Chem. **1992**, *57*, 4336–4339; c) D. Hoppe, T. Hense, *Angew. Chem.* **1997**, *109*, 2376–3410; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2282–2316.

[3] For leading references see: a) P. Beak, A. Basu, D. J. Gallagher, Y. S. Park, S. Thayumanavan, *Acct. Chem. Res.* **1996**, *29*, 552–560; b) A. R. Katritzky, M. Qi, *Tetrahedron* **1998**, *54*, 2647–2668.

[4] For leading references see: R. W. Hoffmann, R. K. Dress, T. Ruhland, A. Wenzel, *Chem. Ber.* **1995**, *128*, 861–870.

[5] a) R. W. Hoffmann, A. Kusche, *Chem. Ber.* **1994**, *127*, 1311–1316; b) R. W. Hoffmann, M. Julius, F. Chemla, T. Ruhland, G. Frenzen, *Tetrahedron* **1994**, *50*, 6049–6060; c) W. Klute, M. Krüger, R. W. Hoffmann, *Chem. Ber.* **1996**, *129*, 633–638.

[6] V. Schulze, R. W. Hoffmann, *Chem. Eur. J.* **1999**, *5*, 337–344.

[7] B. J. Wakefield, *Organomagnesium Methods in Organic Synthesis*, Academic Press, London, **1995**, p. 58.

[8] C. Cardellicchio, V. Fiandanese, F. Naso, A. Scilimati, *Tetrahedron Lett.* **1992**, *33*, 5121–5124.

[9] a) C. Cardellicchio, V. Fiandanese, F. Naso, *J. Org. Chem.* **1992**, *57*, 1718–1722; b) T. Satoh, K. Takano, H. Someya, K. Matsuda, *Tetrahedron Lett.* **1995**, *36*, 7097–7100; c) C. Cardellicchio, A. Iacuone, F. Naso, P. Tortorella, *Tetrahedron Lett.* **1996**, *37*, 6017–6020.

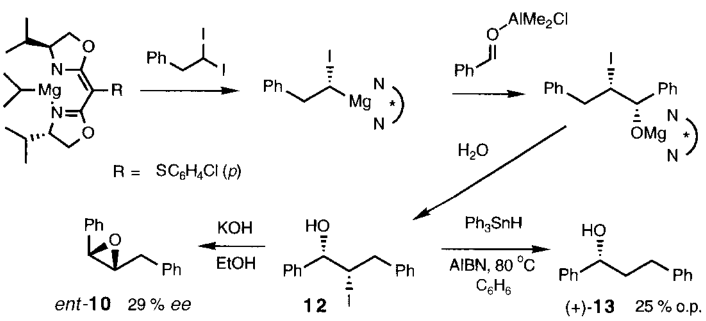
[10] T. Satoh, K. Takano, H. Ota, H. Someya, K. Matsuda, K. Yamakawa, *Tetrahedron* **1998**, *54*, 5557–5574.

[11] T. Satoh, T. Sato, T. Oohara, K. Yamakawa, *J. Org. Chem.* **1989**, *54*, 3130–3136.

[12] T. Satoh, K. Horiguchi, *Tetrahedron Lett.* **1995**, *36*, 8235–8238.

[13] a) M. Hojo, R. Masuda, T. Saeki, K. Fujimori, S. Tsutsumi, *Synthesis* **1977**, 789–791; b) T. Satoh, Y. Mizu, T. Kawashima, K. Yamakawa, *Tetrahedron* **1995**, *51*, 703–710; c) T. Satoh, K. Takano, *Tetrahedron* **1996**, *52*, 2349–2358.

