Preparation and Palladium Complex Formation of Several (2-Phosphaethenyl)benzenes

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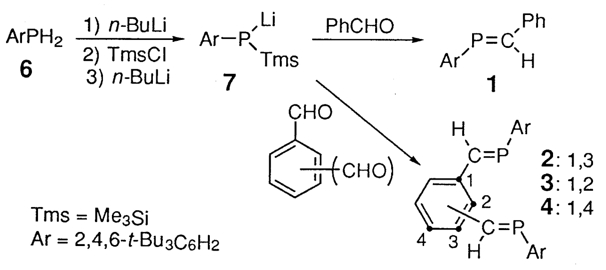
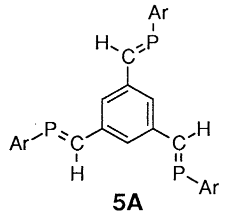
Phenylphosphaethenes carrying two to four phosphorus-carbon double bonds on a benzene ring were prepared and their palladium complex formations were studied. The palladium complexes reacted with alkyllithium reagents to give the corresponding *o*-alkylation products.

Since Bickelhaupt *et al.* reported on the isolation of sterically protected 1-mesityl-2,2-diphenyl-1-phosphaethene,[1] several sterically protected phosphaethenes have been prepared. Utilizing a very bulky 2,4,6-tri-*t*-butylphenyl group (hereafter abbreviated to the Ar group), we were successful in preparation of 1-(2,4,6-tri-*t*-butylphenyl)-2-phenyl-1-phosphaethene (**1**) as a very stable compound[2] and reported some reactions including transition-metal complex formations.[3] Very recently, Geoffroy *et al.* have reported on the formation and properties of *m*- (**2**) and *o*-benzodiphosphaalkenes (**3**).[4,5] We now wish to report our independent results on the synthesis and properties of the benzodiphosphaethenes carrying two C=P double bonds at the 1,2- (**3**) and 1,4-positions (**4**), as well as 1,3,5-tris- (**5A**) and 1,2,4,5-tetrakis(2-phosphaethenyl)benzenes (**5B**).[6]

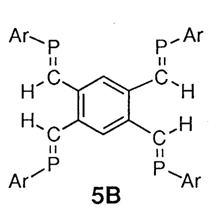


The phosphaethenes (**3**—**5**) were prepared according to the method employed for compound **1**.[2] Starting from 2,4,6-tri-*t*-butylphenylphosphine (**6**, 1.1 g, 4.0 mmol), the corresponding trimethylsilylphosphide **7** was prepared and was allowed to react with *o*-phthalaldehyde (0.26 g, 1.9 mmol) in THF (10 mL) to give **3** (0.68 g, 1.0 mmol) in 54% yield based on **6**. **3**: yellow prisms, mp 222.5–223.0 °C (decomp); ^{31}P NMR (81 MHz, $CDCl_3$) δ_P = 263.8 (d, $^2J_{PH}$ = 22.8 Hz). Similarly, the phosphaethenes **4**, **5A**, and **5B** were obtained from the corresponding aldehydes and **7**.[7]

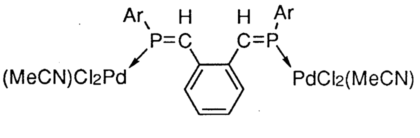
Geoffroy *et al.* reported on the formation of palladium complexes derived from **2** and **3** as a bidentate ligand and $(PhCN)_2PdCl_2$ in CH_2Cl_2.[4a,5] Phosphaethene **3**, under similar conditions with $(MeCN)_2PdCl_2$ in THF, gave transiently **8** (δ_P = 173.0) at room temperature, but gradually led to **9**[5] in 86% yield.[8] Although compounds **4** and **5A** failed to give the corresponding palladium complexes, a similar reaction of **5B** occurred to give bis(palladium) complex **10** in 60% yield.[8] According to the ^{31}P-NMR monitoring of the reaction, there appeared an intermediate signal of **11** (δ_P = 195.5) after 30-min stirring at 25 °C and an additional 4-h stirring gave **10** due to HCl elimination. It seems likely that a C–H activation occurs on the aromatic ring carrying the C=P bonds when palladium metal is located in an appropriate position, as has been demonstrated for azobenzenes,[9] imines,[10,11] and aldehydes.[12]



5A



5B



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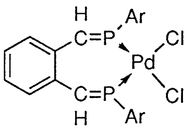

