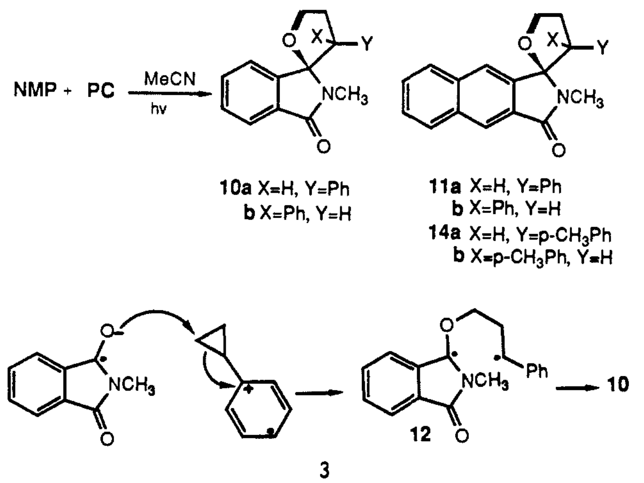
Scheme II



When *N*-methylphthalimide (NMP) and PC were irradiated in acetonitrile the reaction gave two isomeric products **10**, each in 11% yield. In a similar manner, irradiation of *N*-methyl-2,3-naphthalimide (NMN) and PC in acetonitrile gave the corresponding pair of naphthalene derivatives in a 1:1 ratio and a combined yield of 56%.[11] The structures of these products were firmly established by ^{1}H NMR, and 2-D NMR confirmed the coupling relationships.

The infrared spectra of **10** and **11** showed a carbonyl absorption at 1690 cm^{-1}. Finally an X-ray crystallographic structure determination confirmed the structure of **11a**.[12] A proposed stepwise mechanism for the formation of **10** (**11**) is outlined in Scheme II although a concerted processes is a distinct possibility.

In the case of (*p*-methylphenyl)cyclopropane, we observed, in addition to the expected cycloadducts **14**, an equal amount of the photoreduction product **15** which must arise from proton transfer from the **13** to NMN$^{\bullet-}$ followed by coupling of the radical pair. This observation demonstrates that proton transfer remains a viable process in this system and suggests that if the cyclopropane ring in the PC radical cation were not intact, **16** would likely proton transfer to give the allyl radical **17**.

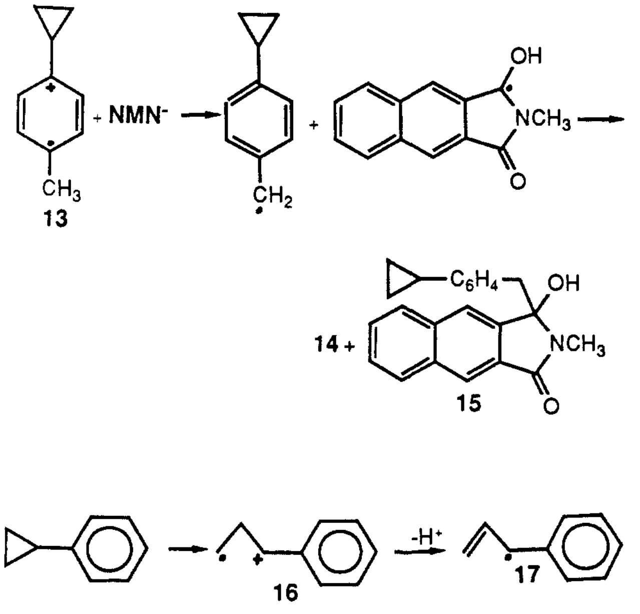
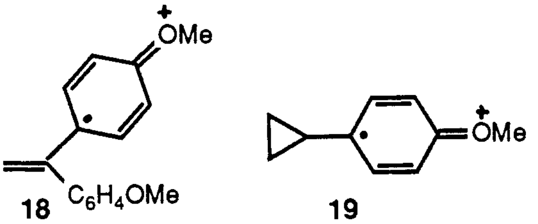


Table I. Fluorescence Quenching Data for Substituted Phenylcyclopropanes

R-Ph-*c*-C_3H_5	E_{ox}, V^a	ΔG_{ET}, kcal/mol	$k_{q,calcd}$, $\times 10^{-10}$	$k_{q,exptl}$, $\times 10^{-10}$	Φ rel
MeO	1.42	−9.51	1.21	1.94	no reaction
Me	1.57	−6.05	0.986	1.20	0.56
H	1.83	−0.051	0.133	0.089	1
Cl	1.86	0.641	0.073	0.051	0.85
CN	2.17	7.79	$<10^{-5}$	0	no reaction

^{a}Vs. SCE; working electrode Au; CH_3CN/0.1 M TEAP.

