3$ and $Pt(PPh_3)_3$ are bright yellow crystals after multiple recrystallizations, but they turn pale gold and orange, respectively, in room light.

(9) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purifications of Laboratory Chemicals*; Pergamon: Oxford, **1966**.

(10) 2-Methyltetrahydrofuran was purified according to the procedure outlined for tetrahydrofuran in: Gordon, A. J.; Ford, R. A. *The Chemist's Companion, A Handbook of Practical Data, Techniques, and References*; Wiley: New York, **1972**, p 436.

(11) Nocera, D. G.; Winkler, J. R.; Yocom, K. M.; Bordignon, E.; Gray, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 5145.

0002-7863/88/1510-2145$01.50/0

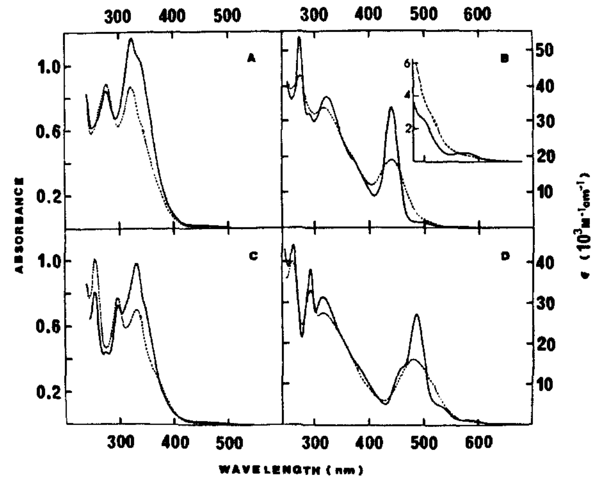

Figure 1. Absorption spectra of $Pd(PPh_3)_3$ (A), $Pd_2(dppm)_3$ (B), $Pt(PPh_3)_3$ (C), and $Pt_2(dppm)_3$ (D) at room temperature (···) and 77 K (—).

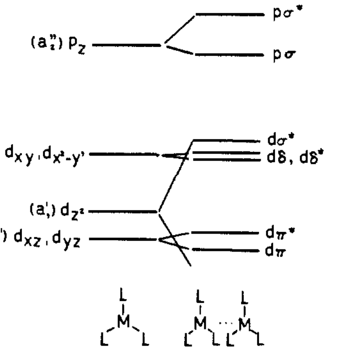

Figure 2. Molecular orbital energy level diagram for d^{10} ML_3 and d^{10}–d^{10} $(ML_3)_2$ complexes.

in Figure 1.[12-14] Because of the extreme air sensitivity of the $M(PPh_3)_3$ complexes, molar absorptivities were not determined. However, several experiments[15] indicate that ε(320 nm) is between 12000 and 16000 M^{-1} cm^{-1} at room temperature for both Pd and Pt. In D_{3h} d^{10} ML_3 complexes, the relative energies of the highest occupied orbitals are $d_{xz},d_{yz} < d_{z^2} < d_{xy},d_{x^2-y^2}$ and the lowest unoccupied orbital[5] is p_z (Figure 2). The very large energy gap (~15000 cm^{-1}) between the lowest observed electronic absorption and emission bands in $M(PPh_3)_3$ cannot be accounted for by an excited-state distortion.[16] Thus there must be one or more forbidden transitions in the 400–500-nm tail absorption,[17] and reasonable candidates are $^1E'' \leftarrow {}^1A_1'$ and $^3E'' \leftarrow {}^1A_1'$ derived from $p_z \leftarrow d_{xy}$, $d_{x^2-y^2}$ excitations.

Intense absorptions that sharpen at low temperature are observed in the 400–500-nm spectra of the binuclear complexes (440 nm, ε 33800 M^{-1} cm^{-1} for $Pd_2(dppm)_3$; 487 nm, ε 27400 M^{-1} cm^{-1} for $Pt_2(dppm)_3$ at 77 K). Low-energy weak absorptions (575 (530) and 580 nm (1200 M^{-1} cm^{-1}) for Pd_2 and Pt_2, respectively, at 77 K) are ~2000–4000 cm^{-1} from the centers of emission systems (details are given in Table I; emission spectra are shown in Figure 3). There are additional weak absorption features in the 77 K absorption spectra of Pd_2 (500 nm) and Pt_2 (455, 530 nm) (Figure 1).

