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Alkali Metal Induced Rupture of a Phosphorus−Phosphorus Double Bond. Electrochemical and EPR Investigations of New Sterically Protected Diphosphenes and Radical Anions [ArPPAr]$^{\bullet-}$

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The synthesis and characterization of the new diphosphenes DmtP═PDmt (**2a**) (Dmt = 2,6-dimesityl-*p*-tolyl) and DxpP═PDxp (**3a**) (Dxp = 2,6-di(*m*-xylyl)phenyl) are described. The electrochemical behavior of **2a**, **3a**, and DmpP═PDmp (**1a**) (Dmp = 2,6-dimesitylphenyl) has been examined by cyclic voltammetry. Compounds **1a**−**3a** display reversible reductions in THF (room temperature, 0.1 M $^{n}Bu_4NBF_4$) at −2.08, −2.15, and −2.08 V vs SCE, respectively. Chemical and electrochemical reduction of solutions of **1a**−**3a** led to the stable radical anions [DmpPPDmp]$^{\bullet-}$ (**1b**), [DmtPPDmt]$^{\bullet-}$ (**2b**), and [DxpPPDxp]$^{\bullet-}$ (**3b**) which were studied by EPR spectroscopy. The EPR data indicate the unpaired spins reside in P═P π^* molecular orbitals. Chemical reduction of **1a**−**3a** with either Na metal or sodium naphthalenide yields sodium salts Na[ArPPAr], which show additional EPR signals that have been attributed to the presence of ion-paired species. No ion pairing was detected by EPR spectroscopy for the corresponding magnesium, potassium, or lithium salts of **1a**. Reduction of DmpP═PDmp with excess potassium metal in THF led to dark, EPR silent, solutions. Analysis of such solutions by ^{31}P NMR indicated the presence of DmpP(H)K. Quenching of this species with degassed H_2O or CF_3COOH affords $DmpPH_2$.

Compounds having multiple bonding between two heavier main group elements, such as phosphorus, have long fascinated chemists.[1] Coupling of $PhPH_2$ and $PhPCl_2$ under basic condition was originally thought to lead to phosphobenzene, PhP═PPh. Although this species was later found to be actually oligomeric, utilization of ligands which provide steric encumbrance to oligomerization reactions has yielded many interesting and important compounds.[2−6] A stable diphosphene having a true P═P double bond was first successfully isolated in 1981.[7] Kinetic stabilization of the P═P array was achieved by use of sterically demanding supermesityl or Mes* (2,4,6-tri-*tert*-butylphenyl) groups which prevent oligomerization to higher homologs. This compound, Mes*P═PMes*, has allowed the nature of the P═P double bond to be probed by numerous theoretical and spectroscopic methods.[3] It is generally agreed that the LUMO is the antibonding P═P π^* molecular orbital. Details of the HOMO orbital are more ambiguous, owing to the P═P π and n_+ (in phase combination of lone pairs on phosphorus) molecular orbitals being close in energy. Transition metal complexes of diphosphenes exhibit a variety of binding geometries, and these have been reviewed.[3]

We recently reported the synthesis and structural characterization of the stable diphosphene DmpP═PDmp (**1a**) (Dmp = 2,6-dimesitylphenyl).[8] Many new and exciting main group and organometallic compounds have been isolated using the steric umbrella afforded by the Dmp system.[9−17] Herein we report the facile reversible reduction of **1a** to the radical anion [DmpPPDmp]$^{\bullet-}$ (**1b**), as studied by electrochemistry, as well as EPR studies of **1b**. We have also prepared the new diphosphenes DmtP═PDmt (**2a**) (Dmt = 2,6-dimesityl-*p*-tolyl) and DxpP═PDxp (**3a**) (Dxp = 2,6-di(*m*-xylyl)phenyl). Reduction of **2a** and **3a** leads to analogous radical anions [DmtPPDmt]$^{\bullet-}$ (**2b**) and [DxpPPDxp]$^{\bullet-}$ (**3b**). Comparisons of the electrochemistry and EPR data of **1**−**3** with that of the related diphosphenes (and corresponding radicals derived from) Mes*P═PMes* (**4a**)[7,18−21] and TsiP═PTsi (**5a**)[21,22] (Tsi

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(1) Köhler, H.; Michaelis, A. *Ber. Dtsch. Chem. Ges.* **1877**, *10*, 807.

(2) Norman, N. C. *Polyhedron* **1993**, *12*, 2431−2446.

(3) Weber, L. *Chem. Rev.* **1992**, *92*, 1839−1906.

(4) Cowley, A. H. *J. Organomet. Chem.* **1990**, *400*, 71−80.

(5) Cowley, A. H.; Norman, N. C. *Prog. Inorg. Chem.* **1986**, *34*, 1−63.

(6) Cowley, A. H.; Jones, R. A.; Mardones, M. A. In *ACS Symposium Series*; American Chemical Society: Washington, DC. 1992; Vol. 486, pp 56−63.

(7) Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587−4589.

(8) Urnezius, E.; Protasiewicz, J. D. *Main Group Chem.* **1996**, *1*, 369−372.

(9) Ruhlandt-Senge, K.; Ellison, J. J.; Wehmschulte, R. J.; Pauer, F.; Power, P. P. *J. Am. Chem. Soc.* **1993**, *115*, 11353−11357.

