## Addition of a Diphosphirenium Salt to Palladium(0) **Complexes:** The First Examples of Diphosphametallacyclobutenes

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Summary: P-Bis(diisopropylamino)-C-(diisopropylamino)diphosphirenium tetrafluoroborate (1) reacts with palladium tetrakis(triphenylphosphine), affording the tetrafluoroborate salt of 2,2-bis(triphenylphosphine)-1,3diphospha-2-pallada(II)cyclobutene 2 in 70% yield. Exchange of the triphenylphosphine ligands occurs with diphenylmethylphosphine, dimethylphenylphosphine, trimethylphosphine, and 1,2-bis(diphenylphosphino)ethane, leading to the corresponding complexes 3-6 in good yields.

The interaction of transition-metal complexes with strained cyclopropenylium cations A has been widely studied.<sup>1-3</sup> Due to the aromatic and cationic character of  $\mathbf{A}$ ,<sup>4</sup> both the  $\eta^3$  and  $\eta^1$  ligations are to be expected,<sup>1,2</sup> but the  $\eta^2$  coordination mode with varying extents of intrusion of the metal into a C-C bond is the most fascinating.<sup>3</sup> The last kind of complexes represent points on the energy surface for the conversion of a metallatetrahedrane ( $\eta^3$ -cyclopropenyl) to a metallacyclobutadiene complex (complete insertion of the metal into the C-C bond),<sup>5</sup> a process which has been recognized to play an important role in alkyne metathesis.<sup>6</sup> In the phosphorus series, a stable nickel  $\eta^3$ -phosphirenyl complex has recently been prepared by Nixon et al.;<sup>7</sup> this complexation mode has been explained by the aromatic character<sup>8</sup> of the three-membered phosphorus heterocycle  $\mathbf{B}^{.9}$  The ligation of the phosphirenium salts



 $\mathbf{C}^{10}$  the related  $\sigma^4$ -phosphorus cation, has never been described, although it is quite likely that it would just behave as a simple olefin since the interaction between the cationic phosphorus center and the C=C double bond is weak.<sup>8a</sup> In contrast, several coordination modes are predictable for diphosphirenium salt 1<sup>11</sup> (Chart 1), and here we report our preliminary results concerning the reactivity of this compound with palladium(0)complexes.

Treatment of a dichloromethane solution of diphosphirenium salt 1 with an equimolar amount of palladium tetrakis(triphenylphosphine), at -40 °C, cleanly led to complex 2, which was isolated as a yellow oil in 70% yield.<sup>12</sup> The low solubility in nonpolar solvents strongly argued for the ionic nature of 2, which was confirmed by the presence of a sharp singlet at 0 ppm in the <sup>11</sup>B NMR spectrum due to  $BF_4^-$ . The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum revealed a multiplet at low field (+253 ppm) and a very complex signal at high field (+33.1 to)+14.9 ppm) corresponding to one and three phosphorus nuclei, respectively. All attempts to solve the  ${}^{31}P{}^{1}H{}$ NMR spectrum or to obtain crystals suitable for an X-ray diffraction study failed. Therefore, we carried out

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<sup>(1)</sup> See for examples: (a) Gowling, E. W.; Kettle, S. F. A. Inorg. Chem. **1964**, 3, 604. (b) Shen, J.-K.; Tucker, D. S.; Basolo, F.; Hughes, Chem. 1904, 3, 004. (0) Snen, J.-R., Tucker, D. S., Dason, J., Jason, T., Jason, R. P. J. Am. Chem. Soc. 1993, 115, 11312. (c) Lichtenberger, D. L.; Hoppe, L. M.; Subramanian, L.; Kober, E. M.; Hughes, R. P.; Hubbard, J. L.; Tucker, D. S. Organometallics 1993, 12, 2025. (d) Dichfield, R.; Hughes, R. P.; Tucker, D. S.; Bierwagen, E. P.; Robbins, J.; Robinson, J. J.; Zakutansky, J. A. Organometallics 1993, 12, 2258. (e) Hughes,
R. P.; Tucker, D. S.; Rheingold, A. L. Organometallics 1993, 12, 3069. (2) (a) Gompper, R.; Bartmann, E.; Nöth, H. Chem. Ber. 1979, 112, 218. (b) DeSimone, D. M.; Desrosiers, P. J.; Hughes, R. P. J. Am. Chem.

Soc. 1982, 104, 4842. (c) Gompper, R.; Bartmann, E. Angew. Chem., Int. Ed. Engl. 1985, 24, 209.