[14] The *cis* arrangement of the substituents in the epoxide **10** is deduced from the characteristic[17] ^{1}H NMR signal at $\delta = 4.18$ for H-2. The absolute configuration of **10** was secured in the context of a related study into the enantioselective iodine/magnesium exchange:[6] a sample of enantio-enriched iodohydrin **12** was converted once to the epoxide *ent*-**10** of 29% *ee* and once by reduction with triphenyltin hydride to the dextrorotatory alcohol **13** ($[\alpha]_D^{25} = +3.9$ ($c = 3.60$, ethanol)) of known absolute configuration[18] in 95% yield (Scheme 5).



Scheme 5. AIBN = 2,2′-azobisisobutyronitrile; o.p. = optical purity.

[15] For leading references see: A. R. Katritzky, X. Lan, J. Z. Yang, O. V. Denisko, *Chem. Rev.* **1998**, *98*, 409–548.

[16] a) W. T. Miller, D. M. Whalen, *J. Am. Chem. Soc.* **1964**, *86*, 2089–2090; b) J. Villiéras, *Bull. Soc. Chim. Fr.* **1967**, 1511–1520; c) G. Köbrich, F. Ansari, *Chem. Ber.* **1967**, *100*, 2011–2020.

[17] Y. Tamura, S. M. Bayomi, K. Sumoto, M. Ikeda, *Synthesis* **1977**, 693–695.

[18] J. L. von dem Bussche-Hünnefeld, D. Seebach, *Tetrahedron* **1992**, *48*, 5719–5730.

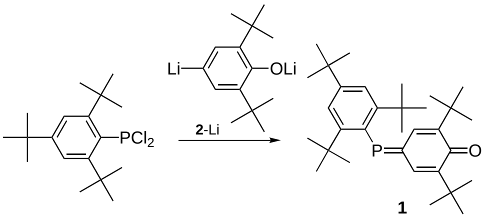
Synthesis, Structure, and Radical Anion of the First Stable *p*-Phosphaquinone**

Shigeru Sasaki, Fumiki Murakami, and
Masaaki Yoshifuji*

*Dedicated to Professor Edgar Niecke
on the occasion of his 60th birthday*

Quinoid compounds have attracted considerable interest for a long time owing to their unique structure, properties, and large potential for application.[1] Thus, a variety of quinoid compounds such as quinones, quinodimethanes, and quinodiimines has played an important role in a wide range of research areas. On the other hand, stable quinoid compounds which contain heavier main group elements had not been known until recently, in spite of progress in the chemistry of heavier main group elements, where double bonds between the most of the typical elements and carbon become available. There have been several reports of matrix isolation[2] of the reactive quinoid molecules and isomeric structures such as tetrathiotetracene,[3] but *p*-diphosphaquinone, characterized and reported by Märkl et al.,[4] is the only example of a stable quinoid molecule containing heavier main group elements. However, it has not been obtained in pure form, since not only the quinoid structure but also the double bond between carbon and a heavier element make the species inherently unstable. Here we report the synthesis, structure, redox properties, and generation of the radical anion of the first stable *p*-phosphaquinone **1**. Employment of the 3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene moiety, which has been one of the most frequently utilized structures in the chemistry of the quinoid molecules, was essential for the synthesis as well as the effective kinetic protection of **1**.

To construct the quinoid skeleton of **1**, we used the 2,6-di-*tert*-butyl-4-lithiophenoxide ion **2** as a key synthetic intermediate [Eq. (1)], since we expected the extremely high



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[**] This work was supported by The Japan Securities Scholarship Foundation and a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan (nos. 08454193 and 09239101). Shin-Etsu Chemical Company is gratefully acknowledged for the donation of silicon chemicals. We also thank the Instrumental Analysis Center for Chemistry, Graduate School of Science, Tohoku University for obtaining 600-MHz NMR spectra, mass spectra, and elemental analysis. This work was partially carried out in the Advanced Instrumental Laboratory for Graduate Research of the Department of Chemistry, Graduate School of Science, Tohoku University.