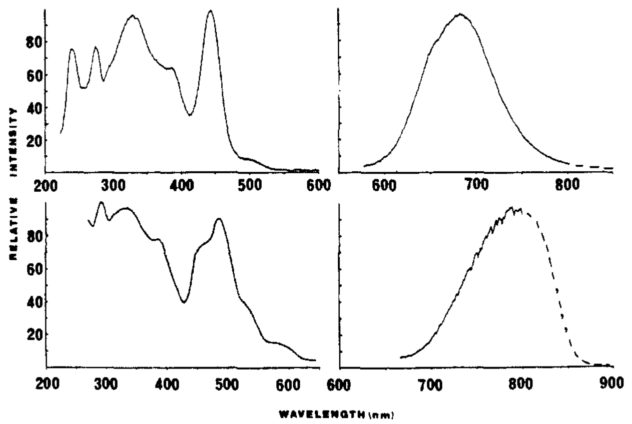

Figure 3. Corrected excitation (left) and emission (right) spectra for $Pd_2(dppm)_3$ (up) and $Pt_2(dppm)_3$ (down) in 2-MeTHF at 77 K ((- - -) is uncorrected emission). Experimental conditions for the Pd and Pt complexes, respectively: λ_{exc} = 450 and 500 nm; λ_{em} = 700 and 820 nm.

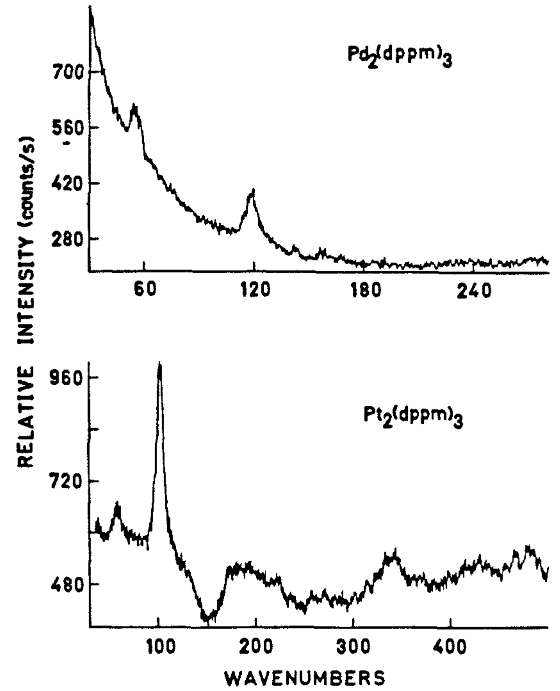

Figure 4. Resonance Raman spectra of solid $M_2(dppm)_3$ at room temperature. Experimental conditions: laser power 2 mW at the sample, microscopic objective 25×, spacing/data point 0.5 cm^{-1}, and 4 s/point. Irradiation wavelengths: 454.5 and 514.5 nm for the Pd and Pt complexes, respectively.

By analogy to well-established patterns in d^8–d^8 species,[1-3] the dσ–dσ* splitting in d^{10}–d^{10} complexes is expected to be much greater than dδ–dδ*, and for this reason the pσ ← dσ* and pσ ← dδ* transitions are likely to appear in the same region (Figure 2). The intense low-energy band in $M_2(dppm)_3$ (Pd_2, 440 nm; Pt_2, 487 nm) is attributable to $^1A_2'' \leftarrow {}^1A_1'$ (pσ ← dσ*), and the 455 nm feature in the Pt_2 spectrum is assigned to the singlet pσ ← dδ* transition. For Pd_2, ^{1}(pσ ← dδ*) probably falls under the ^{1}(pσ ← dσ*) band. This interpretation suggests that the orbital energies are dσ* > dδ, dδ* for Pt_2 and dσ* ~ dδ, dδ* for Pd_2.