<sup>(3) (</sup>a) McClure, M. D.; Weaver, D. L. J. Organomet. Chem. 1973, 54, C59. (b) Tuggle, R. M.; Weaver, D. L. Inorg. Chem. 1972, 11, 2237. (c) Frisch, P. D.; Khare, G. P. Inorg. Chem. **1979**, 18, 781. (d) Blunden, R. B.; Cloke, F. G. N.; Hitchcock, P. B.; Scott, P. Organometallics **1994**, 11, 2917. (e) Hughes, R. P.; Tucker, D. S.; Rheingold, A. L. Organo-

<sup>(4) (</sup>a) Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Ya. Aromaticity and Antiaromaticity; Wiley: New York, 1994. (b) Garratt, P. J. Aromaticity; Wiley: New York, 1986.
(5) (a) Jemmis, E. D.; Hoffmann, R. J. Am. Chem. Soc. 1980, 102, 1970. (b) Lin Z. Leil, M. P. Oct. W. 1994. (c) 10203

<sup>2570. (</sup>b) Lin, Z.; Hall, M. B. Organometallics 1994, 13, 2878.

<sup>(6)</sup> Schrock, R. R. Acc. Chem. Res. 1986, 19, 342.

<sup>(7)</sup> Avent, A. G.; Cloke, F. G. N.; Flower, K. R.; Hitchcock, P. B.; Nixon, J. F.; Vickers, D. M. Angew. Chem., Int. Ed. Engl. 1994, 33, 2330.

<sup>(8) (</sup>a) Mathey, F. Chem. Rev. 1990, 90, 997. (b) Maclagen, G. A. R. Chem. Phys. Lett. 1989, 163, 349.

<sup>(9)</sup> The first successful generation and characterization of a comound of type **B** has recently been reported: Laali, K. K.; Geissler, B.; Wagner, O.; Hoffmann, J.; Armbrust, R.; Eisfeld, W.; Regitz, M. J. Am.

Chem. Soc. 1994, 116, 9407. (10) (a) Forgers, K. S.; Hogeveen, H.; Kingma, R. F. Tetrahedron Lett. 1983, 24, 643. (b) Breslow, R.; Doering, L. A. Tetrahedron Lett. 1984, 25, 1345. (c) Marinetti, A.; Mathey, F. J. Am. Chem. Soc. 1985, C. Comparis, A. Barter, S. C. Comparis, A. Barter, S. C. Comparis, A. 107, 4700. (d) Vural, J. M.; Weissman, S. A.; Baxter, S. G.; Cowley, A. H.; Nunn, C. M. J. Chem. Soc., Chem. Commun. 1988, 462.

<sup>(11) (</sup>a) Castan, F.; Baceiredo, A.; Fischer, J.; De Cian, A.; Com-menges, G.; Bertrand, G. J. Am. Chem. Soc. **1991**, *113*, 8160. (b) Soleilhavoup, M.; Canac, Y.; Polozov, A. M.; Baceiredo, A.; Bertrand, G. J. Am. Chem. Soc. 1994, 116, 6149.



**Figure 1.** Experimental <sup>31</sup>P{<sup>1</sup>H} NMR spectrum (32.438 MHz) of **5** in CDCl<sub>3</sub> at 298 K (bottom) and simulated spectrum (top) using  $\delta_A - 30.8$  ppm,  $\delta_B - 26.1$  ppm,  $\delta_C 27.9$  ppm,  $\delta_X 244.6$  ppm, J(AB) = 52 Hz, J(AC) = 31 Hz, J(AX) = 20 Hz, J(BC) = 559 Hz, J(BX) = 4 Hz, and J(CX) = 57 Hz.

exchange reactions of the triphenylphosphine ligands with a variety of other phosphines.

