Electronic Supplementary Information

A New Oxapalladacycle Generated via Ortho C-H Activation of Phenylphosphinic Acid: Efficient Catalyst for Markovnikov-Type Additions of E-H Bonds to Alkynes

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General. All reactions were carried out under nitrogen atmosphere in a sealed NMR or a Schlenk tube unless otherwise noted. Solvents were dried and purified under nitrogen before use by standard procedure. $^1$H, $^{13}$C and $^{31}$P NMR spectra were recorded on a JEOL LA-500 instrument (500 MHz for $^1$H, 125.4 MHz for $^{13}$C, and 201.9 MHz for $^{31}$P NMR spectroscopy). Unless otherwise noted, CDCl$_3$ was used as the solvent. Chemical shift values for $^1$H and $^{13}$C were referred to internal Me$_4$Si (0 ppm), and that for $^{31}$P was referred to H$_3$PO$_4$ (85% solution in D$_2$O, 0 ppm). Mass spectra were measured on a Shimadzu GCMS-QP2010 spectrometer (EI). HRMS and elemental analysis was performed by the Analytical Center at the National Institute of Advanced Industrial Science and Technology. Preparative GPC was carried out on a Japan Analytical Industry LC-908 instrument (1H and 2H columns) with CHCl$_3$ as eluent.

X-ray Crystallography. Data collection was performed on a Bruker Smart Apex CCD diffractometer (Mo Kα radiation, graphite monochromator). Data were corrected for absorption. For complex 3, the structures were solved by the Patterson method. Structure refinement was carried out by full-matrix least squares on $F^2$. All non-hydrogen atoms were refined anisotropically, with a similar U restraint for some of carbon atoms (C8-C12). All hydrogen atoms were located at calculated positions and refined with a riding model. Structure solution and refinement were performed using Crystal Structure software package with SHELX-97 program.  

Characterizations of Adducts

\[ \text{n-C}_6\text{H}_{13} \quad \text{P(O)Ph}_2 \]

This compound is known: Han, L.-B.; Hua, R.-M.; Tanaka, M. Angew. Chem. Int. Ed.
1998, 37, 94.

\[
\text{t-Bu} \quad \text{P(O)} \quad \text{Ph}_2
\]

\(^1\)H NMR: \(\delta 7.69-7.64\) (m, 4H), \(7.52-7.49\) (m, 2H), \(7.46-7.42\) (m, 4H), 5.99 (d, \(J_{P-H} = 45.2\) Hz, 1H), 5.20 (d, \(J_{P-H} = 22.0\) Hz, 1H), 1.27 (s, 9H). \(^{31}\)P NMR: \(\delta 34.8\). M/S (m/z) 284 (42, M^-), 228 (60), 227 (100), 201 (36). This compound is known: (a) Dobashi, N.; Fuse, K.; Hoshino, T.; Kanada, J.; Kashiwabara, T.; Kobata, C.; Nune, S. K.; Tanaka, M. Tetrahedron Lett. 2007, 48, 4669. (b) Takaki, K.; Takeda, M.; Koshiji, G.; Shishido, T.; Takehira, K. Tetrahedron Lett. 2001, 42, 6357.

\[
\text{Ph}_2(\text{O})\text{P} \quad \text{Ph}
\]

This compound is known: Han, L.-B.; Hua, R.-M.; Tanaka, M. Angew. Chem. Int. Ed. 1998, 37, 94.

\[
n-\text{C}_6\text{H}_{13} \quad \text{P(O)} \quad \text{Me}_2
\]

\(^1\)H NMR: \(\delta 5.92\) (d, \(J_{P-H} = 19.5\) Hz, 1H), 5.86 (d, \(J_{P-H} = 39.1\) Hz, 1H), 2.24-2.19 (m, 2H), 1.55 (d, \(J_{P-H} = 12.2\) Hz, 6H), 1.56-1.49 (m, 2H), 1.37-1.31 (m, 6H), 0.90 (t, \(J_{H-H} = 6.1\) Hz, 3H). \(^{13}\)C NMR: \(\delta 145.8\) (d, \(J_{C-P} = 87.8\) Hz), 125.9 (d, \(J_{C-P} = 7.2\) Hz), 32.1, 31.6 (d, \(J_{C-P} = 11.4\) Hz), 29.4, 28.5 (d, \(J_{C-P} = 6.2\) Hz), 23.0, 16.6 (d, \(J_{C-P} = 69.2\) Hz), 14.5. \(^{31}\)P NMR: \(\delta 35.3\). M/S (m/z) 187 (M^-1), 173, 159, 145, 131, 104, 93, 78. HRMS Calcd for C\(_{10}\)H\(_{21}\)OP: 188.1330; found: 188.1325.

