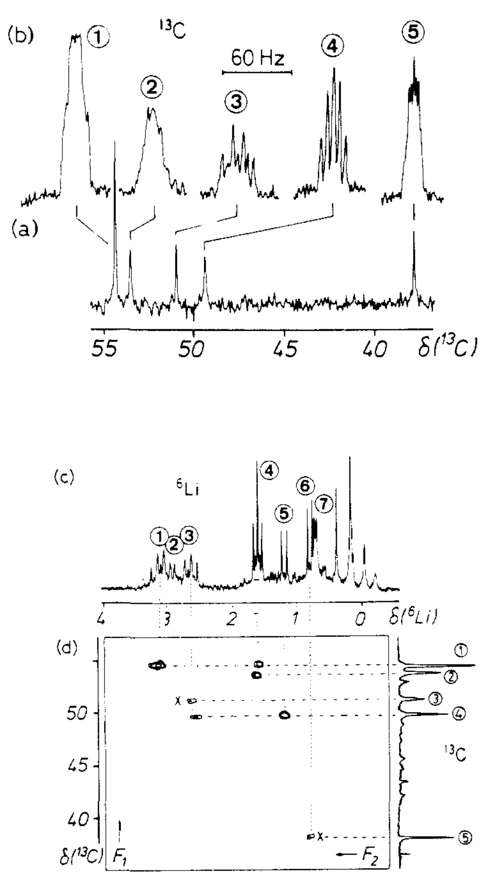

Figure 3. (a) ^{13}C NMR (100.61 MHz) spectrum of ^{13}C and ^{6}Li labeled **1a** with ^{1}H and ^{6}Li broadband decoupling at −103 °C; internal reference TMS. (b) Multiplets of the ^{6}Li coupled ^{13}C spectrum. (c) ^{1}H decoupled ^{6}Li NMR (58.86 MHz) spectrum of ^{13}C and ^{6}Li labeled **1a** with fine structure due to scalar ^{6}Li,^{13}C coupling: −103 °C, external reference 1 M LiBr in THF-d_8. (d) ^{6}Li,^{13}C shift correlation for **1a** based on the pulse sequence[10] $90^\circ_x(^6\mathrm{Li})-\Delta-90^\circ_x(^{13}\mathrm{C})-t_1/2-180^\circ_x(^6\mathrm{Li})-t_1/2-90^\circ_\phi(^{13}\mathrm{C}),t_2(^6\mathrm{Li})$; the standard BRUKER phase program for the selection of double quantum coherences was used; spectral windows were 500 Hz (^{6}Li=F$_2$) and 4 kHz (^{13}C=F$_1$), digital resolution after zero-filling 2.0 and 7.8 Hz, respectively; 128 t_1 increments of 0.125 ms, 24 transients, Δ = 50 ms (optimized for $J(^{13}\mathrm{C},^6\mathrm{Li})$ = 10 Hz), relaxation delay 6 s, acquisition time 0.512 s, total experimental time 5.6 h; window functions exp(F_2) and sin F_1. The probehead was tuned to ^{6}Li excitation and observation, ^{13}C excitation, ^{1}H decoupling at 400 MHz, and ^{19}F lock at 384 MHz; the ^{19}F resonance of $C_2F_4Br_2$ was used as external lock. Correlations 2/3 and 7/5 (X) were obtained by selective ^{13}C decoupling experiments.

COSY experiment[12] established that no direct contact exists between different dianionic carbons or between different ^{6}Li sites. In this way subspectra composed of the following ^{13}C and ^{6}Li signals could be recognized: (a) C(3),C(4),Li(2),Li(3), Li(5); (b) C(5),Li(6),Li(7); (c) C(1),C(2),Li(4). Simulation of subspectra (a) and (b) using the scalar coupling constants extracted directly from the line splittings gave good agreement with the experimentally observed ^{13}C as well as ^{6}Li multiplets.

On the basis of these results it is possible to propose partial structures **a**, **b**, and **c** for the aggregates of **1a** present in THF solution at −103 °C (Chart I). Especially revealing is the arrangement **a**, which includes besides Li(2), Li(3), and Li(5) C(3) and C(4). A similar chain of three Li and two C atoms is found in the solid-state structure of the $(\mathbf{1a})_6\cdot\mathrm{Li_2O}\cdot(\mathrm{thf})_{10}$ complex (Figure 2).

A feature of particular interest is the first experimental demonstration of C atoms in organolithium compounds in solution which carry two different Li atoms, a bonding situation which gives rise to two different ^{13}C,^{6}Li coupling constants (**a** and **b**). All substructures are characterized by a high ^{6}Li/^{13}C ratio, a fact which clearly establishes that **1a** is a true dilithiomethane derivative also in solution.