The dσ*pσ singlet–triplet separations in a number of d^8–d^8 complexes range from 3000 to 4800 cm^{-1}.[1,2] The 575-nm (Pd_2) and 580-nm (Pt_2) absorptions are 5300 and 3600 cm^{-1}, respectively, from the singlet pσ ← dσ* peaks; thus, they are assigned to transitions to $^3A_2''$(dσ*pσ). The 500-nm (Pd_2) and 530-nm

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(12) Both $Pt(PPh_3)_3$[13] and $Pt_2(dppm)_3$[14] possess the same planar PtP_3 geometry: D_{3h} symmetry is adopted for the designation of orbitals and states.

(13) Albano, V.; Bellon, P. L.; Scatturin, V. *J. Chem. Soc., Chem. Commun.* **1966**, 507.

(14) Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1982**, 1155. Manojlovic-Muir, L.; Muir, K. W.; Grossel, M. C.; Brown, M. P.; Nelson, C. D.; Yavari, A.; Kallas, E.; Moulding, R. P.; Seddon, K. R. *J. Chem. Soc., Dalton Trans.* **1986**, 1955.

(15) The samples were rapidly weighed on a precision balance in ambient atmosphere and then transferred in an air-tight precision cell prior to vacuum transfer of the solvent.

(16) Aggregation also can be ruled out, because the emission energy and lifetime do not depend on complex concentration. Ligand dissociation does not occur in solution at room temperature: Mann, B. E.; Musco, A. *J. Chem. Soc., Dalton Trans.* **1975**, 1673. Tolman, C. A.; Seidel, W. C.; Gerlach, D. H. *J. Am. Chem. Soc.* **1972**, *94*, 2669.

(17) Neither an increase in complex concentration nor a decrease in temperature resolves any bands in the 400–550-nm region, but the same emission is observed with 532-nm laser excitation.

(Pt_2) shoulders are attributable to $^3(p\sigma \leftarrow d\delta^*)$.

The emission that is observed for $M_2(dppm)_3$ is assumed to arise from the $^3A_2''$ excited state. Spin-orbit coupling probably controls the emission lifetimes ($\tau_e(Pd) > \tau_e(Pt)$; Table I); it also manifests itself in the intensities of the weak absorptions associated with transitions to the spin triplets ($Pt_2 > Pd_2$).

The solid-state resonance Raman spectra of $M_2(dppm)_3$ are shown in Figure 4. Peaks attributable to metal–metal stretching vibrations are at 120.0 (Pd_2) and 102.5 cm^{-1} (Pt_2). Woodruff's equations[18] relating bond distance (r/Å) and force constant (F/mdyn Å^{-1}) for M_2 complexes of the 4d and 5d series are shown in eq 1 and 2. We obtain r = 3.024 Å for $Pt_2(dppm)_3$, which

$$r(4d) = 1.83 + 1.45 \exp(-F/2.53) \qquad (1)$$

$$r(5d) = 2.01 + 1.31 \exp(-F/2.36) \qquad (2)$$

is in good agreement with the published value (3.025 Å).[14] No crystallographic data exist for $Pd_2(dppm)_3$; eq 1 estimates the metal–metal separation to be 3.043 Å. The force constant in $Pd_2(dppm)_3$ (0.45 mdyn Å^{-1}) is smaller than the one in $Pt_2(dppm)_3$ (0.60 mdyn Å^{-1}), thereby indicating that weaker metal–metal interactions occur. The blue shift of the singlet $p\sigma \leftarrow d\sigma^*$ band from Pt_2 to Pd_2 also suggests that the M–M interaction is weaker in the Pd_2 complex.