A comparison of the photoreactivity and fluorescence quenching efficiency of a series of phenylcyclopropanes with NMN shows good correlations of fluorescence quenching efficiencies with ΔG_{ET} (Table I). We observed no reaction with *p*-cyano-PC, consistent with the fluorescence results, but, surprisingly, *p*-methoxy-PC, which efficiently quenches NMN fluorescence, affords none of the corresponding adduct. Farid and Mattes[1] have suggested that **18** is unreactive to alcohol nucleophiles because the positive charge in the radical cation resides on oxygen which may also explain the lack of reactivity of **19**.



In conclusion, we believe that the first general case of a photochemically generated radical anion radical cation pair undergoing cycloaddition has been observed. We are presently looking for other examples of this process and investigations of the mechanism of this reaction are continuing.

Acknowledgment. We thank the National Science Foundation for funds toward the purchase of an X-ray spectrometer and 400-MHz NMR under Grants CHE-84-02155 and DMB-84-20175, respectively.

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[11] All new products showed acceptable NMR, IR, and analytical data. Details will be published in a full paper.

[12] Crystals of **11** were isolated from ethyl ether. X-ray diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer with Mo Kα radiation (graphite monochromator). Space group $P2_1/n$, a = 7.140 (1) Å, b = 14.038 (1) Å, c = 16.729 (3) Å, β = 97.28 (1)°, Z = 4. 3239 total data collected to θ = 25°; 1739 data 3s above background. Structure solved with direct methods. Structure refinement by full-matrix least squares. Final R = 0.040, R_w = 0.041.

Detection and Kinetics of Formation and Disproportionation of the Mixed-Valence Pt_2(II,III) Complex $Pt_2(\mu\text{-}P_2O_5H_2)_4^{3-}$

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Recently the photophysics of the diplatinum(II) complex anion $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}$ has been the subject of intense study. The primary thrust of this earlier work has been to develop a better understanding of the bonding and energy levels in both the ground and excited states. From quenching measurements being made in parallel with these studies, it is apparent that the excited state $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-*}$ is both a strong oxidant and reductant.[2] Nevertheless, despite this recent spate of published work, little is yet known about the 1-electron-oxidized and -reduced platinum

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[1] (a) Tulane University. (b) Center for Fast Kinetics Research.

[2] Che, C.-M.; Butler, L. G.; Gray, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 7796–7797. Heuer, W. B.; Totten, M. D.; Rodman, G. S.; Herbert, E. J.; Tracy, H. J.; Nagle, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 1163–1164.

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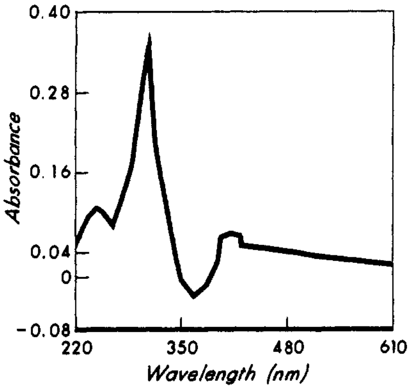

Figure 1. Difference spectrum measured 13.5 μs after the pulse of electrons, showing the appearance of the 310-nm band for $Pt_2(\mu\text{-}P_2O_5H_2)_4^{3-}$ and the bleaching of the 368-nm absorption due to $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}$.

complex intermediates formed in these processes.[3,4]

By pulse radiolysis techniques, the 1-electron-reduced complex $Pt_2(\mu\text{-}P_2O_5H_2)_4^{5-}$ has been previously observed in aqueous solution.[5] By contrast the 1-electron-oxidized complex $Pt_2(\mu\text{-}P_2O_5H_2)_4^{3-}$ has been implicated both in the photoinduced $S_{RN}1$ reaction of $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}$ with aryl halides[6] and in the thermal reactions of the diplatinum(II) complex with both H_2O_2 and 1-electron oxidants.[7] Nevertheless, no published work has appeared which offers any spectroscopic characterization of $Pt_2(\mu\text{-}P_2O_5H_2)_4^{3-}$. We now report that this Pt₂(II,III) complex is formed both by the photoionization of $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}$ in aqueous solution[4] and by the thermal reaction of $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}$ with hydroxyl radicals generated by pulse radiolysis.