Note Added in Proof: X-ray structure analysis of the *octahedral crystals* of **1a** shows a chiral $(\mathbf{1a})_4\cdot(\mathrm{thf})_7$ complex (C_2) with a C–Li chain of the type (Li5–C4–Li3–C3)$_2$Li2.

Acknowledgment. We express our gratitude to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous support of this work.

Supplementary Material Available: Crystal data and crystallographic data for $(\mathbf{1a})_6\cdot\mathrm{Li_2O}\cdot(\mathrm{thf})_{10}$ and tables of atomic positional and thermal parameters and bond distances and angles (9 pages); tables of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

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Electronic Properties of Phosphazene Substituents on Ferrocene

Reginaldo A. Saraceno, Geoffrey H. Riding,
Harry R. Allcock,* and Andrew G. Ewing*

Department of Chemistry, Penn State University
University Park, Pennsylvania 16802

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There has been considerable debate over the last 20 years about the electronic structure of phosphazenes.[1-5] Although the bonding arrangements are still not fully understood, we present here some thermodynamic data from ferrocene-substituted phosphazenes[6-8] which lend new insights into the electronic structure of these materials. Variations in the shifts in the oxidation potential of ferrocene (280–780 mV) are detected with changes in both ferrocene bonding to the phosphazene (pendent versus transannular) and the nature of the remaining cosubstituents on the phosphazene ring. These shifts indicate that phosphazenes are highly electron-withdrawing units. Oxidation products of ten of these species are stable on the time scale of seconds, and, in fact, one species with an oxidation potential shifted 740 mV has an unusual stability for the ferricenium ion. Cosubstituents attached to the phosphazene ring determine the electron-withdrawing properties of the phosphazene and, hence, control the oxidation potential of the ferrocene unit. Electron-withdrawing properties are equally controlled by cosubstituents attached to any phosphorus atom of the phosphazene ring.

The oxidation–reduction chemistry of a wide variety of ferrocenyl cyclic phosphazenes was studied by using cyclic voltammetry at platinum disk electrodes (radius = 2.03 mm). All these compounds displayed diffusion-controlled electrochemistry under the conditions employed. Table I lists the oxidation peak potentials for 15 ferrocenyl phosphazenes. Four examples of the cyclic phosphazenes studied are shown below to illustrate their structure.

Although the oxidation peak potentials varied with the mode of attachment of the ferrocenyl unit and the cosubstituents present on the phosphazene, all were oxidized at considerably more positive

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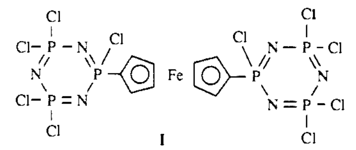

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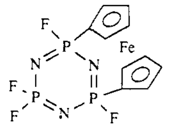
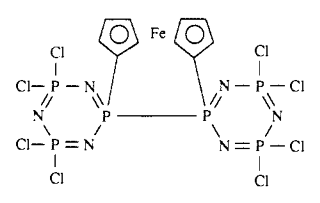
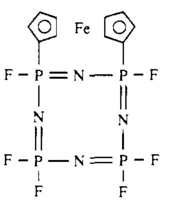


III



IV



VIII

potentials than observed for ferrocene. In fact, cyclic voltammograms obtained in solutions of transannular linked II and III, shown in Figure 1, display an unprecedented shift in oxidation potential for substituted ferrocene compounds, 740 and 710 mV, respectively.

Deviations from coplanarity and changes in the ring–iron distance in bridged ferrocenes are known to affect the thermodynamics of ferrocene oxidation.[9–13] Examination of the X-ray crystal structure of compound III[8] shows the cyclopentadienyl rings to be essentially coplanar with a dihedral angle of 2.5° and iron–ring distances identical, within experimental error, with those in ferrocene. Also, compound VI, which is more distorted than III, does not have a greater oxidation potential than III. These results indicate that strain on the ferrocenyl unit does not appear to contribute to the oxidation potential shifts observed. Electron-donating/withdrawing properties of substituents are known to have a pronounced effect on the thermodynamics of ferrocene oxidation,[14–22] and it is likely that the large shifts in oxidation potentials are mainly the result of inductive effects from the highly electron-withdrawing phosphazene rings.[23–26]

The transannular linked ferrocenyl phosphazene compounds have shifts in oxidation peak potentials approximately twice those of the pendent analogues. This indicates that each phosphorus atom in the phosphazene skeleton has equal electron-withdrawing properties and the inductive effects of the phosphazene operating via each cyclopentadienyl ring of the ferrocene are cumulative.

Different cosubstituents present on the phosphazene ring were found to change the oxidation peak potentials observed in a regular fashion. As expected, the oxidation potentials follow the strength of the electron-withdrawing abilities of the cosubstituents. Thus, the fluorine-substituted phosphazene compounds have considerably larger oxidation potentials than the trifluoroethoxy-substituted analgoues, which in turn have higher potentials than the phenoxy-substituted analogues.