nucleophilicity[5] to be sufficient for the attack at the phosphorus atom of the starting phosphane, assistance of the oxide ion in the elimination of chloride ion to afford the quinoid system **1**, and effective steric protection of the resultant *p*-phosphaquinone structure by the two *tert*-butyl groups. Thus, 2,6-di-*tert*-butyl-4-iodophenol[6] was lithiated with two equivalents of *n*-butyllithium and added to a solution of dichloro(2,4,6-tri-*tert*-butylphenyl)phosphane in THF.[7] Although the mechanism is not clear, the reaction proceeded as expected and formation of a 10:3 mixture of **1** and bis(2,4,6-tri-*tert*-butylphenyl)diphosphene[7] was confirmed by ^{31}P NMR spectroscopy. Repeated extraction with *n*-pentane, chromatographic separation on silica gel, and purification by gel permeation chromatography (GPC) afforded almost pure phosphaquinone **1**. Further recrystallization from benzene gave analytically pure **1** in 30% yield as air-stable orange plates suitable for an X-ray crystallographic analysis.

The proton-coupled ^{31}P NMR spectrum of **1** (81 MHz) shows a doublet at $\delta = 327.4$ with $J(\mathrm{P,H}) = 12.0$ Hz. The significant deshielding suggests a low-lying excited state due to the quinoid structure of **1**, and the large coupling of the phosphorus atom with the proton in the position *cis* to the lone pair is consistent with the structure and an empirical rule that the ^{31}P nucleus of phosphaalkenes has a larger coupling with nuclei *cis* to its lone pair than those *trans* to it.[8] In the ^{1}H NMR spectrum of **1**, the signals at $\delta = 7.41$ ($J(\mathrm{H,H}) = 2.3$, $J(\mathrm{P,H}) = 12.5$ Hz) and 5.74 ($J(\mathrm{H,H}) = 2.3$, $J(\mathrm{P,H}) = 4.1$ Hz) were easily assigned based on the coupling pattern to the vinyl protons *cis* and *trans* to the phosphorus lone pair, respectively. The vinyl and *tert*-butyl protons *cis* to the 2,4,6-tri-*tert*-butylphenyl group are strongly shielded, probably due to the ring current of the aromatic ring. The ^{13}C NMR signal of the P=C carbon atom appears as a doublet; its chemical shift ($\delta = 167.61$) and coupling constant ($J(\mathrm{P,C}) = 40.0$ Hz) are within the range of typical phosphaalkenes.[9] The signal at $\delta = 185.90$ ($J(\mathrm{P,C}) = 6.7$ Hz) as well as the IR band ($\tilde{\nu}_{\mathrm{CO}} = 1598\ \mathrm{cm}^{-1}$) of the carbonyl group are typical for the 3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene system.[10] The UV/Vis spectrum of **1** in hexanes shows one broad peak at $\lambda_{\mathrm{max}} = 372$ ($\varepsilon = 22100$, $\pi \rightarrow \pi^*$), which is responsible for the orange color of **1**.

The structure of **1** was unambiguously confirmed by an X-ray crystallographic analysis (Figure 1). The P=C bond length of 1.705(2) Å is within the range of known phosphaalkenes, though slightly longer than the average.[9] The bond lengths and angles within the 3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene moiety show values similar to those for the known 3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene structures.[11] Thus, the six-membered ring is composed of two double bonds (C2=C3 1.347(2), C5=C6 1.350(2) Å) and four single bonds (C1-C2 1.446(2), C3-C4 1.497(2), C4-C5 1.482(2), C6-C1 1.444(2) Å). Interestingly, the C=P bond points slightly in the less crowded direction with bond angles of 126.5(1)° and 115.9(1)° for P1-C1-C2 and P1-C1-C6, respectively, probably due to the bulkiness of the 2,4,6-tri-*tert*-butylphenyl moiety. All the spectroscopic as well as crystallographic data are consistent with the quinoid structure of **1**.