Hydroxyl radicals are produced in an aqueous solution of $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}$ saturated with N_2O using a pulsed beam of electrons from a Van der Graaf generator.[8] Using transient difference spectroscopy subsequent to the pulse, we observe a bleaching in the absorption band at 368 nm ($\epsilon = 3.45 \times 10^4$ M^{-1} cm^{-1}) caused by the loss of $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}$, along with the appearance of a new absorption band at 310 nm (Figure 1). The rate of formation of this new complex follows a second-order rate law (rate = $k_1[Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}][\dot{O}H]$) with a rate constant $k_1 = 8 \times 10^9$ M^{-1} s^{-1}. This intermediate complex then subsequently decays by a second-order pathway (rate = $k_2[Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}]^2$) with a rate constant $k_2 = 6.7 \times 10^8$ M^{-1} s^{-1}.[9] This rate constant is calculated from the rate of loss of the 310-nm band. In agreement with a disproportionation reaction, we observe the recovery of the bleached 368-nm band due to $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}$ to an intensity midway between its initial and bleached values.[10]

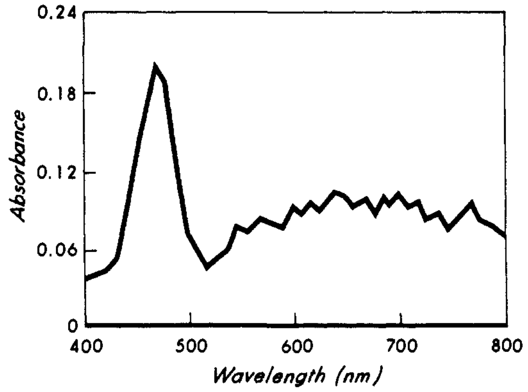

Figure 2. Difference spectrum measured 7 ns after the laser pulse, showing the presence of the 470-nm band for $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-*}$ and the broad 700-nm band for $e(H_2O)_n^-$.

These results prove that the band at 310 nm can be assigned to $Pt_2(\mu\text{-}P_2O_5H_2)_4^{3-}$, which then disproportionates to $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}$ and $Pt_2(\mu\text{-}P_2O_5H_2)_4^{2-}$ (λ_{max} = 248 nm) (eq 1).[11]

$$Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-} + \dot{O}H \xrightarrow{k_1} Pt_2(\mu\text{-}P_2O_5H_2)_4^{3-} + OH^-$$

$$2Pt_2(\mu\text{-}P_2O_5H_2)_4^{3-} \xrightarrow{k_2} Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-} + Pt_2(\mu\text{-}P_2O_5H_2)_4^{2-} \tag{1}$$

Excitation of an aqueous solution of $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}$ with a Nd-YAG laser at 355 nm leads to an initial increase in the absorption maxima at 330 and 470 nm due to $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-*}$.[2,12] Subsequent to the laser pulse, this absorption band decays and is replaced by one at 310 nm due to $Pt_2(\mu\text{-}P_2O_5H_2)_4^{3-}$. Similar spectral changes are observed when the solution is purged with O_2 rather than with N_2 prior to the laser pulse, indicating that O_2 is a triplet state rather than an electron transfer quencher. If the experiment is carried out with the solution buffered to pH 6, an additional broad absorption band at λ_{max} = 700 nm is observed due to the hydrated electron (Figure 2).[4,13] This band decays at a diffusion-controlled rate due to protonation, and indeed this band is unobservable under solution conditions of higher acidity. Clearly, in accordance with earlier studies,[4] the excited state $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-*}$ undergoes photoionization according to eq 2 to give $Pt_2(\mu\text{-}P_2O_5H_2)_4^{3-}$ and a hydrated electron. As final

$$Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-*} \rightarrow Pt_2(\mu\text{-}P_2O_5H_2)_4^{3-} + e(H_2O)_n^- \tag{2}$$

proof of this reaction, we have repeated the reaction with the solution saturated with N_2O rather than with N_2. Under these conditions we observe the additional *slow* growth in the formation of $Pt_2(\mu\text{-}P_2O_5H_2)_4^{3-}$ *subsequent* to the laser pulse. This secondary formation of the Pt₂(II,III) complex results from the reaction between N_2O and $e(H_2O)_n^-$ to give hydroxyl radicals, which then undergo a subsequent thermal reaction with $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}$ to give $Pt_2(\mu\text{-}P_2O_5H_2)_4^{3-}$.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society,

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(4) Since completion of this study, others have suggested that $Pt_2(\mu\text{-}P_2O_5H_2)_4^{3-}$ is formed in this reaction (Cho, K. C.; Che, C. M. *Chem. Phys. Lett.* **1986**, *124*, 313–316).

