Communication

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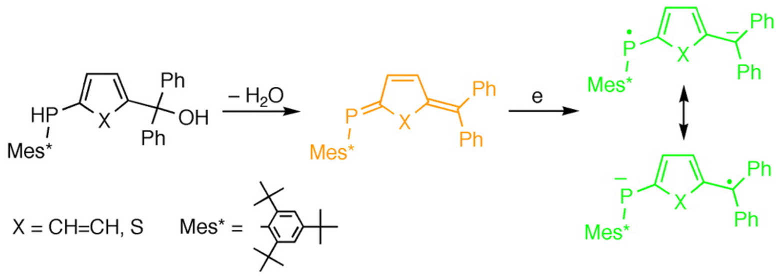

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Phosphaquinomethane and Phosphathienoquinomethanes, and Their Anion Radicals

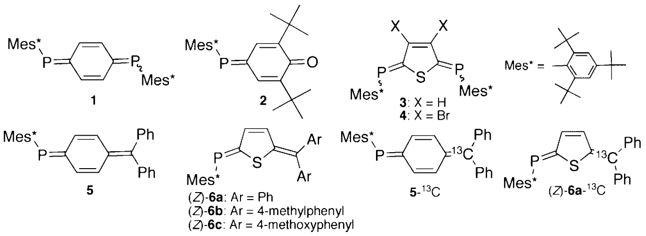
Fumiki Murakami, Shigeru Sasaki, and Masaaki Yoshifuji*

Department of Chemistry, Graduate School of Science, Tohoku University, Aoba, Sendai 980-8578, Japan

Received April 8, 2005; E-mail: yoshifj@mail.tains.tohoku.ac.jp

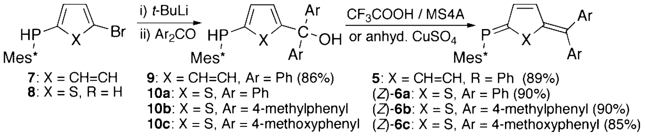
Only a few phosphaquinoid compounds, a hybrid of low-coordinated phosphorus compounds with quinoid skeletons, have been isolated to date despite continuing synthetic effort on the low-coordinated phosphorus compounds for the last two decades[1] as well as enormous research on quinoid molecules (Scheme 1). Sterically protected diphosphaquinone **1**[2] was synthesized by Märkl and co-workers and was isolated as chromium(0) complexes (Mes* = 2,4,6-tri-*tert*-butylphenyl). We synthesized phosphaquinone **2**[3] and diphosphathienoquinones **3** and **4**[4] and revealed the structural similarity to that of the conventional quinoid compounds. The phosphaquinoid compounds **2** and **3** are two-step redox systems, but anion radicals obtained by alkaline metal reduction of them, phosphasemiquinone radicals, have significant unpaired electron density on the phosphorus atoms and formulated as phosphinyl radicals. Herein, we report synthesis, structure, and redox properties of phosphaquinomethane **5** and phosphathienoquinomethanes **6**, which behave as quinoid molecules not only in the neutral but also in the anion radical state.

Scheme 1. Phosphaquinoid Compounds



Phosphaquinoid compounds **1**, **2**, **3**, and **4** were synthesized by 1,6-elimination of the corresponding aromatic precursors. As a route to phosphaquinomethanes, dehydration from the precursors, 1-hydroxymethyl-4-phosphinobenzene **9** and 2-hydroxymethyl-5-phosphinothiophene **10**, was employed (Scheme 2). Carbinol **9** was prepared by the halogen−metal exchange of bromobenzene **7**[4] followed by reaction with benzophenone. Dehydration of **9** catalyzed by trifluoroacetic acid in benzene with MS4A afforded **5**.[5] On the other hand, reaction of the thienyllithium derived from **8** with benzophenones afforded not only the carbinols **10** but also the phosphathienoquinomethanes **6**. Therefore, the mixture was subjected to complete conversion without isolation of **10**, and refluxing with anhydrous $CuSO_4$ in benzene[6] afforded **6** in excellent yields as sterically favored *Z*-isomers.[5]