Excitation in $^1(p\sigma \leftarrow d\sigma^*)$ yields two Raman peaks in the 20–200-cm^{-1} region, one metal–metal stretch (in agreement with the assignment of the electronic transition) and one P–M–P 50–60-cm^{-1} bend. Because of the strongly allowed character of the electronic band, the latter mode presumably is totally symmetric.

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[18] Woodruff, W. H., unpublished results. A brief account of Woodruff's correlation for 4d species has appeared: Miskowski, V. M.; Dallinger, R. F.; Christoph. G. G.; Morris, D. E.; Spies, G. H.; Woodruff, W. H. *Inorg. Chem.* **1987**, *26*, 2127.

Cis and Trans Olefin Radicals: Equilibrium and Photoisomerization

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Abstract: Electrochemical reduction of 1,2-bis(1-methyl-4-pyridino)ethylene dication gives the same reduction potentials (−0.53 and −0.72 V vs SCE in CH_3CN) for both cis and trans isomers. Only the absorbance spectrum of the trans radical (ϵ(max) 57 000 M^{-1} cm^{-1} at 517 nm) is observed. However, by using pulse radiolysis the radicals of both cis and trans isomers are observed in aqueous solution. Although their absorbance spectra are similar, the extinction coefficients are very different. The cis radical is intrinsically stable but undergoes rapid electron exchange with the trans dication isomer. Cis and trans radicals equilibrate through electron exchange, the limiting rate constants in both directions of the equilibrium being 2×10^9 M^{-1} s^{-1} (cis to trans) and 3×10^8 M^{-1} s^{-1} (trans to cis). The photoisomerization of the olefin radicals is essentially one-way: the quantum yield for the cis radical is 0.2, while that of the trans is less than 0.01.

Little is known about the photoisomerization of olefin radicals. The first suggestion that it might occur comes from the observations by Shida and Hamill during their study of stilbene cation spectra in solid matrices.[1] Study of the photoisomerization of olefin radicals in solution requires detection and spectral characterization of both cis and trans radical isomers. Furthermore, the temporal stability of these radicals must be ascertained to allow for photolysis.

The existence of distinct cis and trans isomeric radical cations of stilbene in solid matrices was shown by Shida and Hamill.[1] Later Szwarc and co-workers proved in a series of papers that, contrary to past belief, even in solution the cis radical anion of stilbene is long-lived and has distinct properties from the trans radical anion.[2,3] Perhaps because of the complexity of the reactions observed and of the failure of identifying cis radical isomers for other olefins,[4] it is still believed that cis radical isomers of olefins cannot be observed in solution due to their very short lifetimes or simply because they do not exist.[5-7]

To address the considerations just cited, this study first establishes the distinct properties of cis and trans radicals of the olefin 1,2 bis(1-methyl-4-pyridinio)ethylene, BPE[2],[8] whose structures are shown in Figure 1. Then by means of a pulse radiolysis–flash photolysis setup, the photoisomerization of the olefin radicals is examined.

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(1) Shida, T.; Hamill, W. H. *J. Chem. Phys.* **1966**, *44*, 2375.

(2) Jachimowicz, F.; Levin, G.; Szwarc, M. *J. Am. Chem. Soc.* **1978**, *100*, 5426.

(3) Wang, H. C.; Levin, G.; Szwarc, M. *J. Am. Chem. Soc.* **1977**, *99*, 2642.

(4) Happ, J. W.; Ferguson, J. A.; Whitten, D. G. *J. Org. Chem.* **1972**, *37*, 1485.

(5) Takagi, K.; Aoshima, K.; Sawaki, Y.; Iwamura, H. *J. Am. Chem. Soc.* **1985**, *107*, 47.

(6) Takagi, K.; Ogata, Y. *J. Org. Chem.* **1982**, *47*, 1409.

(7) Lewis, F. D.; Petisce, J. R.; Oxman, J. D.; Nepras, M. J. *J. Am. Chem. Soc.* **1985**, *107*, 203.

(8) Ebbesen, T. W.; Previtali, C. M.; Karatsu, T.; Arai, T.; Tokumaru, K. *Chem. Phys. Lett.* **1985**, *119*, 489.

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