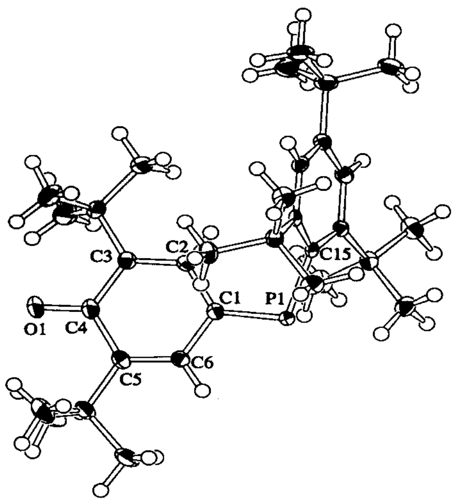


Figure 1. ORTEP drawing of the molecular structure of **1** with 50% probability ellipsoids. Selected bond lengths [Å] and angles [°]: P1−C1 1.705(2), P1−C15 1.847(2), C1−C2 1.446(2), C2−C3 1.347(2), C3−C4 1.497(2), C4−C5 1.482(2), C5−C6 1.350(2), C1−C6 1.444(2), O1−C4 1.238(2); C1-P1-C15 101.58(7), P1-C1-C2 126.5(1), P1-C1-C6 115.9(1), C2-C1-C6 117.5(1), C1-C2-C3 122.8(1), C2-C3-C4 118.7(1), O1-C4-C3 120.5(2), O1-C4-C5 120.7(1), C3-C4-C5 118.8(1), C4-C5-C6 118.4(1), C1-C6-C5 123.4(2).

Since benzoquinones are known to undergo a two-step reversible reduction,[1, 12] and some sterically protected phosphaalkenes are also reported to give redox systems stable enough to allow observation of the corresponding radical anion,[13] we became interested in the redox properties of **1** and measured its cyclic voltammogram (Figure 2). The first redox wave appearing at −1.43 V vs. Ag/Ag^{+} is reversible. However, the second reduction at −2.45 V is irreversible, and scanning to this second reduction makes the first one also irreversible. The first reduction potential is intermediate in value of those of quinones[12] and phosphaalkenes.[13] The difference of the first and second reduction peak potentials ($\Delta E = 0.90$ V) is larger than that of *p*-benzoquinones and quinone methides ($\Delta E = 0.6-0.8$ V).[12]

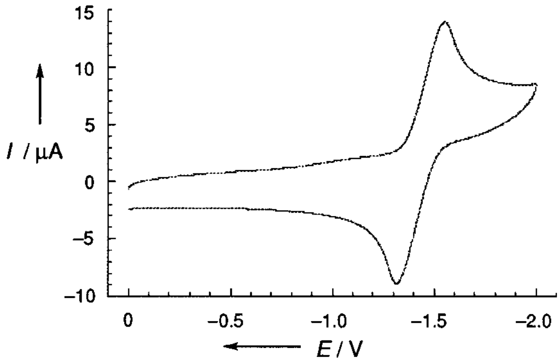
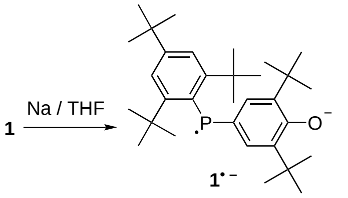


Figure 2. Cyclic voltammogram of **1** (10^{-4} M in THF; supporting electrolyte: 0.1 M $n\mathrm{Bu_4NClO_4}$; working electrode: glassy carbon; counter electrode: Pt wire; reference electrode: Ag/0.01 N $\mathrm{AgNO_3}$ in acetonitrile with 0.1 M $n\mathrm{Bu_4NClO_4}$ ($E_{1/2}$(ferrocene/ferrocenium) = 0.180 V); scan rate: 100 mV s^{-1}; 22 °C). I = current, E = potential.