\[
\text{t-Bu} \quad \text{P(O)} \quad \text{Me}_2
\]

\(^1\)H NMR: \(\delta 5.75\) (d, \(J_{P-H} = 42.7\) Hz, 1H), 5.54 (d, \(J_{P-H} = 22.0\) Hz, 1H), 1.64 5.76 (d, \(J_{P-H} = 12.2\) Hz, 6H), 1.32 (s, 9H). \(^{13}\)C NMR: \(\delta 156.5\) (d, \(J_{C-P} = 82.7\) Hz), 122.6 (d, \(J_{C-P} = 11.4\) Hz), 38.0 (d, \(J_{C-P} = 9.3\) Hz), 30.4 (d, \(J_{C-P} = 4.1\) Hz), 20.4 (d, \(J_{C-P} = 70.3\) Hz). \(^{31}\)P NMR: \(\delta 39.2\). HRMS Calcd for C\(_8\)H\(_{17}\)OP: 160.1017; found: 160.1013.

\[
n-\text{C}_6\text{H}_{13} \quad \text{P(O)(OEt)} \quad \text{Ph}
\]

This compound is known: Han, L.-B.; Zhang, C.; Yazawa, H.; Shimada, S. J. Am. Chem. Soc. 2004, 126, 5080.
**t-Bu P(O)(OEt)Ph**

$^1$H NMR: $\delta$ 7.81-7.77 (m, 2H), 7.53-7.30 (m, 1H), 7.48-7.43 (m, 2H), 5.90 (d, $J_{P-H} = 44.0$ Hz, 1H), 5.82 (d, $J_{P-H} = 22.0$ Hz, 1H), 4.13-4.06 (m, 1H), 3.98-3.90 (m, 1H), 1.32 (t, $J_{H-H} = 7.4$ Hz, 3H), 1.22 (s, 9H). $^{13}$C NMR: $\delta$ 152.1 (d, $J_{C-P} = 117.8$ Hz), 133.1 (d, $J_{C-P} = 129.2$ Hz), 132.165 (d, $J_{C-P} = 3.1$ Hz), 132.161 (d, $J_{C-P} = 10.3$Hz), 128.7 (d, $J_{C-P} = 12.4$ Hz), 127.5 (d, $J_{C-P} = 10.3$ Hz), 60.9 (d, $J_{C-P} = 6.2$ Hz), 37.0 (d, $J_{C-P} = 11.4$ Hz), 30.7 (d, $J_{C-P} = 4.1$ Hz), 16.8 (d, $J_{C-P} = 6.2$ Hz). $^{31}$P NMR: $\delta$ 34.9. HRMS Calcd for C$_{14}$H$_{21}$O$_2$P: 252.1279; found: 252.1280.

This compound is known: Han, L.-B.; Tanaka, M. *J. Am. Chem. Soc.* 1996, 118, 1571.

**n-C$_6$H$_{13}$ P(O)(OMe)$_2$**

$^1$H NMR: $\delta$ 6.03 (d, $J_{P-H} = 23.2$ Hz, 1H), 5.90 (d, $J_{P-H} = 48.8$ Hz, 1H), 3.72 (d, $J_{P-H} = 11.0$ Hz, 6H), 1.23 (s, 9H). $^{13}$C NMR: $\delta$ 147.9 (d, $J_{C-P} = 163.3$ Hz), 128.7 (d, $J_{C-P} = 8.3$ Hz), 52.6 (d, $J_{C-P} = 5.2$ Hz), 36.0 (d, $J_{C-P} = 11.4$ Hz), 30.4 (d, $J_{C-P} = 5.2$ Hz). $^{31}$P NMR: $\delta$ 23.0. HRMS Calcd for C$_8$H$_{17}$O$_3$P: 192.0915; found: 192.0925.

