AM1-optimized geometry which gave $^{13}C$ hfs of −22.2 and +16.5 G for $HC{\equiv}C^{13}CO_2^{\bullet}$ and $HC{\equiv}^{13}CCO_2^{\bullet}$, respectively,[23] and with an experimental value of −13.3 G measured for $C_6H_5{}^{13}CO_2^{\bullet}$ in an acetyl benzoyl peroxide single crystal at 35–40 K.[26]

The peroxide precursors of **1** and **2** were also subjected to 308 nm LFP and were found to yield transient absorptions in the visible region of the spectrum, as we have found previously for aroyloxyl[7] and alkoxycarbonyloxyl[8] radicals. We assign these absorptions to the expected alkenylcarbonyloxyl and alkynylcarbonyloxyl radicals for the usual reasons, e.g., "instantaneous" (≤4 ns) formation following LFP, lifetimes that are the same in $N_2$-saturated as in $O_2$-saturated solutions, etc.[7,8] LFP measurements[7,8] indicate that the alkenylcarbonyloxyl radical is of comparable reactivity to benzoyloxyl[7c] and that the alkynylcarbonyloxyl radical has a reactivity greater than benzoyloxyl[7c] but generally somewhat lower than alkoxycarbonyloxyl[8] radicals. For example, in $CCl_4$ at ambient temperatures the bimoleuclar rate constants for reactions of *trans*-$Me_3CCH{=}CHCO_2^{\bullet}$, $C_6H_5CO_2^{\bullet}$, $Me_3CC{\equiv}CCO_2^{\bullet}$, and $CH_3CH_2CH_2OCO_2^{\bullet}$ with styrene are 0.33, 0.51, 5.3, and $20 \times 10^8$ $M^{-1}$ $s^{-1}$, respectively, and with 1,4-cyclohexadiene 1.3, 0.66, 9.2, and $9.9 \times 10^8$ $M^{-1}$ $s^{-1}$, respectively. As before,[8] we attribute differences in the reactivities of different $XCO_2^{\bullet}$ radicals to variations in the importance that polar, canonical structures (e.g., $[XCO_2^- \, RH^{\bullet +}]^{\bullet}$) contribute to the stabilization of the transition state for the reaction.

The detection of carbonyloxyl radicals by EPR spectroscopy under normal experimental conditions opens a new avenue for the exploration of the chemical and spectroscopic properties of these highly reactive and industrially important species.

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(25) For $HCC{\equiv}CCO_2^{\bullet}$ the AM1-optimized geometry of the carboxyl moiety is $r$(C–O) = 1.343 and 1.235 Å, $r$(C–C) = 1.423 Å, and <(O–C–O) = 116.6°. In the case of a forced $C_{2v}$ geometry the AM1-optimization gives $r$(C–O) = 1.284 Å, $r$(C–C) = 1.422 Å, and ⟨(O–C–O) = 122.1°, and the calculated $^{13}C$ hfs increases to −36.8 G. We are indebted to Dr. W. Müller, Universität Essen, for carrying out these calulations.

(26) Merril, R. A. Ph.D. Thesis, Yale University, 1986; *Disser. Abstr. Int., B* **1987**, *47*, 3372. We are indebted to Dr. J. M. McBride for drawing this work to our attention.

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## Luminescent Exciplex Formation Involving Tetrakis(μ-diphosphito)diplatinate(II) and -thallium(I) in Aqueous Solution

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The formation of exciplexes involving singlet organic excited states is well documented.[1-3] While the properties of such exciplexes are often easily probed as a result of strong fluorescence, such is not the case for triplet exciplexes; like most other triplet organic excited states little or no luminescence is observed and only indirect measures of their properties are available.[4,5] This situation is found also for triplet exciplexes involving metalloporphyrins and various electron acceptors[6,7] and for copper (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)$_2$ and various Lewis bases.[8] However, there have been recent reports of luminescent triplet exciplex formation involving rhenium (4,7-dimethyl-1,10-phenanthroline)$(CO)_3Cl$ and *N*,*N*-dimethylbenzeneamine in decahydronaphthalene solution[9] and ruthenium (2,2′-bipyridine)$_3^{2+}$ and $Ag^+$ in aqueous solution.[10]