(10) Ellison, J. J.; Ruhlandt-Senge, K.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1178−1180.

(11) Ellison, J. J.; Power, P. P. *Inorg. Chem.* **1994**, *33*, 4231−4234.

(12) Protasiewicz, J. D. *J. Chem. Soc., Chem. Commun.* **1995**, 1115−1116.

(13) Li, X.-W.; Pennington, W. T.; Robinson, G. H. *Organometallics* **1995**, *14*, 2109−2111.

(14) Ellison, J. J.; Ruhlandt-Senge, K.; Hope, H. H.; Power, P. P. *Inorg. Chem.* **1995**, *34*, 49−54.

(15) Li, X.-W.; Pennington, W. T.; Robinson, G. H. *J. Am. Chem. Soc.* **1995**, *117*, 7578−7579.

(16) Li, X.-W.; Xie, Y.; Schreiner, P. R.; Gripper, K. D.; Crittendon, R. C.; Campana, C. F.; Schaefer, H. F.; Robinson, G. H. *Organometallics* **1996**, *15*, 3798−3803.

(17) Grigsby, W. J.; Power, P. P. *J. Am. Chem. Soc.* **1996**, *118*, 7981−7988.

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= tris(trimethylsilyl)methyl) lead to several unexpected and novel results. First, the electrochemical potentials obtained for the diphosphenes run counterintuitive to predictions based on electrochemical studies of previously described diphosphenes. Second, we have gathered EPR evidence for unprecedented counterion binding to radical anions of the form $[\text{RPPR}]^{\bullet -}$. Third, we have discovered that an unusually facile cleavage of the P═P double bond occurs by reduction of **1a** with potassium metal and suggest that P═P bond cleavage may be promoted by ion pairing to the radical ion.

Experimental Section

General. DmpP═PDmp (**1a**) was prepared as previously described.[8] DxpI was prepared as described.[23] CH_2Cl_2 was purified by distillation from P_2O_5 under N_2. THF, pentane, toluene, hexanes, and diethyl ether were purified by distillation from purple Na−benzophenone solutions under N_2. ^1H and ^{31}P NMR spectra were recorded using a 300 MHz Varian Gemini spectrometer. ^{31}P NMR are referenced to external 85% H_3PO_4, while ^1H NMR are referenced to residual proton solvent signals of $CDCl_3$ or C_6D_6. UV−vis results were obtained on a Varian Cary 5G spectrophotometer. X-band EPR Spectra were measured on a Varian E-112 Century Series spectrophotometer. All EPR spectra were referenced to DPPH. Mass spectroscopic analyses were performed at the Washington University Resource for Biomedical and Bio-organic Mass Spectrometry and at the CWRU departmental facility.

2,6-Dibromo-4-methyliodobenzene.[24] A modified procedure similar to that described for 2,6-dibromoiodobenzene was used.[25] A solution of sodium nitrite (4.32 g, 0.062 mol) in 20 mL of water was added dropwise at 0−5 °C to a solution of 2,6-dibromo-4-methylaniline (Aldrich, 15.9 g, 0.06 mol) in 60 mL of concentrated HCl and glacial acetic acid (50:50 mixture). The diazonium solution was stirred for 1.5 h and poured through a glass wool filter into a solution of potassium iodide (99.3 g) in 150 mL of water. After the solution was stirred for 1 h, 200 mL of CH_2Cl_2 and 20 mL of 1 N Na_2SO_3 were successively added. Upon separation, the aqueous layers were extracted with CH_2Cl_2, and the combined organic layers were washed successively with 10% aqueous NaOH and distilled water and then dried with magnesium sulfate. After solvent removal, the orange-white residue was extracted with warm hexanes to remove a white insoluble impurity. The residue after removal of the hexanes was recrystallized from warm hexanes to give 16.1 g (71%) of 2,6-dibromo-4-methyliodobenzene, mp (51−54 °C): ^1H NMR δ 2.23 (s, 3H), 7.36 (s, 2H); HRMS calcd for $C_7H_5Br_2I$ 373.7802, found 373.7812.

2,6-Dimesityl-4-methylbenzene (DmtI). DmtI was synthesized by a procedure analogous to that for DmpI.[25] The crude product was recrystallized from warm toluene to give DmtI (57%), mp 208−210 °C: ^1H NMR (C_6D_6) δ 1.98 (s, 3H), 2.10 (s, 12H), 2.22 (s, 6H), 6.71 (s, 2H), 6.90 (s, 4H); HRMS calcd for $C_{25}H_{27}I$ 454.1157, found 454.1145.

$DmtPCl_2$ and $DxpPCl_2$. Procedures analogous to that described in the literature for $DmpPCl_2$ were utilized.[8] The crude products were washed several times with pentane to give $DmtPCl_2$ (73%) and $DxpPCl_2$ (52%). **$DmtPCl_2$**: ^1H NMR (C_6D_6) δ 2.08 (s, 12H), 2.38 (s, 6H), 2.45 (s, 3H), 6.97 (s, 6H); ^{31}P NMR (C_6D_6) δ 162.3 ppm; HRMS calcd for $C_{25}H_{27}PCl_2$ $(M + H)^+$ 429.1306, found 429.1309. **$DxpPCl_2$**: ^1H NMR (C_6D_6) δ 2.06 (s, 12H), 6.69 (dd, $J_{HH} = 7.6$, $J_{HP} = 3.0$ Hz, 2H), 6.98−7.11 (m, 7H); ^{31}P NMR (C_6D_6) δ 160.0; HRMS calcd for $C_{22}H_{21}PCl_2$ 386.0760, found 386.0763.