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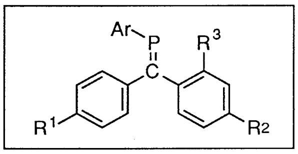
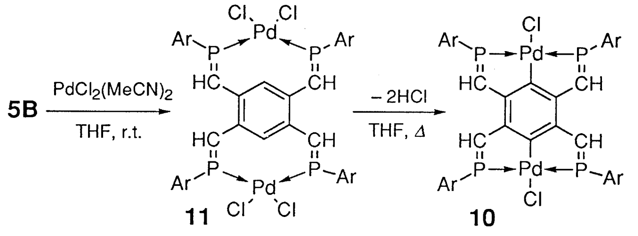
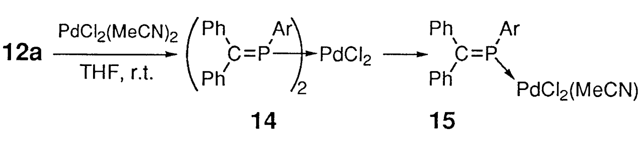


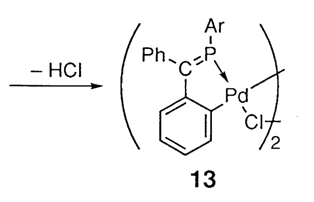
12 **a**: R1= R2= R3= H;
b: R1= R3= H, R2= *t*-Bu;
c: R1= *t*-Bu, R2= R3= H.

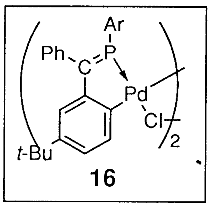
17 **a**: R1= *t*-Bu, R2= H, R3= Me;
b: R1= R2= H, R3= Me;
c: R1= R2= H, R3= *n*-Bu;
d: R1= R2= H, R3= Ph;
e: R1= H, R2= *t*-Bu, R3= Me.

18 R1= R2= H, R3= C(O)OMe









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Furthermore, it turned out that one P=C bond is enough for *o*-palladation reaction. A THF solution of a mixture of 2,2-diphenylphosphaethene **12a** (0.31 g, 0.70 mmol)[3] and bis(acetonitrile)dichloropalladium(II) (0.18 g, 0.70 mmol) was stirred at room temperature for 5 h and the solvent was removed in vacuo. Trituation with hexane gave precipitates of palladium complex **13** (0.39 g, 0.70 mmol) in 97% yield. The formation of **13** appeared to successively proceed *via* **14** (δ_P = 182.1) and **15** (δ_P = 151.0) due to the NMR studies. **13**: orange prisms, mp >300 °C (decomp); δ_P = 205.5. Although the crystallographic analysis of **13** was not successful, the structure of **16**, a similar palladium complex derived from **12b**,[13] was confirmed by X-ray analysis.[14] **16**: mp > 300 °C (decomp); δ_P = 201.5; Found: C, 66.18; H, 7.19; Cl, 5.43%. Calcd for $C_{70}H_{92}Cl_2P_2Pd_2$: C, 65.83; H, 7.10, Cl, 5.55%. Figure 1 depicts the molecular structure of dimeric feature for **16**, where a well-known four-membered ring[15] is formed by two palladium atoms, coordinated by the lone-pair electrons of the phosphorus atoms, and two chlorine atoms, taking a dihedral angle of 157.5° along with the Cl(1)-Cl(2) axis. The atoms Pd(1), P(1), C(1), C(2), C(3), and Cl(2) are almost coplanar within 0.1 Å.

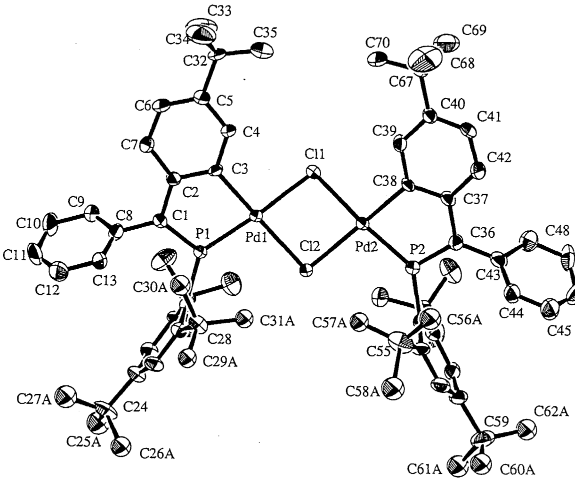

Figure 1. Molecular structure of complex **16**, where the notation A's denote disordered atoms with the predominant occupancy factors. Some important bond lengths (Å) and bond angles (°): P(1)-Pd(1), 2.198(3); Pd(1)-C(3), 2.010(9); Pd(1)-Cl(1), 2.391(3); Pd(1)-Cl(2), 2.437(3); P(1)-Pd(1)-C(3), 80.5(3); Cl(1)-Pd(1)-Cl(2), 83.73(9); P(1)-Pd(1)-Cl(1), 172.8(1); C(3)-Pd(1)-Cl(2), 179.2(3).