**t-Bu POO**

$^1$H NMR: $\delta$ 5.88 (d, $J_{P-H} = 23.2$ Hz, 1H), 5.60 (d, $J_{P-H} = 50.0$ Hz, 1H), 2.39-2.33 (m, 2H), 1.59-1.54 (m, 2H), 1.52 (s, 6H), 1.37-1.30 (m, 6H), 1.34 (s, 6H), 0.88 (t, $J_{H-H} = 6.1$ Hz, 3H). $^{13}$C NMR: $\delta$ 141.4 (d, $J_{C-P} = 166.4$ Hz), 126.7 (d, $J_{C-P} = 9.3$ Hz), 88.6, 33.3 (d, $J_{C-P} = 11.4$ Hz), 32.0, 29.2, 28.4 (d, $J_{C-P} = 5.2$ Hz), 25.4 (d, $J_{C-P} = 2.1$ Hz), 24.5 (d, $J_{C-P} = 4.1$ Hz), 23.0, 14.5. $^{31}$P NMR: $\delta$ 31.1. HRMS Calcd for C$_{14}$H$_{27}$O$_3$P: 274.1698; found: 274.1695.

**t-Bu P(O)(OMe) 2**

$^1$H NMR: $\delta$ 5.93 (d, $J_{P-H} = 24.4$ Hz, 1H), 5.73 (d, $J_{P-H} = 50.0$ Hz, 1H), 1.51 (s, 6H), 1.32 (s, 6H), 1.27 (s, 9H). $^{13}$C NMR: $\delta$ 151.4 (d, $J_{C-P} = 158.1$ Hz), 124.7 (d, $J_{C-P} = 8.3$ Hz).
Hz), 88.4, 36.0 (d, \( J_{C\text{-}P} = 13.4 \text{ Hz} \)), 30.9 (d, \( J_{C\text{-}P} = 5.2 \text{ Hz} \)), 25.4 (d, \( J_{C\text{-}P} = 4.1 \text{ Hz} \)), 24.3 (d, \( J_{C\text{-}P} = 5.2 \text{ Hz} \)). \(^{31}\text{P NMR: } \delta = 31.0\). HRMS Calcd for \( C_{12}H_{23}O_3P \): 246.1385; found: 246.1381.

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\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
n-C_6H_{13} & \\
\end{align*}
\]

\(^{1}\text{H NMR: } \delta = 5.76 \text{ (d, } J_{P\text{-}H} = 25.6 \text{ Hz, } 1\text{H}), 5.38 \text{ (d, } J_{P\text{-}H} = 56.1 \text{ Hz, } 1\text{H}), 2.41\text{-}2.35 \text{ (m, } 2\text{H}), 1.54\text{-}1.49 \text{ (m, } 2\text{H}), 1.35\text{-}1.27 \text{ (m, } 6\text{H}), 1.26 \text{ (s, } 12\text{H}), 1.13 \text{ (s, } 12\text{H}), 0.88 \text{ (t, } J_{H\text{-}H} = 7.4 \text{ Hz, } 3\text{H}). \(^{13}\text{C NMR: } \delta = 151.6 \text{ (d, } J_{C\text{-}P} = 204.6 \text{ Hz}), 121.0 \text{ (d, } J_{C\text{-}P} = 7.2 \text{ Hz}), 78.7, 33.3 \text{ (d, } J_{C\text{-}P} = 11.4 \text{ Hz}), 32.2, 29.6, 28.6 \text{ (d, } J_{C\text{-}P} = 8.3 \text{ Hz}), 24.9 \text{ (d, } J_{C\text{-}P} = 4.1 \text{ Hz}), 24.2 \text{ (d, } J_{C\text{-}P} = 6.2 \text{ Hz}), 23.1 \text{ (d, } J_{C\text{-}P} = 1.0 \text{ Hz}), 14.5. \(^{31}\text{P NMR: } \delta = -31.6.\) This compound is known: L.-B. Han, Y. Ono, Q. Xu, S. Shimada, *Bull. Chem. Soc. Jpn.* in press.