DmtP═PDmt (2a). Compound **2a** was synthesized according to the procedure for synthesis of **1a** to give **2a** in 86%:[8] ^1H NMR ($CDCl_3$) δ 1.66 (s, 24H), 2.26 (s, 6H), 2.30 (s, 12H), 6.71 (s, 8H), 6.73 (s, 4H); ^{31}P NMR ($CDCl_3$) 492.7 ppm; HRMS calcd for $C_{50}H_{54}P_2$ $(M + H)^+$ 717.3749, found 717.3779; UV−vis (heptane) 459 ($\epsilon = 364$), 374 ($\epsilon = 5890$), 280 (sh, $\epsilon = 2260$).

DxpP═PDxp (3a). Compound **3a** was synthesized according to the procedure for synthesis of **1a** to give **3a** in 79%:[8] ^1H NMR ($CDCl_3$) δ 1.70 (s, 24H), 6.92 (m, 12H), 7.08 (m, 4H), 7.30 (t, $J_{HH} = 7.6$ Hz, 2H); ^{31}P NMR ($CDCl_3$) δ 494.4; HRMS calcd for $C_{44}H_{42}P_2$ 632.2764, found 632.2775; UV−vis (heptane) 459 ($\epsilon = 586$), 368 ($\epsilon = 10100$), 264 ($\epsilon = 18700$)

DmpP═PDmp (1a). For comparison: UV−vis (heptane) 456 ($\epsilon = 365$), 372 ($\epsilon = 6190$), 313 ($\epsilon = 4200$), 264 (sh, $\epsilon = 12400$).

Reaction of DmpP═PDmp with K and reaction with CF_3COOH. A solution of 0.200 g of DmpP═PDmp (0.291 mmol) in 20 mL of THF was stirred with excess potassium (70 mg, 1.79 mmol) for 2 h. The resulting dark solution was filtered to remove unreacted potassium. Addition of 0.5 mL of degassed CF_3COOH (6.55 mmol) immediately resulted in a colorless solution and upon removal of THF, pentane extraction, and removal of pentane yielded white $DmpPH_2$ as the only product as ascertained by ^{31}P and ^1H NMR spectroscopy.

Electrochemistry. Tetrabutylammonium tetrafluoroborate was recrystallized twice from hot ethyl acetate and dried under vacuum at 130−140 °C for 2−3 h. The experiments were performed inside a nitrogen-filled Vacuum Atmospheres drybox using a conventional three-electrode cell, a Model RDE 3 Pine Instruments potentiostat, and a Houston Instruments X−Y recorder. A glassy carbon working electrode (approximate area, 0.070 cm^2) was used for the cyclic voltammetry experiments whereas a platinum gauze electrode (area, 10 cm^2) was used for the bulk electrolysis. Silver wire was used as a quasi-reference electrode, and a platinum wire was the counter electrode. The purity of the solutions was verified by running background voltammograms. All systems studied by cyclic voltammetry were prepared using either 10 mL of THF or CH_2Cl_2, 0.1 M in the supporting electrolyte (tetrabutylammonium tetrafluoroborate), and 0.001 M in the relevant diphosphene. All potentials were corrected to SCE using the Fc^+/Fc couple. The reversibility of the redox couples was ascertained by comparison to peak separations for the Fc^+/Fc couple and by observation that ratios of cathodic to anodic peak currents were found to be essentially unity and invariant to scan rate. Scan rate dependency studies also revealed linear plots for i_p (peak current) versus $v^{1/2}$ (available as Supporting Information). A 0.02 M solution of DmpP═PDmp in 10 mL of THF was used for the bulk electrolysis.

Computational Studies. *Ab initio* studies of PhP═PPh were carried at the 6-31G** level (restricted Hartree−Fock method (RHF) for neutral species and unrestricted Hartree−Fock method (UHF) for radical anions) using SPARTAN on an Indigo2 SGI workstation.[26]

Results and Discussion

The new orange diphosphenes DmtP═PDmt (**2a**) and DxpP═PDxp (**3a**) were prepared in a manner analogous to that reported for DmpP═PDmp, as outlined in

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(18) Cowley, A. H.; Kilduff, J. E.; Newman, T. H.; Pakulski, M. *J. Am. Chem. Soc.* **1982**, *104*, 5820−5821.

(19) Cetinkaya, B.; Hudson, A.; Lappert, M. F.; Goldwhite, H. *J. Chem. Soc., Chem. Commun.* **1982**, 609−610.

(20) Cetinkaya, B.; Hitchcock, P. B.; Lappert, M. F.; Thorne, A. J.; Goldwhite, H. *J. Chem. Soc., Chem. Commun.* **1982**, 691−693.