Although **1** did not afford a two-step reversible redox system like the *p*-benzoquinones, the first reversible wave suggested considerable stability of the phosphasemiquinone radical anion $\mathbf{1}^{\bullet-}$. Thus, the reduction of **1** with sodium metal was carried out [Eg. (2)] and monitored by EPR spectroscopy. The orange color of a solution of **1** in THF became green upon contact with the sodium mirror, and an EPR signal consisting of a doublet due to hyperfine coupling with one ^{31}P nucleus (a(P) = 9.3 mT at $g = 2.0069$) was observed at room temperature (Figure 3 a). The appearance of the spectrum, where the upfield peak is broader due to large anisotropy of the hyperfine coupling, is typical of radical anions of low-coordinated phosphorus compounds. The EPR spectrum of the frozen solution of $\mathbf{1}^{\bullet-}$ at 77 K (Figure 3 b) was also characterized by large anisotropy of hyperfine coupling with the ^{31}P nucleus. The spectrum was approximately reproduced by assigning $g_{xx} = 2.0094$, $g_{yy} = 2.0094$, $g_{zz} = 2.0022$, $a_{xx}(P) = 0.25$, $a_{yy}(P) = 1.7$, and $a_{zz}(P) = 26.1$ mT. From these principal values of the hyperfine coupling tensor, isotropic (contact) and anisotropic (dipolar) coupling constants of 9.35 and 8.38 mT were obtained. Comparison of the isotropic and anisotropic coupling constants of $\mathbf{1}^{\bullet-}$ with those of the phosphorus atom[14] suggests that about 2 and 64 % of the unpaired electron is localized on the 3s and 3p orbitals of phosphorus, respectively. The appearance of the spectra of both solution and frozen solution originating from large anisotropy of hyperfine coupling is similar to those for the known radical anions of low-coordinated phosphorus compounds such as phosphaalkenes[13] and diphosphenes.[15] However, both $a_{zz}(P)$ and $a_{iso}(P)$ are considerably larger than those for the radical anions of other low-coordinate phosphorus compounds, but very similar to those of diarylphosphanyl radicals $Ar_2P^{\bullet}$.[16] This indicates significant contribution of the canonical structure shown in Equation (2).



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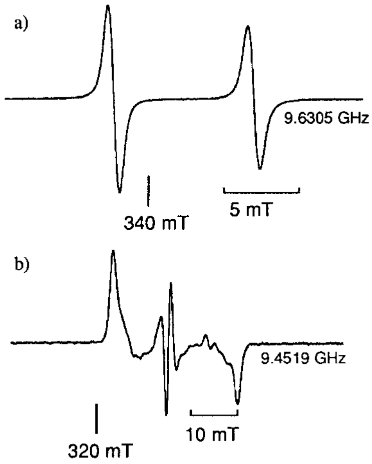

Figure 3. EPR spectra of $\mathbf{1}^{\bullet-}$ generated by the reduction of **1** with sodium metal in THF a) at 295 K and b) at 77 K.