Scheme 2. Synthesis of Phosphaquinomethanes



Phosphaquinomethane **5** and phosphathienoquinomethane (*Z*)-**6a** show a ^{31}P NMR signal at δ 244.4 (s) and 201.4 (s), respectively, supporting formation of a P═C double bond. More shielded value of (*Z*)-**6a** is ascribed to electron donation by the sulfur atom similarly to diphosphathienoquinones.[4] ^{1}H and ^{13}C NMR spectra of **5** reflect the phosphaquinoid structure, where a vinyl proton cis to Mes* shows more upfield shift with a smaller J_{PH} value (δ 5.48, J_{PH} = 9.6 Hz) than that cis to the lone pair (δ 7.11, J_{PH} = 13.8 Hz).[7] The carbon adjacent to the phosphorus appears in a low field (δ 170.35, d, J = 29.1 Hz) similarly to phosphaalkenes.[1] The exocyclic carbon (δ 134.68, d, J = 28.5 Hz) has considerable coupling with the ^{31}P nucleus owing to an extended π-conjugated system. ^{1}H and ^{13}C NMR spectra of (*Z*)-**6a** are also consistent with its formulation as the phosphathienoquinomethane. Deshielded chemical shift and considerably large J_{PH} values of the proton adjacent to the phosphinidene moiety (δ 6.96, J_{PH} = 8.1 Hz) reflect the *Z*-configuration. Phosphaquinomethane **5** and (*Z*)-**6a** have a deep orange color (λ_{max} (log ϵ/hexanes) 440 (4.49) (**5**); 446 (4.49) ((*Z*)-**6a**) nm) which is similar to phosphaquinone **2** (λ_{max} (log ϵ/hexanes) 372 (4.34) nm)[3] due to the low-lying excited state. Phosphathienoquinomethanes (*Z*)-**6b** and (*Z*)-**6c** display ^{1}H, ^{13}C, and ^{31}P NMR and UV−vis data similar to those of (*Z*)-**6a**, reflecting little influence of substituents at the 4-positions of the aryl groups on the phosphaquinoid skeleton. Molecular structure of (*Z*)-**6b** obtained by X-ray crystallography is shown in Figure 1.[8] The P═C bond length (1.704(2) Å) lies in the longest category in the reported values (1.61−1.71 Å),[1] but is similar to those of the phosphaquinoid compounds (1.705(2) (**2**),[3] 1.712(2), 1.714(2) (**4**)[4] Å). The C−P═C angle reflects the absence of severe steric interaction among substituents and takes a small value (98.48(6)°) as low-coordinated phosphorus compounds carrying a Mes* group. The bond lengths within the phosphathienoquinomethane skeleton show apparent bond alternation, where C1−C2 (1.450(2) Å) and C3−C4 (1.441(2) Å) are longer than C2−C3 (1.349(2) Å) and C4−C5 (1.365(2) Å). The whole phosphathienoquinomethane skeleton, except for the P═C double bond, has bond lengths similar to those reported for thienoquinomethanes.[9] The phosphathienoquinomethane is planar with the maximum deviation from the least squares plane (S1, P1, C1−C6, C13, C20) as 0.0634(13) Å (C3).

Cyclic voltammetries of **5** and (*Z*)-**6** consist of two-step irreversible waves, which do not become reversible even when scanned within the range of one wave (Figure 2). The first reduction

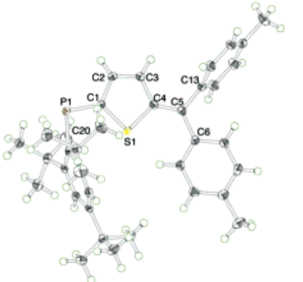


Figure 1. ORTEP drawing of (*Z*)-**6b** with 50% thermal ellipsoids.

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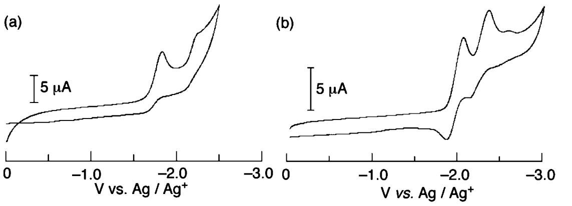

Figure 2. Cyclic voltammograms of (a) **5** and (b) (*Z*)-**6a** in tetrahydrofuran with 0.1 M *n*-Bu_4NClO_4. Scan rate = 30 mV s^{-1}, working electrode is glassy carbon, reference electrode is Ag/0.01 M $AgNO_3$ in acetonitrile with 0.1 M *n*-Bu_4NClO_4, counter electrode is Pt. $Fc/Fc^+ = 0.18$ V.