(21) Bard, A. J.; Cowley, A. H.; Kilduff, J. E.; Leland, J. K.; Norman, N. C.; Pakulski, M.; Heath, G. A. *J. Chem. Soc., Dalton Trans.* **1987**, 249−251.

(22) Culcasi, M.; Gronchi, G.; Escudié, J.; Couret, C.; Pujol, L.; Tordo, P. *J. Am. Chem. Soc.* **1986**, *108*, 3130−3132.

(23) Lüning, U.; Baumgartner, H.; Manthey, C.; Meynhardt, B. *J. Org. Chem.* **1996**, *61*, 7922−7926.

(24) We acknowledge that this material has been assigned a registry number [175278-10-1] by CAS Registry Services under private contract without reference.

(25) Du, C. J. F.; Hart, H.; Ng, K.-K. D. *J. Org. Chem.* **1986**, *51*, 3162−3165.

(26) SPARTAN, Version 4.1, Wavefunction, Inc., Irvine, CA, 1996.

Scheme 1

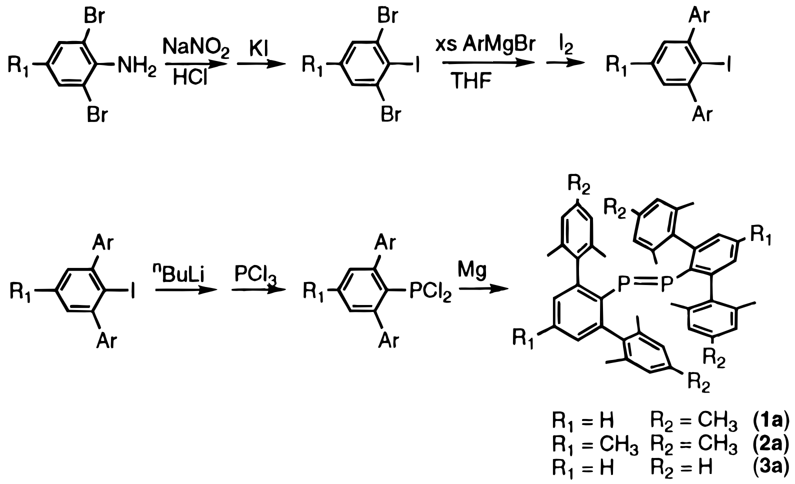

Table 1. Summary of CV and EPR Data for Compounds 1−5

	DmpP═Pmp **1a/1b**	DmtP═PDmt **2a/2b**	DxpP═PDxp **3a/3b**	Mes*P═PMes* **4a/4b**	TsiP═PTsi **5a/5b**
$E_{1/2}$ (V vs SCE)	−2.08[a]	−2.15[a]	−2.08[a]	−1.93[a,b]/−1.74[c,d]	−1.84[a,b]/−1.73[e,f]
$E_{(ox)}$ (V vs SCE)	1.06[g]	0.98[g]	1.12[g]		1.6[b,h]/1.14[e,f]
$a(^{31}P)$ (G)	46[i]	46[i]	45.5[i]	55[b,c]	43[b]/43.5[e]
g	2.008[i]	2.007[i]	2.009[i]	2.013[b]/2.010[c]	2.018[b]/2.011[e]

[a] THF, 0.1 M $^nBu_4NBF_4$. [b] Data from ref 21. [c] Data from ref 20. [d] CH_3CN, $^nBu_4NBF_4$. [e] Data from ref 22. [f] CH_3CN, $^nBu_4NPF_6$. [g] CH_2Cl_2, 0.1 M $^nBu_4NBF_4$. [h] Reversible oxidation, CH_2Cl_2, 0.1 M $^nBu_4NBF_4$, −78 °C. [i] THF, room temperature, Na(18-crown-6)$^+$ salt, THF, 0.1 M $^nBu_4NPF_6$.

Scheme 1.[8] Overreduction of the dichlorophosphines $ArPCl_2$ by small amounts of excess magnesium during syntheses of **1a**−**3a** leads to purple solutions, which were ascribed to formation of trace amounts of the radical anions $[ArPPAr]^{\bullet-}$. This assumption was confirmed by facile formation of stable (in the absence of air or water) purple THF solutions of **1b**−**3b** by chemical reduction of **1a**−**3a** by lithium, magnesium, and sodium metal. Similar purple solutions were also generated by electrochemical reduction of **1a** in the presence of $^nBu_4NBF_4$.

Cyclic voltammetry (0.1 M $^nBu_4NBF_4$ in THF) of **1a**−**3a** revealed one electron reversible reduction waves (Table 1). No evidence for reversible oxidation to stable cation radicals of **1a**−**3a** was obtained by analogous CV experiments conducted at room temperature in CH_2Cl_2. The irreversible oxidation potentials observed in CH_2Cl_2 are reported in Table 1. Unexpectedly, **1a**−**3a** are reduced at more *negative* potentials than either **4a** or **5a**. Easier reduction of **1a**−**3a** compared to that of **4a** or **5a** might be expected upon replacement of three *tert*-butyl groups for two less electron donating mesityl rings.[27]