When diphenylmethylphosphine, dimethylphenylphosphine, or trimethylphosphine was added to complex 2, clean reactions occurred leading to the corresponding complexes 3, 4, and 5, which were isolated as yellow oils in near-quantitative yields.<sup>12</sup>

The  ${}^{31}P{}^{1}H$  NMR spectra of complexes 2-5 are similar and exhibit resonances of the type ABCX (Table 1). When the phosphine ligands are changed, the chemical shifts of the X (244-259 ppm) and C (25-32 ppm) parts change only slightly and therefore can be assigned to the phosphorus atoms arising from diphosphirenium salt 1; moreover, the proton-coupled <sup>31</sup>P NMR spectra demonstrate that  $P_C$  bears the amino groups. The simplest spectrum was obtained for complex 5 and is shown along with the simulated spectrum in Figure 1. The presence of an ABCX system excludes the  $\eta^1$  complex **D**, the two phosphines being magnetically equivalent. Since the value of the coupling constant between the phosphorus atom substituted by amino groups and one of the phosphine ligands is quite large ( $J_{P_BP_C} = 559$  Hz), the  $\eta^2$  complex of type **E** can also be excluded. Thus, the reasonable remaining possibility was a structure of type  $\mathbf{F}$ , featuring a completely or partially opened diphosphirenium moiety

Table 1.  $\delta({}^{31}\text{P})$  Chemical Shifts (ppm) Obtained by Simulation of the Spectra of Complexes 2–6

	$\delta_{\rm A}$	$\delta_{\rm B}$	$\delta_{ m C}$	$\delta_{\mathbf{X}}$
2	+16	+19	+25	+253
3	-4.8	+4.2	+25.4	+259.0
4	-19.0	-14.5	+27.5	+250.0
5	-30.8	-26.1	+27.9	+244.6
<b>6</b> <sup><i>a</i></sup>	+32	+32	+32	+249

<sup>a</sup> It has not been possible to solve the ABC part of the system observed for 6; +32 is the center of the multiplet.



(Chart 2). Note that the value of the coupling constant between the two phosphorus atoms of the ring  $(J_{P_CP_X} =$ 57 Hz) does not rule out a PP interaction, and the presence of only one large coupling constant ( $J_{P_BP_C} =$ 559 Hz) is rather surprising, since two trans P-Pd-P arrangements are expected.

The exact structure of these complexes came from the reaction of **2** with 1,2-bis(diphenylphosphino)ethane,<sup>12</sup> since complex **6** was obtained in 90% yield as orange crystals (mp 169–171 °C) suitable for an X-ray analy-

<sup>(12)</sup> Synthesis of comlex 2: To a dichloromethane solution (5 mL) of 1 (0.46 g, 1 mmol) at -40 °C was added a stoichiometric amount of palladium tetrakis(triphenylphosphine) (1.10 g, 1 mmol). After the solution was warmed to room temperature, the solvent was removed in vacuo, and the residue was washed with toluene and ether, leading to complex 2 as a yellow oil (0.76 g, 70% yield). Synthesis of complexes 3-6: To a dichloromethane solution (10 mL) of 2 (1.09 g, 1 mmol) at room temperature was added 2 equiv of phoshine (diphenylmeth-ylphosphine) (3), phenyldimethylphosphine (4), or trimethylphosphine (5)) or a stoichiometric amount of 1,2-bis(diphenylphosphino)ethane (6). After 30 min at room temperature, the solvent was removed in vacuo, and the residue was washed several times with toluene and ether to eliminate triphenylphosphine. Complexes 3 (0.82 g, 85% yield), 4 (0.69 g, 82% yield), and 5 (0.63 g, 88% yield) were obtained as yellow oils, and complex 6 (0.87 g, 90% yield) was obtained as orange crystals from a THF/ether solution.



sis.<sup>13</sup> The ORTEP view of the molecule is illustrated in Figure 2, along with the atom labeling and the pertinent metric parameters. No interaction between the cation and the anion  $(BF_4^-)$  is observed. The P(1)-P(3) distance of 2.655(1) Å is longer than a normal P-P single bond, which is about 2.22 Å,<sup>14</sup> and is also longer than that observed in the related 1,3-diphospha-2,4disilabicyclo[1.1.0]butane (2.34 Å).<sup>15</sup> Bond lengths do not always correlate with bond orders in a simple way; however, as the C(2) atom lies only 0.1899(34) Å out of the [P(1),Pd(1),P(3)] plane, we can rule out a bicyclic structure and therefore a P(1)-P(3) interaction. The palladium atom has a slightly distorted square-planar geometry (the value of the twist angle between the [P(1),Pd(1),P(3)] and [P(25),Pd(1),P(28)] planes is  $16.44(7)^{\circ}$ ), probably due to the strain in the fourmembered ring (P(1)-Pd-P(3), 70.27(3)°; P(1)-C(2)-P(3), 96.2(2)°), and can be considered as Pd(II). Since the P(1)-C(2) bond length (1.745(3) Å) falls in the range observed for C-amino-substituted phosphaalkenes,<sup>16</sup> complex 6 and 2-5 have to be considered as the first examples of diphosphametallacyclobutene (Scheme 1). It is quite likely that the mechanism leading to