Experimental Section

1: 2,6-Di-*tert*-butyl-4-iodophenol (1.06 g, 3.18 mmol) dissolved in THF (10 mL) was treated with *n*-butyllithium (6.44 mmol, 1.61 mol L^{-1} in *n*-hexane) at −78 °C and allowed to warm to room temperature. The resultant colorless solution was added to dichloro(2,4,6-tri-*tert*-butylphenyl)phosphane (1.09 g, 3.13 mmol) in THF (10 mL) at −78 °C. After being stirred for 15 min at −78 °C, the dark yellow-green solution was warmed to room temperature and stirred for 2 h to afford a dark purple solution. Disappearance of the starting material and formation of **1** and bis(2,4,6-tri-*tert*-butylphenyl)diphosphene (10:3 ratio) were monitored by ^{31}P NMR spectroscopy. The solution was diluted with *n*-pentane (20 mL), and insoluble salts were removed by filtration. The filtrate was concentrated and purified by repeated extraction with *n*-pentane, column chromatography (SiO_2, *n*-hexane/CH_2Cl_2/Et_3N), and GPC (Jaigel 1H + 2H, chloroform). Recrystallization from benzene afforded orange plates of **1** (30 %). M.p. 172.0 °C (decomp); ^1H NMR (200 MHz, $CDCl_3$, 22 °C, TMS): $\delta = 7.48$ (d, J(P,H) = 1.1 Hz, 2H; $H_{arom.}$), 7.41 (dd, J(H,H) = 2.3 Hz, J(P,H) = 12.5 Hz, 1H; vinyl H *trans* to Ar), 5.74 (dd, J(H,H) = 2.3 Hz, J(P,H) = 4.1 Hz, 1H; vinyl H *cis* to Ar), 1.41 (s, 18H; *o*-$C(CH_3)_3$), 1.36 (s, 9H; *p*-$C(CH_3)_3$), 1.33 (s, 9H; $C(CH_3)_3$ *trans* to Ar), 0.96 (s, 9H; $C(CH_3)_3$ *cis* to Ar); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 22 °C, TMS): $\delta = 185.90$ (d, J(P,C) = 6.7 Hz; C=O), 167.61 (d, J(P,C) = 40.0 Hz; C=P), 155.13 (s; *o*-$C_{arom.}$), 151.46 (s; *p*-$C_{arom.}$), 145.02 (d, J(P,C) = 33.3 Hz; =$CC(CH_3)_3$ *trans* to Ar), 143.86 (d, J(P,C) = 23.2 Hz; =$CC(CH_3)_3$ *cis* to Ar), 134.46 (d, J(P,C) = 57.3 Hz; *ipso*-$C_{arom.}$), 133.93 (d, J(P,C) = 41.1 Hz; =CH *trans to* Ar), 128.00 (d, J(P,C) = 13.1 Hz; =CH *cis* to Ar), 121.71 (s; *m*-$C_{arom.}$), 38.03 (s; *o*-$C(CH_3)_3$), 35.14 (s; $C(CH_3)_3$ *trans* to Ar), 35.05 (s; *p*-$C(CH_3)_3$), 34.84 (s; $C(CH_3)_3$ *cis* to Ar), 33.58 (d, J(P,C) = 6.0 Hz; *o*-$C(CH_3)_3$), 31.26 (s; *p*-$C(CH_3)_3$), 29.67 (s; $C(CH_3)_3$ *trans* to Ar), 29.32 (s; $C(CH_3)_3$ *cis* to Ar); ^{31}P NMR (81 MHz, $CDCl_3$, 22 °C, ext. 85 % H_3PO_4): $\delta = 327.4$ (d, J(P,H) = 12.0 Hz); IR (KBr): $\tilde{\nu} = 2954, 2908, 2868, 1631, 1598, 1556, 1475, 1456, 1394, 1365, 1250, 1207, 1128, 1018, 930, 885, 820, 752, 648, 600, 490$ cm^{-1}; UV/Vis (hexanes): λ_{max} (ε) = 372 nm (22100); MS (low resolution, 70 eV, EI): *m/z* (%): 480 (100) $[M]^+$, 465 (61) $[M - Me]^+$, 423 (20) $[M - tBu]^+$, 57 (25) $[tBu]^+$; C,H analysis calcd for $C_{32}H_{49}OP$: C 79.95, H 10.27; found: C 79.89, H 10.27.