The greater difficulty in reducing **1a**−**3a** may be attributed to shorter P═P bonds and, hence, slightly higher lying and less accessible π^* orbitals (compound **1a**, $d_{P=P}$ = 1.985(2) Å, compound **4a**, $d_{P=P}$ = 2.034(2) Å).[28] Addition of an electron is expected to populate the P═P π^* orbital of a diphosphene on the basis of EPR and He-1 photoelectron spectroscopy of **4a**.[20]

A stronger π bond, however, should also manifest differences in the $\pi \rightarrow \pi^*$ transitions in the electronic spectra of these materials. The UV−vis spectra of **1a**−**3a** show little variance for the two lowest energy transitions (456−459 and 368−374 nm in heptane) and are somewhat comparable to those of **4a** (460 and 340 nm).[7] Diphosphenes are orange owing to these transitions, and these transitions have been attributed to the promotion of electrons from the n_+ and π molecular orbitals to the π^* molecular orbitals. The $n_+ \rightarrow \pi^*$ transitions are believed to be lower in energy on the basis of intensities and the results of various computational efforts. The $\pi \rightarrow \pi^*$ transitions are notably lower for **1a**−**3a** than for **4a**, but these values represent the $\pi \rightarrow \pi^*$ gap and not the absolute energy of the π^* orbital. Exact interpretation of the high energy transitions of **1a**−**3a** is more difficult owing to overlap with absorptions arising from electron rich flanking aryl groups.

The solid state structure of **4a** reveals the aromatic π systems to be non-coplanar to the P═P π bond (61.5° dihedral angle). In comparison, the structure of **1a** reveals one of the central aromatic rings to be nearly coplanar (12.9°) and the other nearly orthogonal (81.3°) to the P═P π bond. Owing to the extreme nature of the steric protecting groups in these systems, the effect of locking these aromatic rings into certain arrangements may have ramifications on their reduction potential due to conjugation of the P═P π system with the aromatic groups. This possibility was investigated through a series of *ab initio* calculations at the 6-31G** level of theory. Table 2 shows the results of these calculations for phosphobenzene (PhP═PPh) as a model of the current complexes. Full geometry optimization at this level of theory reproduced the results (energies,

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(27) Electronic communication through conjugation to the outer mesityl rings is expected to be limited owing to the strong preference for these substituents to adopt conformations nearly perpendicular to the inner phenyl ring.

(28) Preliminary structural details for DxpP═PDxp reveal an average P═P bond length of 1.954 Å (for two molecules per asymmetric unit). Burdette, S.; Protasiewicz, J. D. Unpublished results.

Table 2. PhP═PPh *ab Initio* Calculations

	dihedral angles			
	0, 0[a]	0, 0[b]	61.5, 61.5[c]	81.3, 12.9[c]
E_{LUMO}[d]	0.015 70	0.018 41	0.024 51	0.020 35
E_{HOMO}[d]	−0.282 15	−0.284 46	−0.302 35	−0.302 09
$E_{\mathrm{HOMO(-1)}}$[d]	−0.339 01	−0.338 58	−0.337 31	−0.318 56
$E_0 - E$ (kcal/mol)[e]	0	2.93	0.84	0.77
E[d]	−1141.684 485 1	−1141.684 017 7	−1141.683 149 1	−1141.683 255 8
$d_{\mathrm{P=P}}$ (Å)	2.0097	1.98	2.0068	2.0085
PhPP angle (deg)	105.5, 105.5	105.5, 105.5	101.4, 101.6	100.1, 106.0

[a] Full geometry optimization. [b] Single-point calculation, all geometrical parameters equal to (*a*) except $d_{\mathrm{P=P}} = 1.98$ Å. [c] Constrained refinement, PPCC dihedral angles locked at listed values. [d] Hartrees. [e] E_0 = energy for all-planar structure.

Table 3. [PhP═PPh]⁻ *ab Initio* Calculations

	dihedral angles		
	0, 0[a]	61.5, 61.5[b]	81.3, 12.9[b]
E_{LUMO}[c]	0.281 61	0.266 33	0.264 30
E_{HOMO}[c]	−0.070 40	−0.068 73	−0.069 11
$E_{\mathrm{HOMO(-1)}}$[c]	−0.158 56	−0.150 15	−0.147 93
E[c]	−1141.720 310 8	−1141.711 531 00	−1141.712 041 10
$E_0 - E$ (kcal/mol)[d]	0	5.51	5.19
$d_{\mathrm{P=P}}$ (Å)	2.1202	2.1277	2.1287
PhPP angle (deg)	104.01	99.45, 99.71	104.5, 97.5

[a] Full geometry optimization. [b] Constrained refinement, PPCC dihedral angles locked at listed values. [c] Hartrees. [d] E_0 = energy for all-planar structure.

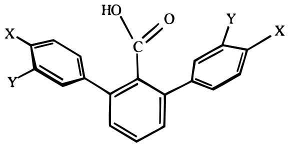
distances, and angles) obtained earlier and showed a preference for the aryl rings to be coplanar with the P═P π bond.[29]

Minimizations performed while constraining the PPCC dihedral angles to values appropriate for the structures of **1a** (81.3, 12.9°) and **4a** (61.5, 61.5°) revealed slightly higher energy structures (0.77 and 0.84 kcal/mol, respectively) and slightly elongated PP bond lengths (2.0085 and 2.0068 Å, respectively). Notable modulations in the Ph−P−P bond angles also occur concurrently with these constraints. The LUMO in each calculation was predominantly P═P π* in nature. The HOMO was comprised predominantly of the n_+ combination of the phosphorus lone pairs, while the HOMO(−1) was mainly P═P π bond in nature for the all planar and the Mes*P═PMes* model phosphobenzene. For the DmpP═PDmp, the π MO becomes slightly favored as the HOMO.