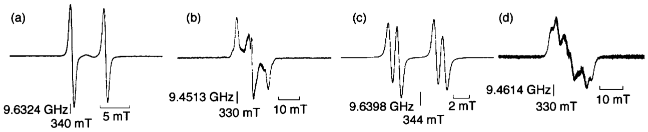

Figure 3. EPR spectra obtained after sodium reduction of **5** (a) at 293 K and (b) 77 K, and **5**-^{13}C (c) at 293 K and (d) 77 K in THF.

potentials of **5**, **6a**, **6b**, and **6c** ($E_{red} = -1.83$ V (**5**), −2.05 (**6a**), −2.15 (**6b**), and −2.12 (**6c**) V vs Ag/Ag^+) are close to those of phosphaethenes (ca. −2 V)[10] but higher than those of **2**[3] and **4**[4] ($E_{red} = -1.55$ V (**2**), −1.60 V (**4**)). The differences between the first and the second reduction potentials ($\Delta E_{red} = 0.41$ (**5**), 0.30 (**6a**), 0.32 (**6b**), 0.36 (**6c**) V), which are much smaller than those for **2** and **4** ($\Delta E_{red} = 0.90$ (**2**), 0.89 (**4**) V), suggest different properties of the corresponding anion radicals.

Reduction of **5** and **6**, as well as ^{13}C-labeled compounds **5**-^{13}C and (*Z*)-**6a**-^{13}C, which were prepared analogously to **5** and (*Z*)-**6a** from $Ph_2{}^{13}CO$, was studied by EPR (Figure 3).[11] The orange solutions of **5** and **6** in tetrahydrofuran became green upon contact with the sodium mirror. The EPR spectra of the anion radicals of **5** and **6** in fluid solution consist of two lines due to hfc with one ^{31}P nucleus. The isotropic hfc constants ($a(^{31}P) = 5.7$ (**5**), 5.2 (**6a**) mT) are similar to those of phosphaalkenes[10] and diphosphenes[12] (5.4−5.6 mT) and much smaller than those of the anion radical of phosphaquinoid compounds **2**[3] and **4**[4] ($a(^{31}P) = 9.3$ (**2**), 9.3 (**4**) mT), where significant contribution of the diarylphosphinyl radical[13] was postulated. The spectra of the anion radicals of **5**-^{13}C and (*Z*)-**6a**-^{13}C consist of four lines due to further splitting by a ^{13}C nucleus. Considerably large isotropic hfc constants with a ^{13}C nucleus ($a(^{13}C) = 1.1$ (**5**-^{13}C) and 1.0 (**6a**-^{13}C) mT), which are twice that of $a(^{13}C)$ of the anion radical of phosphaethenes ($-P{=}^{13}C<$),[10] suggest delocalization of an unpaired electron through the whole phosphaquinoid skeleton, although lack of apparent hfc with protons suggests limited spin density in the central ring. On the other hand, the EPR spectra of the anion radicals of **5** and **6** in the frozen solution are axial symmetric and can be interpreted by dominant contribution of $a_{//}(^{31}P)$ (15.3 (**5**), 13.8 (**6a**) mT). From the comparison between isotropic (5.5 (**5**), 4.7 (**6a**) mT) as well as anisotropic (4.9 (**5**), 4.4 (**6a**) mT) hfc constants and the atomic hfc constants,[14] 1 and 30−40% of the unpaired electrons of **5** and **6a** are estimated to be localized in the 3s and 3p orbitals of the phosphorus, respectively. Frozen solutions of the anion radicals of **5**-^{13}C and **6a**-^{13}C give EPR spectra similar to those of **5** and **6a**. The spectra become broader due to hfc with a ^{13}C nucleus. Anion radicals of phosphaquinomethane and phosphathienoquinomethane are concluded to be delocalized radicals, in contrast to diarylphosphinyl-type structures of those of phosphaquinone and diphosphathienoquinones.