Table I. Oxidation Peak Potentials of Ferrocene-Substituted Phosphazenes

compound		$E_{\mathrm{p,a}}$,[a] (V)	$E_{\mathrm{p,a}} - E_{\mathrm{p,ferrocene}}$,[a] (V)
(I)	$N_6P_6Cl_{10}(\eta\text{-}C_5H_4)_2Fe^b$	1.25	0.78
(II)	1,5-$N_4P_4F_6(\eta\text{-}C_5H_4)_2Fe$	1.21	0.74
(III)	$N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe^b$	1.18	0.71
(IV)	$N_6P_6Cl_8(\eta\text{-}C_5H_4)_2Fe^b$	1.18	0.71
(V)	$N_3P_3F_3(OCH_2CF_3)(\eta\text{-}C_5H_4)_2Fe^b$	1.14	0.67
(VI)	$N_6P_6(OCH_2CF_3)_{10}(\eta\text{-}C_5H_4)_2Fe$	1.13	0.66
(VII)	$N_3P_3F_3(OC_6H_5)(\eta\text{-}C_5H_4)_2Fe^b$	1.12	0.65
(VIII)	1,3-$N_4P_4F_6(\eta\text{-}C_5H_4)_2Fe$	1.09	0.62
(IX)	1,5-$N_4P_4(OCH_2CF_3)_6(\eta\text{-}C_5H_4)_2Fe$	1.06	0.59
(X)	$N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Fe$	1.04	0.57
(XI)	1,3-$N_4P_4(OCH_2CF_3)_6(\eta\text{-}C_5H_4)_2Fe$	0.98	0.51
(XII)	$N_3P_3(OC_6H_5)_4(\eta\text{-}C_5H_4)_2Fe$	0.94	0.47
(XIII)	$N_3P_3F_5(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$	0.86	0.39
(XIV)	$N_4P_4F_7(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$	0.85	0.38
(XV)	$N_3P_3(OCH_2CF_3)_5(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$	0.75	0.28

[a] Potentials are versus Ag wire pseudo reference. [b] These reactions are chemically irreversible following oxidation.

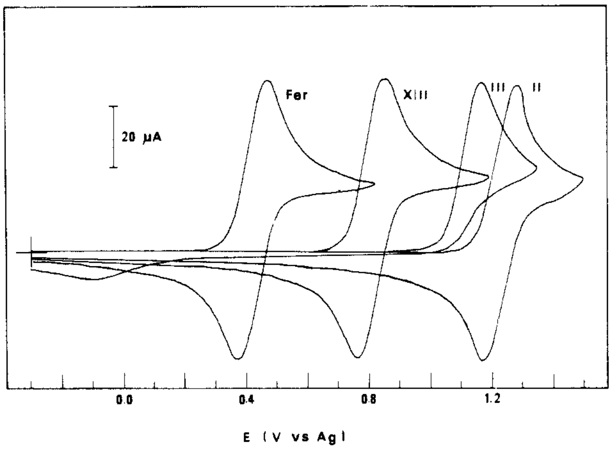


Figure 1. Cyclic voltammetry in 1 mM solutions of ferrocene (Fer) and fluorine-substituted ferrocenyl cyclic phosphazenes from Table I in 0.1 M tetraethylammonium perchlorate/acetonitrile. Scan rate: 100 mV/s.

The oxidation peak potentials were found to be surprisingly sensitive to changes in a substituent group at a non-geminal site. The substitution of a non-geminal fluorine atom in III by a trifluoroethoxy V or phenoxy VII group decreases the oxidation potential for the ferrocene moiety by approximately 25% when compared to the change in potential when all four fluorine atoms are replaced by the same substituent (X or XII, respectively). This long range effect may explain the observation that the 1,3-bridged tetrameric phosphazenes, VIII and XI, have lower oxidation potentials than corresponding 1,5-isomers II and IX.

Substituted ferrocenes with high oxidation potentials are generally less stable as ferricenium ions.[27] This trend was also observed in the present work. Four of the five ferrocenyl phosphazenes with the highest positive peak potentials were found to be unstable as the ferricenium ion as evidenced by chemical irreversibility following oxidation. However, the cyclic tetramer II displays one of the largest thermodynamic shifts detected for oxidation of substituted ferrocenes[14–22,28] and is stable as the ferricenium ion.