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(8) Electron pulses of 100-ns duration were delivered to samples contained in a quartz cell.

(9) This value of k_2 was calculated by using the second-order rate constant evaluated from an analysis of the 310-nm decay curve. The extinction coefficient of the 310-nm band for $Pt_2(\mu\text{-}P_2O_5H_2)_4^{3-}$ was calculated to be 7.6 × 10^4 M^{-1} cm^{-1}. This was estimated from the bleaching of $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}$ (Figure 1) by assuming that this transient has $\epsilon_{368} = 0.23\epsilon_{310}$. The concentration of $Pt_2(\mu\text{-}P_2O_5H_2)_4^{3-}$ was then calculated from the absorbance extinction coefficient ratio. Under certain pH conditions the rate curve for the formation of $Pt_2(\mu\text{-}P_2O_5H_2)_4^{3-}$ fits to two first-order reactions. This further reaction corresponds to a proton-transfer step which occurs because of the different pK_a's of Pt₂(II) and Pt₂(II,III) complexes.

(10) The corresponding $t_{1/2}$ from the rate of reappearance of $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}$ is 370 μs. The absorbance at 248 nm corresponds to that expected for $Pt_2(\mu\text{-}P_2O_5H_2)_4^{2-}$.

(11) We assign this 310-nm band to the dσ → dσ* transition. From Gray's simplified MO model (Mann, K. R.; Gordon, J. G. II; Gray, H. B. *J. Am. Chem. Soc.* **1975**, *97*, 3553–3555) the splitting in d_{z^2} (dσ and dσ*) and p_z (pσ and pσ*) are caused by the intermetallic interactions along the *z* axis. If we assume that the Pt–Pt separation in Pt₂(II,III) (See Che, C.-M.; Herbstein, F. H.; Schaefer, W. P.; Marsh, R. E.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 4604-4607) is intermediate between that in Pt₂(II) and Pt₂(III), we expect that the dσ–dσ* splitting in Pt₂(II,III) will be greater than in Pt₂(II) but less than in Pt₂(III). Correspondingly, we expect the dσ*–pσ separation in Pt₂(II,III) to be intermediate between that in Pt(II) and in Pt₂(III). Since the dσ* → pσ transition in Pt₂(II) is at 368 nm, and the dσ → dσ* transition in Pt₂(III) is at 248 nm, the 310-nm band in Pt₂(II,III) is best assigned to dσ → dσ*.

(12) The peak at 470 nm is a transition from $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-*}$, since its decay rate precisely parallels that of the 330-nm band.

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An Electron-Deficient Thallium Zintl–Metal Carbonylate: Structure and Bonding of $[Et_4N]_6[Tl_6Fe_{10}(CO)_{36}]$

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Cluster anions of the heavy main-group elements are well-known except for those of group 13 where the high degree of electron deficiency inhibits cluster bonding.[1] Those elements can, however, be incorporated into more electron-rich, heteroelement clusters such as $[Tl_2Te_2]^{2-}$,[2] $[TlSn_9]^{3-}$,[3] and $[TlSn_8]^{3-}$.[3] Thallium interacts with transition-metal carbonyls to form traditional complexes such as $TlCo(CO)_4$,[4] $Tl[Co(CO)_4]_3$,[4,5] $Tl[Mn(CO)_5]_3$,[6] and $[Tl[Co(CO)_4]_4]^-$.[7] A report of $Tl_2Fe_3(CO)_{12}$,[8] which has not been structurally characterized, has appeared. This latter report coupled with our recent discovery of $[Et_4N]_2[Bi_4Fe_4(CO)_{13}]$[9] suggested that the Tl–Fe system might yield some examples of unusual bonding situations.

When $Fe(CO)_5$/KOH/MeOH solutions are treated with thallium salts, deep yellow-brown solutions result from which an anionic metal carbonyl complex can be isolated and is proposed to be $[Et_4N][Tl[Fe(CO)_4]_2]$[10] (**1**), which may be structurally related to the known $[M[Fe(CO)_4]_2]^{2-}$ ions (M = Zn, Cd, Hg).[11] When methanol solutions of this complex stand at room temperature black crystals, **2**, deposit slowly which will not redissolve in methanol. On the basis of analyses, spectroscopic data and X-ray analysis, **2** is shown to be $[Et_4N]_4[Fe_2(CO)_6(\mu\text{-}CO)[\mu\text{-}Tl[Fe(CO)_4]]_2]_2$, an aggregate of **1** produced by loss of CO. Details of the structure of **2**, which is structurally similar to Burlitch's recently reported $Co_2(CO)_6(\mu\text{-}CO)(\mu\text{-}ZnCo(CO)_4)_2$, will appear elsewhere.[13] An X-ray diffraction study of crystals of a minor product showed it to be the highly unusual cluster compound **3** which can be viewed as a derivative of **2** in which the μ-CO's are replaced by $[\mu\text{-}TlFe(CO)_4]^-$. The structure and bonding of this complex whose formula is $[Et_4N]_6[Tl_6Fe_{10}(CO)_{36}]$ is the subject of this paper. The Tl–Fe framework is shown in Figure 1.[14] Bond distances and angles are given in Table I.