As the reduction potentials will also depend on stability of the resultant radical anions, parallel calculations were also performed for the corresponding $[\mathrm{PhPPPh}]^{\bullet -}$ anions. The effects of constraining the dihedral angles is more dramatic upon minimizing the structures of the corresponding radical anions (Table 3). Relative to the fully minimized structure of $[\mathrm{PhPPPh}]^{\bullet -}$ (planar, P═P bond length 2.1202 Å), calculations performed using the above dihedral constraints showed destabilization of 5.19 and 5.51 kcal/mol, respectively.

These calculations thus suggest that greater difficulty in reduction of **1a**−**3a** relative to **4a** does not arise from any particular orientational effects of the aromatic residues relative to the P═P bond. The PP bond length determined for **4a** is 2.034(2) Å, while that for **1a** is 1.985(2) Å. A shorter PP bond might indicate a stronger PP bond and might be expected to give rise to higher lying LUMO orbitals. The higher lying LUMO orbital would thus be more difficult to reduce. Such an expectation was indeed realized when the PP bond in a planar [PhP═PPh] was shortened to 1.98 Å (Table 2), at a cost of only 2.93 kcal/mol. Such calculations do not necessarily prove this effect, owing to the many assumptions that must be made.

An attractive alternative explanation may involve "through space" communication of the π clouds of the flanking aryl groups to the P═P system. By judicious choice of substituent, the pK_a's of structurally related 2,6-bis(*p*-X-phenyl)benzoic and 2,6-bis(*m*-Y-phenyl)benzoic acids (below) could be modulated through 0.74 pK units.[30] The acids having the most donating substituents were the weakest acids, and results showing comparable acidities for *m*- and *p*-substituted acids provided evidence for polar π effects being transmitted through space. Through space effects probably play some role in the greater difficulty in reductions of **1a**−**3a**. Such effects, however, do not manifest notable chemical shift effects in the ^{31}P NMR of **1a**−**3a** relative to **4a** (495 ppm). Likewise, the UV−vis spectra of **1a**−**3a** are very similar to those reported for **4a**.



Additionally, compounds **1a** and **3a**, which differ by *p*-methyl or *p*-hydrogen substituents of the flanking aryl groups, show no discernible differences in their reduction potentials. Changes in through space effects for these two species might be expected to be extremely small owing to only a 0.15 V (4.6 kcal/mol) change in reduction potential between **1a** and **4a** (the maximum on−off through space effect). Significant changes, however, are observed in the irreversible oxidation potentials for **1a** and **3a**. In particular, compound **3** is

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(29) Allen, T. L.; Scheiner, A. C.; Yamaguchi, Y.; Schaefer, H., F., III. *J. Am. Chem. Soc.* **1986**, *108*, 7579−7588.

(30) Chen, C.-T.; Siegel, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 5959−5960.

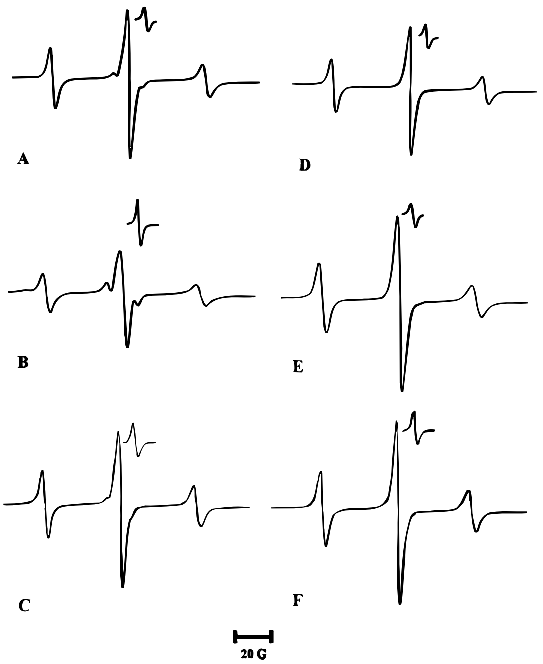

Figure 1. EPR spectra (RT) of Na[DmpPPDmp]$^{\bullet-}$ (top left, A), Na[DmtPPDmt]$^{\bullet-}$ (middle left, B), and Na[DxpPPDxp]$^{\bullet-}$ (bottom right, C) generated by reduction of ArP═PAr with excess Na metal in THF. On the right are the corresponding spectra recorded in the presence of 18-crown-6 (spectra D−F).

more difficult to oxidize by 0.06 V relative to **1a**, possibly indicating that the radical cation formation may be facilitated by polar π through space effects.