Crystal data for **1** ($C_{32}H_{49}OP$): $M_r = 480.71$, orange plates grown from benzene, crystal dimensions $0.50 \times 0.50 \times 0.30$ mm^3, monoclinic, space group $P2_1/c$ (no. 14), $a = 13.887(2)$, $b = 11.094(2)$, $c = 20.087(9)$ Å, $\beta = 102.620(3)^\circ$, $V = 3019(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.057$ g cm^{-3}, $\mu = 0.111$ mm^{-1}, $T = 100(1)$ K, $F(000) = 1056.00$. A Rigaku RAXIS-IV imaging plate area detector with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71070$ Å) was used. Of 4860 reflections measured ($2\theta_{max} = 50.1^\circ$), 4213 were observed $[I > 3.00\sigma(I)]$. The structure was solved by direct methods (SIR92),[17] expanded using Fourier techniques (DIRDIF94),[18] and refined by full-matrix least squares on F for 504 variable parameters. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms isotropically. $R = 0.038$, $R_w = 0.056$, Goodness of fit $S = 1.10$ for observed reflections, and $R = 0.046$, $R_w = 0.064$ for all reflections. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.26 and −0.23 e Å^{-3}, respectively. Structure solution, refinement, and graphical representation were carried out using the teXsan package.[19] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-102095. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Received: July 7, 1998 [Z12108IE]
German version: *Angew. Chem.* **1999**, *111*, 351 – 354

Keywords: EPR spectroscopy · phosphaalkenes · quinones · radical ions · redox chemistry

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[1] *The Chemistry of the Quinoid Compounds, Parts 1 and 2* (Ed.: S. Patai), Wiley, London, **1974**; *The Chemistry of the Quinoid Compounds, Vol. 2, Parts 1 and 2* (Eds.: S. Patai, Z. Rappoport), Wiley, Chichester, **1988**.

[2] H. Bock, S. Mohmand, T. Hirabayashi, G. Maier, H. P. Reisenauer, *Chem. Ber.* **1983**, *116*, 273–281.

[3] J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini, M.-H. Whangbo in *Organic Superconductors (Including Fullerenes): Synthesis, Structure, Properties, and Theory*, Prentice-Hall, New Jersey, **1992**, pp. 11–64.

[4] G. Märkl, R. Hennig, K. M. Raab, *Chem. Commun.* **1996**, 2057–2058.

[5] H. Kurata, T. Tanaka, T. Sauchi, T. Kawase, M. Oda, *Chem. Lett.* **1997**, 947–948.

[6] K. Ley, E. Müller, R. Mayer, K. Scheffler, *Chem. Ber.* **1958**, *91*, 2670–2681.

[7] M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, T. Higuchi, *J. Am. Chem. Soc.* **1981**, *103*, 4587–4589; M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, T. Higuchi, *J. Am. Chem. Soc.* **1982**, *104*, 6167.

[8] E. Fluck, G. Heckmann in *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis* (Eds.: J. G. Verkade, L. D. Quin), VCH, New York, **1987**, pp. 61–113.

[9] R. Appel in *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. Scherer), Thieme, Stuttgart, **1990**, pp. 157–219.

[10] J. Zhou, A. Rieker, *J. Chem. Soc. Perkin Trans. 2* **1997**, 931–938.

[11] G. G. Aleksandrov, Y. T. Struchkov, D. I. Kalinin, M. G. Neigant, *Zh. Strukt. Khim.* **1973**, *14*, 852–858; R. West, J. A. Jorgenson, K. L. Stearley, J. C. Calabrese, *J. Chem. Soc. Chem. Commun.* **1991**, 1234–1235.

[12] J. Q. Chambers in *The Chemistry of the Quinoid Compounds, Part 2* (Ed.: S. Patai), Wiley, London, **1974**, pp. 737–791; J. Q. Chambers in *The Chemistry of the Quinoid Compounds, Vol. 2, Part 2* (Eds.: S. Patai, Z. Rappoport), Wiley, Chichester, **1988**, pp. 719–758.

[13] M. Geoffroy, A. Jouaiti, G. Terron, M. Cattani-Lorente, Y. Ellinger, *J. Phys. Chem.* **1992**, *96*, 8241–8245.

[14] J. R. Morton, K. F. Preston, *J. Magn. Reson.* **1978**, *30*, 577–582.