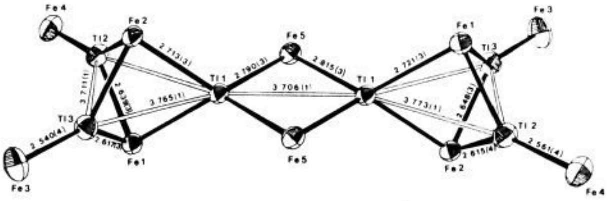

Figure 1. ORTEP diagram of $[Tl_6Fe_{10}(CO)_{36}]^{6-}$ with carbonyl ligands omitted for clarity. Three carbonyls are associated with each of the iron atoms Fe1, Fe1′, Fe2, and Fe2′ while the other irons are ligated by four carbonyls each.

The structure is composed of two thallium triangles held together asymmetrically by two μ_3-$Fe(CO)_3$ moieties without any apparent bonding between the irons (d_{Fe-Fe} = 3.087 (5) Å). The triangles are connected by two $Fe(CO)_4$ bridges. Terminal, trigonal-bipyramidal $Fe(CO)_4$ groups are attached to Tl2, Tl2′, Tl3, and Tl3′, and all metals, with the exception of the μ_3-Fe's, are coplanar.

For purposes of understanding the bonding in **3**, it is useful to consider it to be a dimer of $Tl_3[\mu_3\text{-}Fe(CO)_3]_2[Fe(CO)_4]_3{}^{3-}$ (**4**). On the basis of electron counting rules for cluster compounds,[15] a *closo* trigonal-bipyramidal cluster should possess 12 skeletal electrons. In **4**, two electrons on each Tl atom are utilized for dative bonds to the FeL_4 units. This leaves 10 electrons for cluster bonding and the cluster is electron deficient by Wade's electron counting rules which presuppose the existence of Tl–Tl bonding. The Tl–Tl distances in Figure 1, however, fall nicely in the range of Tl–Tl nonbonded contacts for other structures.[2,16] This is consistent with extended Hückel molecular orbital calculations[17] on **4** which gave a very small Tl–Tl overlap population of 0.025. Localized bonding in the $Tl_3[\mu_3\text{-}Fe(CO)_3]_2$ fragment would also require 12 skeletal electrons for two-center two-electron bonding. The cluster may still be considered to be deficient by two electrons per monomeric **4**.

How does this molecule accommodate the electron deficiency? Our calculations on **4** give five occupied levels of e″, e′, and a_1′ symmetry which are associated with Tl–FeL_3 cluster bonding along with three occupied Tl–FeL_4 bonding orbitals of a_1′ and e′ symmetry.[18] All eight molecular orbitals lie at moderate energies.

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(10) Pentacarbonyl iron (0.68 g) was added to 0.69 g of KOH dissolved in MeOH. To this was added 0.73 g of $TlCl_3 \cdot 4H_2O$. After it was filtered, the solution was treated with aqueous $[Et_4N]Br$ to precipitate $[Et_4N][Tl[Fe(CO)_4]_2]$, which was washed with water and dried under vacuum. IR (MeOH, cm^{-1}) 1983 m, 1912 s. Anal. Calcd.: N, 2.09; Fe, 16.65; Tl, 30.47. Found: N, 1.86; Fe, 15.10; Tl, 30.50. ^{13}C NMR (ppm relative to Me_4Si) 218.0 (carbonyl), 53.3 and 7.6 (Et_4N^+).

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(12) (a) IR (CH_3CN, cm^{-1}) 1987 s, 1968 m, sh, 1958 s, 1920 s, sh, 1910 s, 1895 m, sh, 1740 w. Anal. Calcd. for $[Et_4N]_2[Tl_2Fe_4(CO)_{15}]$: N, 2.13; Tl, 31.13; Fe, 17.02. Found: N, 1.89; Tl, 30.01; Fe, 17.84. (b) X-ray analysis: Rheingold, A. L.; Whitmire, K. H., manuscript in preparation.

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