Solutions of the purple radical anions [ArPPAr]$^{\bullet-}$ displayed prominent EPR signals. Initial investigations of Na[ArPPAr] generated by reduction of ArP═PAr with excess Na metal in THF revealed that these spectra were not as simple as the triplets observed for [Mes*PPMes*]$^{\bullet-}$ or [TsiPPTsi]$^{\bullet-}$. Figure 1 (left) shows that the anticipated triplet is associated with a minor species at nearly the same g values and coupling constants. The EPR spectra of the major species is centered at about $g = 2.008$ with a coupling of 46 G, consistent with the unpaired electron coupling equivalently to both ^{31}P nuclei.[31] The unpaired electron most likely occupies the P═P π* orbital owing to the relatively small coupling constant. Table 1 displays the coupling constants and g values for [ArPPAr]$^{\bullet-}$ and lists data for the radical anions **4b** and **5b** for comparison.

The quantity of the secondary species appears greater for the more electron rich Dmt derivative. The exact nature of the minor species was illuminated by finding that addition of 18-crown-6 to such solutions removed the minor species (Figure 1, right). The minor species also appeared in solutions of the radical anions generated by reduction with sodium naphthalenide in THF, but not for solutions of the radical anion generated by electrochemical means with $^{n}Bu_4NBF_4$ as supporting electrolyte. The more electron rich Dmt (**3b**) analog shows greater amounts of the minor signal, consistent with expectations that ion pairing with Na$^+$ might be expected to be more prevalent in this species.

Oddly, these additional signals for the minor species are absent for reductions with Na metal in Et_2O or DME (reduction in toluene produced purple solutions, but interpretation of the EPR spectra is more complicated). Lowering the temperature of the THF solutions of the Na salts led to the disappearance of the signals for the minor isomer (see Supporting Information). The radical anions could also be generated by chemical reduction of diphosphenes by Li and Mg metal in THF; EPR studies of these salts revealed only simple triplet spectra. Static interactions of Na$^+$ and [ArPPAr]$^{\bullet-}$ might lead to a more complicated signal owing to asymmetric binding of the sodium cation to only one of the two phosphorus atoms, or preferential interactions with the electron rich mesityl rings. Owing to the extremely slight differences between the free and ion-paired radical anion EPR spectral signatures, and the likelihood the ion-paired radical is not static on the EPR time scale, assignment of exactly which species exists under each set of conditions is difficult. EPR investigation of Na[DmpPPDmp]$^{\bullet-}$ in pentane (obtained by generation of Na[DmpPPDmp]$^{\bullet-}$ in THF followed by removal of solvent and dissolution in pentane) revealed a single species with $a(^{31}P) = 49.5$ G and $g = 2.009$.

It is interesting to note that EPR data for the radical anion derived by the sodium naphthalenide reduction of **4a** or **5a** in THF did not display such additional complexity.[19,22] We are currently unable to explain the apparent selectivity of the new radical anions for sodium binding. A lack of similar behavior for the Na$^+$ salts in other solvents or by the Li$^+$ or Mg^{2+} salts in THF may reflect a combination of low concentrations and/or symmetrical binding modes for such ion pairs.[32] Efforts to obtain single crystals of a sodium complex of **1b-3b** are currently underway to address this interesting question.[33]

The importance of ion-pairing effects in stabilizing highly charged phosphides is amply demonstrated for $K_2[{}^tBuPP{}^tBu]\cdot{}^1/_2THF$, the formal product of two-electron reduction of the unknown disphosphene $^tBuP{=}P^tBu$.[34] Addition of either 18-crown-6 or cryptand[2.2.2] in THF renders solubility and allows ^{31}P NMR investigations (eq 1). At low temperatures evidence for the dianionic

$$\underset{\text{insoluble}}{{}^{t}BuP(K)P(K){}^{t}Bu} \xrightarrow[\text{THF}]{\text{18-C-6}} {}^{t}BuP(H)P(K)\,{}^{t}Bu + [{}^{t}BuPP{}^{t}Bu]^{\bullet-} \quad (1)$$

species has been obtained, while at ambient temperatures further reaction occurs to produce the radical anion $[{}^tBuPP{}^tBu]^{\bullet-}$ ($g = 2.010$, $a(^{31}P) = 45.5$ G) and $[{}^tBu(H)PP{}^tBu]^-$. Interestingly, EPR spectroscopy of electrochemically generated (THF, 0.1 M $^{n}BuPF_6$) $[{}^tBuPP{}^tBu]^{\bullet-}$ at reduced temperatures revealed a second unidentified species.

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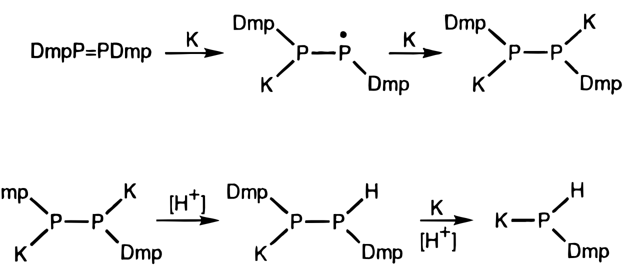
[31] For large coupling constants more complicated spectra will be observed, see: (a) Culcasi, M.; Gronchi, G.; Tordo, P. *J. Am. Chem. Soc.* **1985**, *107*, 7191−7193. (b) Gara, W. B.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1978**, 150−154.