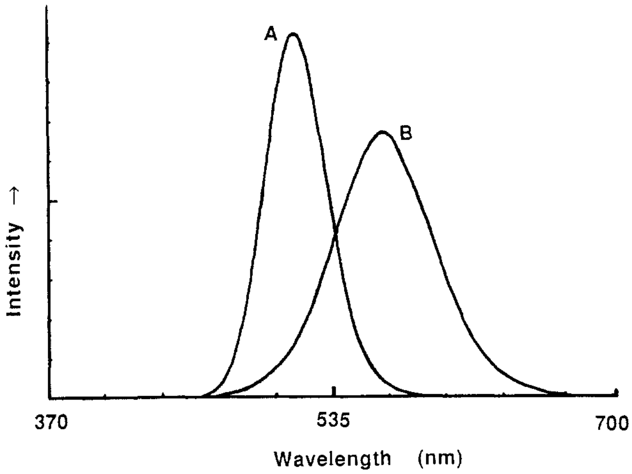

**Figure 1.** Corrected emission spectra of (A) $10^{-5}$ M $Pt_2(P_2O_5H_2)_4{}^{4-}$ and (B) $10^{-5}$ M $Pt_2(P_2O_5H_2)_4{}^{4-}$ and $10^{-3}$ M $TlNO_3$, both in deoxygenated water at room temperature. About 5% of the 514-nm band appears superimposed on the 565-nm band in (B). The absorption (and corrected emission) spectra for (A) and (B) are nearly identical.

Evidence is presented here for the formation of a strongly luminescent triplet exciplex involving $Pt_2(P_2O_5H_2)_4{}^{4-}$ ($Pt_2$; singlet ground state) in its triplet excited state ($Pt_2$*)[11,12] and $Tl^+$ in aqueous solution. As suggested below we believe this to involve Pt–Pt–Tl covalent bonding. Other reports of purely inorganic luminescent exciplexes have appeared[13] but with less direct evidence than reported here. To our knowledge this is the first report of exciplex formation involving a metal–metal-bonded complex.

Figure 1 shows the effect of adding $TlNO_3$ to an aqueous solution of $Pt_2$ irradiated at either 368 or 453 nm. The green 514-nm phosphorescence of $Pt_2$* is replaced by a yellow-green luminescence centered at 565 nm (with intermediate concentrations of $Tl^+$ an isoluminescent point is seen at about 535 nm);[14,15] the 405-nm fluorescence[11] (produced only by 368-nm excitation and not shown on this scale) is unaffected by $Tl^+$. The measured lifetime (10.2 ± 0.2 μs[16]) and quantum yield (0.53 ± 0.03[17]) of

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(2) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978; pp 135–146.

(3) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401–449.

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(7) Hoshino, M.; Seki, H.; Shizuka, H. *J. Phys. Chem.* **1985**, *81*, 470–474.

(8) Palmer, C. E. A.; McMillin, D. R.; Kirmaier, C.; Holten, D. R. *Inorg. Chem.* **1987**, *26*, 3167–3170. McMillin, D. R.; Kirchoff, J. R.; Goodwin, K. V. *Coord. Chem. Rev.* **1985**, *64*, 83–92.

(9) Vogler, A.; Kunkely, H. *Inorg. Chim. Acta* **1980**, *45*, L265–L266.

(10) Ayala, N. P.; Demas, J. N.; DeGraff, B. A. *J. Am. Chem. Soc.* **1988**, *110*, 1523–1529. For the related case of ruthenium (2,2′-bipyarizine)$_3^{2+}$ and $Ag^+$: Lever, A. B. P.; Seymour, P.; Auburn, P. R. *Inorg. Chim. Acta* **1988**, *145*, 43–48.

(11) Zipp, A. *Coord. Chem. Rev.* **1988**, *84*, 47–83. Roundhill, D. M.; Gray, H. B.; Che, C.-M., submitted for publication in *Acc. Chem. Res.*

(12) The $10^7$ ratio of 514–405-nm lifetimes for $Pt_2$*,[11] the $3 \times 10^2$ ratio of 368–453-nm molar absorptivities, and the relative energies of the two absorption and two luminescence bands all support the use of singlet–triplet designations.

(13) Marcantonatos, M. D.; Deschaux, M. *Chem. Phys. Lett.* **1981**, *80*, 327–333. Deschaux, M.; Marcantonatos, M. D. *J. Inorg. Nucl. Chem.* **1981**, *43*, 2915–2917.