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Supporting Information Available: Detailed experimental procedures and X-ray data in cif form. This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) Compound **5**: orange crystals, mp 79.0−82.0 °C (dec); ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.44 (2H, s), 7.34−7.24 (6H, m), 7.21 (2H, dd, $J_{HH} = 1.2$, 3.4 Hz), 7.17 (2H, dd, $J_{HH} = 2.0$, 6.6 Hz), 7.11 (1H, ddd, $J_{HH} = 1.7$, 4.1 Hz, $J_{PH} = 13.8$ Hz), 6.78 (1H, ddd, $J_{HH} = 1.7$, 4.5 Hz, $J_{PH} = 9.7$ Hz), 6.46 (1H, ddd, $J_{HH} = 1.7$, $J_{HH} = 5.6$ Hz, $J_{PH} = 9.6$ Hz), 5.48 (1H, ddd, $J_{HH} = 1.6$, $J_{HH} = 6.2$ Hz, $J_{PH} = 9.6$ Hz), 1.46 (18H, s), 1.33 (9H, s); ^{31}P NMR (81 MHz, CD_2Cl_2) δ 244.4 (s). (*Z*)-**6a**: orange crystals, mp 120.0−122.0 °C (dec); ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.32 (2H, d, $J_{PH} = 1.1$ Hz), 7.24−7.20 (4H, m), 7.10−7.06 (6H, m), 6.96 (1H, dd, $J_{HH} = 5.8$ Hz, $J_{PH} = 8.1$ Hz), 6.72 (1H, dd, $J_{HH} = 5.8$ Hz, $J_{PH} = 4.2$ Hz), 1.42 (18H, s), 1.21 (9H, s); ^{31}P NMR (81 MHz, CD_2Cl_2) δ 201.4 (s). (Z)-**6b**: orange prisms (ether), mp 162.0−163.0 °C (dec); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.36 (2H, d, $^4J_{PH} = 1.0$ Hz), 7.08 (2H, d, $^3J_{HH} = 8.2$ Hz), 7.01 (2H, d, $^3J_{HH} = 8.2$ Hz), 7.00 (2H, d, $^3J_{HH} = 8.3$ Hz), 6.99 (1H, dd, $^4J_{PH} = 8.5$ Hz, $^3J_{HH} = 5.8$ Hz), 6.96 (2H, d, $^3J_{HH} = 8.3$ Hz), 6.78 (1H, dd, $^4J_{PH} = 4.2$ Hz, $^3J_{HH} = 5.7$ Hz), 2.30 (3H, s), 2.23 (3H, s), 1.46 (18H, brs), 1.26 (9H, s); ^{31}P NMR (81 MHz, CD_2Cl_2) δ 198.9 (s). (*Z*)-**6c**: orange crystals, mp 100.0−103.0 °C (dec); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.37 (2H, d, $^4J_{PH} = 1.0$ Hz), 7.08 (2H, d, $^3J_{HH} = 8.2$ Hz), 7.06 (2H, d, $^3J_{HH} = 8.4$ Hz), 7.05 (2H, d, $^3J_{HH} = 8.5$ Hz), 6.98 (1H, dd, $^4J_{PH} = 8.3$ Hz, $^3J_{HH} = 5.8$ Hz), 6.76 (1H, dd, $^4J_{PH} = 4.3$ Hz, $^3J_{HH} = 5.8$ Hz), 6.68 (2H, d, $^3J_{HH} = 8.9$ Hz, arom), 3.76 (3H, s), 3.71 (3H, s), 1.47 (18H, brs), 1.27 (9H, s); ^{31}P NMR (81 MHz, CD_2Cl_2) δ 196.3 (s).

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(8) Crystal data of (*Z*)-**3b**: $C_{37}H_{45}SP$, $M = 552.80$, orange prisms from diethyl ether, $0.40 \times 0.25 \times 0.20$ mm^3, monoclinic, $P2_1/n$ (No. 14), $a = 10.595(6)$, $b = 18.095(4)$, $c = 16.820(3)$ Å, $\beta = 96.04(2)°$, $V = 3206(1)$ Å^3, $D_c = 1.145$ g cm^{-3}, μ (Mo Kα) = 0.174 mm^{-1}, $T = 115(1)$ K, $Z = 4$, $F(000) = 1192.00$. A Rigaku RAXIS-IV imaging plate, GOF = 1.34 for observed reflections, and $R_1/R/R_w = 0.035/0.042/0.048$ for all reflections, max/min residual electron density 0.32/−0.34 e Å^{-3}. CCDC 260774.

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(11) Compound **5**: $g = 2.005$, $a(^{31}P) = 5.7$ mT; $g_\perp = 2.006$, $a_\perp(^{31}P) = 0.6$ mT, $g_{//} = 2.002$, $a_{//}(^{31}P) = 15.3$ mT. **5**-^{13}C: $g = 2.005$, $a(^{31}P) = 5.6$ mT, $a(^{13}C) = 1.1$ mT. (*Z*)-**6a**: $g = 2.004$, $a(^{31}P) = 5.2$ mT; $g_\perp = 2.006$, $a_\perp(^{31}P) = 0.2$ mT, $g_{//} = 2.002$, $a_{//}(^{31}P) = 13.8$ mT. (*Z*)-**6a**-^{13}C: $g = 2.004$, $a(^{31}P) = 5.2$ mT, $a(^{13}C) = 1.0$ mT.

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