Furthermore, the complex **13** reacted with some nucleophiles. Methyllithium (1.13 mmol in ether) was added to a THF (10 mL) solution of **13** (55.6 mg, 0.0476 mmol) in the presence of triphenylphosphine (50.1 mg, 0.191 mmol) at 0 °C and stirred for 1 h at 25 °C to give a methylation product **17b** in 84% yield after the usual work-up. Similarly *o*-alkylation occurred when butyllithium or phenyllithium was employed to give **17c** (54% yield) or **17d** (25% yield).[16] However, the reaction of *t*-butyllithium with **13** failed to give the alkylation product but gave the starting phosphaethene **12a** (39% yield). The reaction of **16** with methyllithium similarly gave **17e** in 55% yield, whereas that of the palladium complex derived from **12c**[13] gave **17a** in 84% yield. Furthermore **13** reacted with carbon monoxide under a pressure of 95 atm (1 atm = 101325 Pa) in a mixture of methanol-benzene (1:1 v/v) at 20 °C for 14 h to give methyl *o*-(2-phosphaethenyl)benzoate **18**[17] in 95% yield.[18] Thus *o*-palladation occurred to (2-phosphaethenyl)benzenes and the complexes could be alkylated or carbonylated with alkyllithiums or carbon monoxide to give *o*-substituted benzenes carrying the C=P bond.

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References and Notes

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6 A part of this work, including the X-ray analysis of **3a**, was presented at the 69th Annual Meeting of Chemical Society of Japan, March 1995 (Kyoto), Abstr. 3H-706.
7 **4**: mp 144.5–145.5 °C, δ_P = 259.8 (${}^2J_{PH}$ = 25.5 Hz), 33% yield; **5A**: mp 284.0–284.5 °C, δ_P = 263.9 (${}^2J_{PH}$ = 24.8 Hz), 17% yield; **5B**: mp 208–210 °C (decomp) δ_P = 267.1 (${}^2J_{PH}$ = 18.4 Hz), 4% yield. All new compounds have been fully characterized spectroscopically.
8 **9**: mp 265–270 °C (decomp), δ_P = 193.3; **10**: mp > 300 °C (decomp), δ_P = 201.9.
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13 Phosphaethenes **12b** and **12c** were prepared from **7** and *t*-butylbenzophenone.[19] **12b**: mp 129–130 °C, δ_P = 239.5, 15% yield; **12c**: pale yellow oil, δ_P = 239.0, 8% yield.
14 Crystal data for **16**: $C_{70}H_{92}Cl_2P_2Pd_2$, FW = 1281.17, monoclinic, $P2_1/n$, a = 17.335(3), b = 23.966(4), c = 17.493(3) Å, β = 109.80(1)°, V = 6838(1) Å^3, Z = 4, D_{calc} = 1.244 g cm^{-3}, R = 0.056, R_w = 0.060; 6352 unique reflections with $I > 3\sigma(I)$. The structure was solved with SHELXS86. The methyl carbon atoms of the *t*-butyl groups of the Ar groups (C25–C27), (C29–C31), (C56–C58), and (C60–C62) are disordered. The predominant occupancy factors were refined to be 0.639, 0.650, 0.604, and 0.599, respectively. Further details of the crystal structure investigations for **16** are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ (UK).
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16 **17a**: colorless oil, δ_P = 239.2; **17b**: mp 146–147 °C, δ_P = 241.8; **17c**: mp 106.5–108.5 °C, δ_P = 242.6; **17d**: mp 160–161 °C, δ_P = 246.9; **17e**: colorless oil, δ_P = 241.8. The yields of alkylation products decreased when triphenylphosphine was not employed.
17 **18**: colorless oil, δ_P = 244.1, IR ($CHCl_3$) 1733 and 1724 (C=O) cm^{-1}.
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