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\begin{align*}
n-C_6H_{13} & \quad \text{SPh} \\
n-C_6H_{13} & \\
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\[
\begin{align*}
n-C_6H_{13} \quad & \quad n-C_6H_{13} \\
n-C_6H_{13} \quad & \quad n-C_6H_{13} \\
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\begin{align*}
t-Bu \quad & \quad t-Bu \\
t-Bu \quad & \quad t-Bu \\
\end{align*}
\]

Preparation of Complex 4b. The mixture of 3 (64.6 mg, 0.2 mmol) and dppe (80.0 mg, 0.2 mmol) in 4 mL CH₂Cl₂ was stirred at room temperature under nitrogen till 3 totally dissolved. Standing of the solution filtrate after adding drops of hexane at room temperature gave a white solid, which was collected and washed with CH₂Cl₂ and hexane. Dec. 168 °C. ¹H NMR (CD₂Cl₂): δ 7.99-7.58 (m, 9H), 7.56-6.99 (m, 17H), 6.87-6.84 (m, 1H), 6.61-6.54 (m, 2H), 2.62-2.37 (m, 2H), 2.34-2.21 (m, 1H), 2.16-2.02 (m, 1H). ³¹P NMR (CD₂Cl₂): δ 61.3 (dd, Jₚ₋ₚ = 29.4 Hz, Jₚ₋ₚ = 7.4 Hz, 1P), 47.2 (dd, Jₚ₋ₚ = 33.1 Hz, Jₚ₋ₚ = 7.4 Hz, 1P), 38.2 (dd, Jₚ₋ₚ = 33.1 Hz, Jₚ₋ₚ = 29.4 Hz, 1P).

Preparation of Complex 5a. The mixture of 3 (0.162 g, 0.5 mmol), dmpe (84 µL, 0.5 mmol) and Ph₂P(O)H (0.101 g, 0.5 mmol) in 5 mL CH₂Cl₂ was stirred at room temperature under nitrogen till 3 totally dissolved. Standing of the solution filtrate after adding drops of hexane at room temperature gave colorless crystals, which were collected and washed with CH₂Cl₂ and hexane. ³¹P NMR (CD₂Cl₂): δ 71.9 (ddd, Jₚ₋ₚ = 447.0 Hz, Jₚ₋ₚ = 34.4 Hz, Jₚ₋ₚ = 7.6 Hz, 1P), 32.1 (ddd, Jₚ₋ₚ = 447.0 Hz, Jₚ₋ₚ = 26.8 Hz, 1P), 23.5 (dd, Jₚ₋ₚ = 9.6 Hz, Jₚ₋ₚ = 11.5 Hz, 1P), 20.3 (ddd, Jₚ₋ₚ = 36.3 Hz, Jₚ₋ₚ = 26.7 Hz, Jₚ₋ₚ = 11.5 Hz, 1P).
Monitoring $^{31}$P NMR Spectra of 4b-Catalyzed Addition of Ph$_2$P(O)H to 1-Octyne. 4b (11 mg, 0.015 mmol, 15 mol%; Chart 1) was added to a mixture of Ph$_2$P(O)H (20.2 mg, 0.1 mmol) and 1-octyne (16 µL, 0.11 mmol) dissolved in CD$_2$Cl$_2$ (0.5 mL) in a NMR tube. After 2 h, $^{31}$P NMR showed the complete conversion of 4b to 5b (ca. 15 mol%; Chart 2). The solvent was changed to d$_8$-toluene, and the tube was heated at 70 °C overnight (19 h). $^{31}$P NMR showed that all starting Ph$_2$P(O)H and 5b were completely disappeared, and 99% yield of the adducts (branched/linear ratio = 99/1) together with 4b (ca. 15 mol%) were obtained (Chart 3).
Chart 2. After 2 h at room temperature of a mixture of 4b with Ph₂P(O)H and 1-octyne: 4b totally converted to 5b (ca. 15 mol%); trace adduct (29.97 ppm) was also observed.
Chart 3. Heating at 70 °C for 19 h: Ph₂P(O)H and 5b completely disappeared to give the adducts (branched/linear 99/1), while 4b was regenerated (cat. 15 mol%).
$^1$H NMR and $^{13}$C NMR Spectra of New Compounds

$^1$H NMR

$^{13}$C NMR
$t\text{-Bu}P(O)\text{Me}_2$

**$^1$H NMR**

**$^{13}$C NMR**
$t$-Bu P(OMe)$_2$ O

$^1$H NMR

$^1$C NMR

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$^{1}H$ NMR

$^{13}C$ NMR
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$^1$H NMR

$^{13}$C NMR
ESI-TOF MS of 3 in CH$_2$Cl$_2$
ESI-TOF MS of 3 (with 1% DMSO) in CHCl₃