complexes 2-6 involves a nucleophilic attack of the



Figure 2. ORTEP view of complex 6. Selected bond lengths (Å) and bond angles (deg): Pd(1)-P(1), 2.317(1); Pd(1)-P(3), 2.2960(7); Pd(1)-P(25), 2.3228(7); Pd(1)-P(28), 2.382(1); P(1)-C(2), 1.745(3); P(3)-C(2), 1.821(4); C(2)-N(4), 1.349(5); P(3)-N(11), 1.686(3); P(3)-N(18), 1.691(3); P(1)-Pd(1)-P(3), 70.27(3); P(1)-Pd(1)-P(25), 95.78(3); P(1)-Pd(1)-P(28), 172.76(3); P(3)-Pd(1)-P(25), 160.45(4); P(3)-Pd(1)-P(28), 111.81(3); P(25)-Pd(1)-P(28), 83.78(3); Pd(1)-P(1)-C(2), 97.1(1); P(1)-C(2)-P(3), 96.2(2).

dicoordinated phosphorus atom of 1, as already observed with lithium salts,<sup>11b</sup> leading to  $\eta^1$ -coordinated 1,3diphosphaallylic cations 7, which then undergo a ring closure (Scheme 1).<sup>17</sup>

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**Supporting Information Available:** Tables giving crystal and intensity collection data, positional and thermal parameters, interatomic distances and angles, and least-squares-plane equations (17 pages). Ordering information is given on any current masthead page.

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<sup>(13)</sup> Crystallographic data for **6** (C<sub>45</sub>H<sub>66</sub>BF<sub>4</sub>N<sub>3</sub>P<sub>4</sub>Pd) were collected at  $-150 \pm 0.5$  °C on an Enraf-Nonius CAD4 diffractometer using Mo K $\alpha$  radiation ( $\lambda = 0.710$  73 Å) and a graphite monochromator. The crystal structure was solved and refined using the Enraf-Nonius MOLEN package. The compound crystallizes in space group PI (No. 2), with a = 10.258(1) Å, b = 20.801 Å, c = 24.435(2) Å,  $\alpha = 66.39(1)^\circ$ ,  $\beta = 88.14(1)^\circ$ ,  $\gamma = 88.38(1)^\circ$ , V = 4773.90(91) Å<sup>3</sup>, Z = 4,  $d_{calc} = 1.344$  g/cm<sup>3</sup>,  $\mu = 5.6$  cm<sup>-1</sup>, and F(000) = 2016. A total of 17.766 unique reflections were recorded in the range  $2^\circ \leq 20 \leq 50.0^\circ$ , of which 5289 were considered as unobserved ( $F^2 < 3.0\sigma(F^2)$ ), leaving 12 477 for solution and refinement. The structure was solved by Patterson methods, yielding a solution for the two palladium atoms. The two molecules contained in the asymmetric unit are identical. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement while using anisotropic temperature factors for all other atoms. A non-Poisson weighting scheme was applied with a *p* factor equal to 0.08. The final agreement factors were R = 0.035,  $R_w = 0.054$ , and GOF = 1.15.

 <sup>(14) (</sup>a) Cowley, A. H. Chem. Rev. 1963, 5, 617. (b) Durig, J. R.;
 Carreira, L. A.; Odom, J. D. J. Am. Chem. Soc. 1974, 96, 2688.

<sup>(15) (</sup>a) Driess, M.; Fanta, A. D.; Powell, D. R.; West, R. Angew.
Chem., Int. Ed. Engl. 1989, 28, 1038. (b) Fanta, A. D.; Driess, M.;
Powell, D. R.; West, R. J. Am. Chem. Soc. 1991, 113, 7806.
(16) Markovski, L. N.; Romanenko, V. D.; Ruban, A. V. The

<sup>(16)</sup> Markovski, L. N.; Romanenko, V. D.; Ruban, A. V. The Chemistry of Acyclic Derivatives of Two-Coordinated Phosphorus; Kirsanov, A. V., Ed.; Naukova Dumka: Kiev, Ukraine, 1988.

<sup>(17)</sup> An alternative mechanism involving a direct insertion into the  $P{-}P$  bond of the  $(R_3P)_2Pd$  fragment acting as a carbene^{15b} has been suggested by a reviewer.