(14) $Tl^+$ luminesces in aqueous solutions but only at substantially higher energies than seen here (Sheperd, T. M. *J. Chem. Soc., Faraday Trans 2* **1979**, *75*, 644–650).

(15) As [$Tl^+$] is increased from $10^{-3}$ M to 0.2 M, the absorption (and excitation) band at 368 nm is replaced by one at 389 nm, and the 565-nm luminescence band is replaced by one at 589 nm. Owing to the absorption change, such effects are not considered further here but are currently being investigated. Note that according to ref 2 (p 140), "The 'instability' of the ground state complex is a somewhat arbitrary feature of the excimer and exciplex definition. The essential idea is that the ground state ... collision complexes are *unstable*, low-structured species, *not* that they lack a measurable absorption spectrum." See also ref 25.

(16) Lifetimes of deoxygenated solutions were determined with a Laser Science VSL-337 pulsed nitrogen laser used to pump a DCM-1 dye laser with PPO-365 dye.

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the 565-nm band are both, within experimental uncertainty, the same as those for the 514-nm band of $Pt_2^*$ in the absence of $Tl^+$.[17,18] These similarities, along with the single exponential luminescence decay observed in both cases, suggest the radiative and nonradiative decay rates for the two species are nearly the same.[10,19]

The 565-nm luminescence is assigned to the exciplex $Pt_2Tl^{+*}$, and a value of $2.0 \pm 0.3 \times 10^4$ at 25 °C for the equilibrium constant for $Pt_2^* + Tl^+ \Leftrightarrow Pt_2Tl^{2+*}$ has been determined,[20] giving $\Delta G° = -25$ kJ mol$^{-1}$. This value can be used in an energy cycle analysis[2,21] to derive a free energy difference of $10 \pm 5$ kJ mol$^{-1}$ for the process $Pt_2Tl^+ \Leftrightarrow Pt_2 + Tl^+$. This free energy difference does not refer to the equilibrium ground state of $Pt_2Tl^+$ but rather to an excited vibrational state having the same internuclear configuration as $Pt_2Tl^{+*}$. This state is produced directly as a result of the deactivation of $Pt_2Tl^{+*}$ via exciplex luminescence.[22]

In 2:1 1,2-ethanediol/water solutions, as the temperature is lowered from 250 to 190 K to give a frozen solution, the 565-nm luminescence disappears as the 514-nm phosphorescence reappears, suggesting the likelihood of a diffusional process for exciplex formation. This interpretation is supported by the lack of an effect of $Tl^+$ on the 405-nm fluorescence of $Pt_2^*$ ($\tau \approx$ 1-3 ps[11]) in water. $HNO_3$ (0.1 M), $KNO_3$ (0.1 M), and $O_2$ (air-saturated solutions) all reduce the 565- to 514-nm luminescence intensity ratio, the first two presumably by ion pairing effects and $O_2$ by competitive quenching of $Pt_2^*$.

The tendency for $Tl^+$ and $Pt_2^*$ to form an exciplex can be viewed in terms of a simple molecular orbital picture.[23] In the present case the half-filled $\sigma^*$ ($5d_{z^2}$) and $\sigma$ ($6p_z$) orbitals of $Pt_2^*$[11] are expected to interact at an axial site with the filled 6s and empty $6p_z$ orbitals of $Tl^+$, respectively,[24] to yield a net two-electron stabilization. Such a covalent interaction (formal bond order of one between $Pt_2^*$ and $Tl^+$) differs from the charge-transfer behavior normally attributed to singlet organic exciplex formation.[1-3] Exciplex luminescence in the present case is then expected to result in a reduction in the formal bond order between $Pt_2$ and $Tl^+$ from one to zero,[23] implying a relatively weak ground-state interaction between $Pt_2$ and $Tl^+$.[25] This suggests a reason why the 368-nm absorption band of $Pt_2Tl^+$ is relatively unaffected under these conditions.

The present results lend support to suggestions that triplet exciplex formation may often involve relatively little charge transfer.[6,8,26] $Pt_2Tl^{+*}$ is the first reported example of an exciplex involving a metal-metal-bonded complex and adds to the growing evidence[6-10] that triplet exciplex formation involving metal complexes may be surprisingly common.

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[17] Determined relative to 0.52 for $Pt_2^*$ (Heuer, W. B.; Totten, M. D.; Rodman, G. S.; Hebert, E. J.; Tracey, H. J.; Nagle, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 1163-1164).