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Laser-Jet Photochemistry: The Photofragmentation of Triplet 1,1,3,3-Tetraarylpropane-1,3-diyls and Their Role in the Photometathesis between Diarylcarbenes and 1,1-Diarylethylenes

R. Marshall Wilson* and Karlyn A. Schnapp

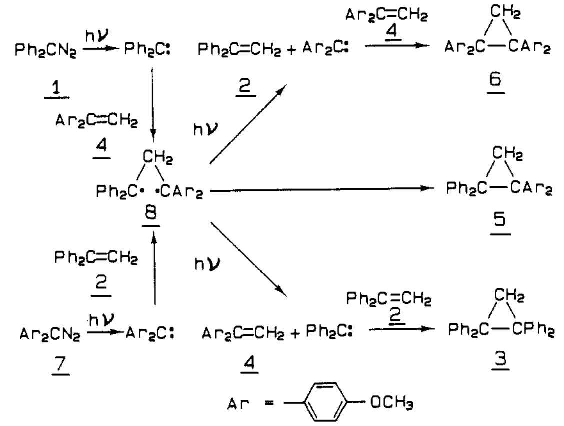
Department of Chemistry, University of Cincinnati
Cincinnati, Ohio 45221

Received August 21, 1987

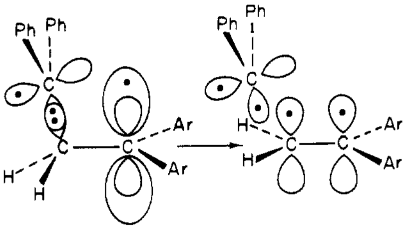
Until recently the only method available for studying the photochemistry of transient photochemical intermediates was to stabilize them in low-temperature matrices where their lifetimes are increased to the point where conventional low intensity light sources can induce photochemistry.[1] During the past several years, pulsed excimer laser sources have made it possible to study the photochemistry of transient intermediates under ambient conditions.[2] We have recently developed a laser-jet technique for the study of transient intermediate photochemistry with a CW argon ion laser.[3] This technique consists of irradiating a high velocity solution microjet (∼4.5 m/s, ∼100 μm in diameter) with the focused output of an argon ion laser (all UV lines, 333–364 nm, ∼3W). Since microjet self-focusing and waveguide properties greatly enhance the light intensity within the jet,[4] and since relatively large quantities of material can be processed by this method, multiphoton products can often be isolated from these jet reactions and characterized by conventional spectroscopic methods. In this report we describe the application of this laser-jet technique to the photochemistry of triplet 1,1,3,3-tetraarylpropane-1,3-diyls generated through the irradiation of diaryldiazomethanes in the presence of 1,1-diarylethylenes.

As a control for the biradical photochemical studies to be reported below and in an effort to compare the argon laser-jet technique with high intensity excimer laser irradiation, we have repeated the photolysis of diphenyldiazomethane (**1**) described by Turro and co-workers.[2b] They observed the formation of tetraphenylethylene (TPE), 9,10-diphenylphenanthrene (DPP), 9,10-diphenylanthracene (DPA), and fluorene (FL). Under laser-jet conditions TPE also was observed to be the predominant product along with DPP and DPA. However, no FL could be detected even by GLC-mass spectrometry. These results are in accord with the earlier observations, since FL formation was ascribed to the further excitation of the very short-lived ^{1}DPC ($\tau \sim 95$ ps in isooctane),[5] while either DPP or DPA may arise from the much longer lived ^{3}DPC. Apparently under laser-jet conditions there is insufficient light intensity or photon energy to affect cyclization of ^{1}DPC to FL.

Scheme I



Scheme II



When **1** is irradiated under low intensity conditions (Rayonet Photochemical Reactor, 350 nm) in the presence of **2**, the predominant product is 1,1,2,2-tetraphenylcyclopropane (**3**)[6] along with small amounts of benzophenone azine. Under jet conditions, this same reaction also gives **3** in addition to TPE, DPP, DPA as well as trace amounts of 1,1,3,3-tetraphenylpropene.[6,7] Michl has observed a similar 1,2-H shift upon irradiation of matrix-isolated 1,3-biradicals.[1g] If **2** is replaced by 1,1-bis(*p*-methoxyphenyl)ethylene (**4** in Scheme I), low intensity irradiation yields the expected unsymmetrical cyclopropane, 1,1-diphenyl-2,2-bis(*p*-methoxyphenyl)cyclopropane (**5**). However, under jet conditions two products not observed in the low intensity reactions are formed as well. These were shown to be **2** and 1,1,2,2-tetrakis(*p*-methoxyphenyl)cyclopropane (**6**).[6,7] In a complementary set of experiments, bis(*p*-methoxyphenyl)diazomethane (**7**)[8] was irradiated in the presence of **2**. Again low intensity irradiation resulted in the unsymmetrical tetraarylcyclopropane **5** as the predominant product, and jet irradiation yielded the intensity dependent products **4** and the symmetrical cyclopropane **3**.[6,7]

The results of these two carbene addition reactions which should both lead to the unsymmetrical biradical ^{3}**8** are most easily correlated by the mechanism outlined in Scheme I.[9] If ^{3}**8** has

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