(32) At low concentrations signals for a symmetrically ion paired species might not be resolved from those larger signals for free ion, owing to somewhat broader EPR line widths in the present complexes (as compared to EPR line widths of [TsiPPTsi]$^-$, for example).

(33) The possibility that the minor species present might be reflective of the presence of a *cis*-[ArPPAr] complex was probed by *ab initio* calculations at the UHF/6-31G** level for [HPPH]$^-$. These calculations yielded a trans/cis preference of 2.6 kcal/mol. Both cis and trans radicals contained elongated PP bonds of 2.14 and 2.13 Å, respectively. Related calculations for *cis*-[PhPPPh]$^-$ were unsuccessful.

(34) Binder, H.; Riegel, B.; Heckmann, G.; Moscherosch, M.; Kaim, W.; Schnering, H.-G. v.; Hönle, W.; Flad, H.-J.; Savin, A. *Inorg. Chem.* **1996**, *35*, 2119−2126.

Scheme 2



During surveys to assay counterion binding effects we attempted to generate K[DmpPPDmp]$^{\bullet-}$ by reduction of **1a** with excess potassium metal. We discovered instead that the dark solutions thus obtained were EPR silent. Analysis of the reaction mixtures by ^{31}P NMR indicated clean formation of a single species resonating at δ −124.4 ppm (d, J_{HP} = 177.4 Hz). Addition of degassed H_2O or CF_3CO_2H to such solutions yielded $DmpPH_2$ as the sole products as ascertained by ^{31}P and ^{1}H NMR spectroscopy. These observations are consistent with cleavage of the P═P bond and formation of DmpP(H)K (Scheme 2). Addition of Me_3SiCl or D_2O to DmpP(H)K yields DmpP(H)SiMe$_3$ or DmpP(H)D, respectively.[35] The unobserved and potential intermediate(s) $DmpPK_2$ or K_2[DmpPPDmp] may abstract a proton from THF to yield DmpP(H)K or K[Dmp(H)PPDmp], the latter being cleaved upon further reduction with potassium (and being subsequently converted to DmpP(H)K). Addition of protons to Na[DmpPPDmp]$^{\bullet-}$, however, yields a mixture of predominantly DmpP═PDmp and minor amounts of DmpP(H)P(H)Dmp.[36] It is interesting to note that the electrochemistry of **1a** shows no evidence for 2e$^-$ (or more) reductions and suggest the requirement for alkali metal binding to facilitate subsequent reduction. Cyclic voltammetry of **5a** suggested the presence of a second one-electron reduction occurs (~0.8 V more negative than first one-electron reduction) near the reduction limits of the solvent THF.[21] Careful reduction of DmpP═PDmp by exactly 1 equiv of potassium naphthalenide allows EPR observation of K[DmpPPDmp]. Only one species is observed for this complex, which has EPR spectral signatures nearly identical to the other salts of [DmpPPDmp]$^{\bullet-}$ ($a(^{31}P)$ = 45.5 G, g = 2.009). As only one signal is observed, and taking into account the very similar EPR spectra for the ion pairs and free ions, the identity of this species is not uniquely identified.

This reductive cleavage reaction may be contrasted to a variety of previously noted oxidative and nucleophile/electrophile coupled promoted cleavages of diphosphenes,[3] and also contrasted to metathesis of P═P bonds of RP═PR by low-valent tungsten species,[37] as well to the four-electron reductive cleavage of azobenzene using tungsten complexes.[38] Our results suggest that reductive cleavage of diphosphenes by alkali metals may be facilitated by counterion association.

Note Added in Proof. After review of this manuscript a paper describing electron deformation density experiments and density functional theory (DFT) calculations of **4a** appeared (Cowley, A. H.; Decken, A.; Norman, N. C.; Krüger, C.; Lutz, F.; Jacobsen, H.; Ziegler, T. *J. Am. Chem. Soc.* **1997**, *119*, 3389−3390) which indicate that the HOMO in **4a** is the n_+ molecular orbital.

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Supporting Information Available: EPR spectra of Li(THF), Mg(THF), $^{n}Bu_4NBF_4$ (THF), and Na (THF, DME and Et_2O) salts of [ArPPAr]$^{\bullet-}$, variable temperature EPR of Na[ArPPAr]$^{\bullet-}$ in THF, and scan rate dependency plots for CV experiments of **1** and **3** (9 pages). Ordering information is given on any current masthead page.

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[35] DmpP(H)SiMe$_3$ has been characterized independently by reaction of DmpP(H)Li with Me_3SiCl. Urnezius, E.; Protasiewicz, J. D. Unpublished results.

[36] DmpP(H)P(H)Dmp has been prepared from DmpP(H)Li and CCl_4 as described for Mes*P(H)P(H)Mes* (ref 18). Shah, S.; Protasiewicz J. D. Unpublished results.

[37] Dillon, K. B.; Gibson, V. C.; Sequeira, L. J. *J. Chem. Soc., Chem. Commun.* **1995**, 2429−2430.

[38] Lockwood, M. A.; Fanwick, P. E.; Eisenstein, O.; Rothwell, I. P. *J. Am. Chem. Soc.* **1996**, *118*, 2762.