[18] Che, C.-M.; Butler, L. G.; Gray, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 7796-7797.

[19] Hui, M.-H.; Ware, W. R. *J. Am. Chem. Soc.* **1976**, *98*, 4718-4727.

[20] The ratio $[Pt_2Tl^{+*}]/[Pt_2^*]$ in deoxygenated solutions with 368-nm excitation was determined by using relative luminescence intensities as a function of $[Tl^+]$ (approximated as the formal concentration of $Tl^+$) over a range of ratios of 2-20 $[Tl^+]/[Pt_2]$ ($[Pt_2] = 10^{-5}$ M). Constant values of $K$ over this range were obtained and support our assignment of a 1:1 $Pt_2^*/Tl^+$ stoichiometry at these concentrations.

[21] Ware, W. R. *NATO Adv. Sci. Inst. Ser., Ser. A* **1983**, *69*, 341-362. Stevens, B. *Adv. Photochem.* **1971**, *8*, 161-226. Beens, H.; Weller, A. In *Organic Molecular Photophysics*; Birks, J. B., Ed.; Wiley: New York, 1975; Vol. 2, Chapter 4. No evidence for diabatic contributions to the process has been obtained (see ref 2, pp 72-73).

[22] The uncertainty in the free energy value is largely due to the estimate of $E_{0-0}$ for $Pt_2^*$ ($245 \pm 4$ kJ mol$^{-1}$: Fordyce, W. A.; Brummer, J. G.; Crosby, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 7061-7064. Rice, S. F.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 4571-4575, ref 17). The decrease in the entropy of the singlet ground state relative to the triplet excited state ($R$ ln 3) has been included in the calculation.

[23] Reference 2, pp 138-139.

[24] See: Nagle, J. K.; Balch, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 319-321, for a consideration of Pt-Tl bonding in $Tl_2Pt(CN)_4^{2-}$.

[25] Although $Tl_2Pt(CN)_4$ exists in the solid state with Pt-Tl bonds of 314.0 (1) pm,[24] $^{195}$Pt NMR results indicate there are no Pt-Tl interactions in $(CH_3)_2SO$ solutions containing $Tl^+$ and $Pt(CN)_4^{2-}$ and no Pt-Pb interactions in aqueous solutions containing $Pb^{2+}$ and $Pt(CN)_4^{2-}$ (Balch, A. L.; Wood, F. E.; Nagle, J. K., unpublished results). Furthermore, recent electronic structure calculations on $Tl_2Pt(CN)_4$ indicate a relatively weak covalent interaction exists between Pt and the $Tl^+$ ions in this compound (Ziegler, T.; Nagle, J. K.; Snijders, J. G.; Baerends, E. J.; Ravenek, W., unpublished results).

[26] Reference 2, p 140.

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## A Stereoselective Synthesis of Functionalized Cyclopentenes via Base-Induced Ring Contraction of Thiocarbonyl Diels-Alder Adducts

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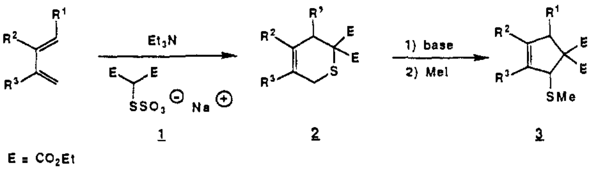
Despite recent advances in the synthesis of cyclopentanoids, interest in this area remains high.[1] One approach which has received relatively little attention is the conversion of 1,3-dienes to cyclopentenes.[2] Considering the enormous number of methods now available for preparing conjugated dienes, this route has considerable potential.

We have developed a two-step procedure for the preparation of usefully functionalized cyclopentenes from conjugated dienes which is both efficient and stereoselective. The overall transformation is presented in eq 1. Bunte salt **1**, prepared from diethyl chloromalonate and sodium thiosulfate, is reacted with triethylamine in the presence of 1,3-dienes. The diethyl thioxomalonate thus generated undergoes smooth cycloaddition in a regioselective fashion.[3,4] When the cycloadducts **2** are exposed to either $LiN(iPr)_2$ or $KN(SiMe_3)_2$ at low temperature followed by quenching with iodomethane, a novel ring contraction occurs, leading to cyclopentenes **3**.



(1)

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