[15] M. Culcasi, G. Gronchi, J. Escudié, C. Couret, L. Pujol, P. Tordo, *J. Am. Chem. Soc.* **1986**, *108*, 3130–3132; A. J. Bard, A. H. Cowley, J. E. Kilduff, J. K. Leland, N. C. Norman, M. Pakulski, G. A. Heath, *J. Chem. Soc. Dalton Trans.* **1987**, 249–251; S. Shah, S. C. Burdette, S. Swavey, F. L. Urbach, J. D. Protasiewicz, *Organometallics* **1997**, *16*, 3395–3400.

[16] M. Geoffroy, E. A. C. Lucken, C. Mazeline, *Mol. Phys.* **1974**, *28*, 839–845; B. Çetinkaya, A. Hudson, M. F. Lappert, H. Goldwhite, *J. Chem. Soc. Chem. Commun.* **1982**, 609–610.

[17] A. Altomare, M. C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi, G. Polidori, *J. Appl. Crystallogr.* **1994**, *27*, 435.

[18] P. T. Beuskens, G. Admiraal, G. Beuskens, W. P. Bosman, R. de Gelder, R. Israel, J. M. M. Smits, The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, **1994**.

[19] Crystal Structure Analysis Package, Molecular Structure Corporation, **1985** and **1992**.

Kinetics and Mechanisms of the Reactions of π-Allylpalladium Complexes with Nucleophiles[**]

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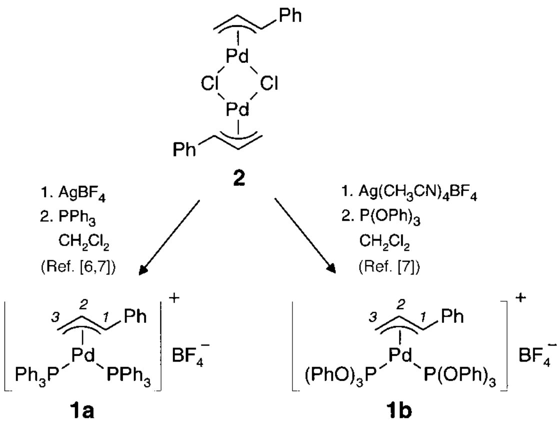
Dedicated to Professor Wolfgang Steglich on the occasion of his 65th birthday

Palladium(0)-catalyzed allylations of nucleophiles proceed under mild conditions, often with high regio- and stereoselectivity.[1] Detailed mechanistic investigations revealed that these reactions generally involve the intermediacy of cationic allylpalladium complexes which have been isolated and characterized by X-ray crystallography.[2] In the course of our program to quanitify the reactivities of cationic electrophiles[3] we have now turned to palladium-stabilized allyl cations. Herein we report on the kinetics of the reactions of the allylpalladium complexes **1a** and **1b** with noncharged nucleophiles, and we demonstrate how to employ the electrophilicity parameters derived therefrom for analyzing the reactivities of these cationic complexes.

The allylpalladium complexes **1a**, **b**[4] were synthesized from **2**[5] using known procedures[6, 7] (Scheme 1). The reaction products **4a–f** were obtained from the nucleophiles **3a–f** and the allyl complexes **1a** and **1b**, either by employing stoichiometric quantities of the allylpalladium tetrafluoroborates **1a**-BF_4 or **1b**-BF_4 or by generating **1a** and **1b** in situ in the presence of the nucleophiles **3** from $[Pd(PPh_3)_4]$ or $[Pd_2(dba)_3 \cdot CHCl_3]/P(OPh)_3$ (10 mol%) and 3-phenylallyl acetate, as specified in Table 1 (Scheme 2; dba = dibenzylideneacetone).



Scheme 1. Synthesis of the complexes **1a**-BF_4 and **1b**-BF_4 from **2**.

To determine the reaction kinetics, the allyl complexes **1a**-BF_4 and **1b**-BF_4 were prepared and combined with 10–50 equivalents of the nucleophiles **3a–f**, and the decay of the

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[**] We thank C. Schlierf for experimental contributions as well as the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.