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## Circumambulatory Rearrangement with Characteristics of a 2:1 Covalent Molecular Bevel Gear

Rosa E. Buló,<sup>†,‡</sup> Florian Allaart,<sup>‡</sup> Andreas W. Ehlers,<sup>‡</sup> Franciscus J. J. de Kanter,<sup>‡</sup> Marius Schakel,<sup>‡</sup> Martin Lutz,<sup>§</sup> Anthony L. Spek,<sup>‡</sup> and Koop Lammertsma<sup>\*‡</sup>

Contribution from the Department of Chemistry, Vrije Universiteit, FEW, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands, Department of Chemistry and Applied Biosciences, ETH Zürich, USI-Campus, Via Giuseppe Buffi 13, 6900 Lugano, Switzerland, and Bijvoet Center for Biomolecular Research, Crystal and Structural Chemistry, Utrecht University, Padualaan 8, NL-3584 CH, Utrecht, The Netherlands

Received May 1, 2006; E-mail: K.Lammertsma@few.vu.nl

**Abstract:** *anti*-W(CO)<sub>5</sub>-complexed 9-methyl-9-phosphabicyclo[6.1.0]nonatriene represents a covalently interlocked molecular bevel gear. Correlated movement of the phosphorus atom and the eight-membered ring by way of a “walk” rearrangement makes gear slippage impossible. The gearing motion is transferred to the four-toothed W(CO)<sub>5</sub> propeller connected to the rotating phosphorus atom, enabling a gearing ratio of 2:1 according to B3LYP and Car–Parrinello Molecular Dynamics calculations. Methyl substitution of the eight-membered ring tempers the gearing process, with the PMeW(CO)<sub>5</sub> entity passing the substituted carbon atom only at temperatures above 50 °C

### Introduction

Captivating molecular devices capable of mechanical work exist for molecular bearings,<sup>1</sup> brakes,<sup>2</sup> gears,<sup>3</sup> ratchets,<sup>4</sup> switches,<sup>5</sup> and turnstiles.<sup>6</sup> Most are held together by weak interactions such as hydrogen bonds or van der Waals and electrostatic forces. Heat, mechanical force, photochemical activation, or proton or electron transfer drive their motion. Friction is a common phenomenon in the molecular machinery. Exemplary are the propeller-like motions<sup>7</sup> of triptycenes<sup>3b</sup> and biphenanthrylidene-derived compounds.<sup>8</sup> Gear slippage occurs when teeth bend, such as for aromatics linked to carbon nanotubes.<sup>9</sup>

Molecular machines and particularly gears with covalently interlocking parts are very rare. An exception is the bishapto circumambulation mimicking the motion of a bevel gear.<sup>10</sup> In such a rearrangement, known as “walk”, a cyclopropane ring

moves over the perimeter of the other ring in a series of [1,*n*]-sigmatropic shifts. The larger ring and the migrating carbon represent the two gearing wheels that are covalently linked by two C–C bonds. To constitute a bevel gear, the substituents on the migrating carbon may not interchange, necessitating inversion at the carbon center at each step.

Such a motion complies with the Woodward–Hoffmann (WH) rules for pericyclic reactions and mandates the participation of 4*n* electrons, such as in the thermal 4*e*-walk of a bicyclo[3.1.0]hexadienyl cation<sup>11</sup> and the 8*e*-walk of a bicyclo[6.1.0]nona-2,4,6-triene.<sup>12</sup> Gear slippage cannot occur in these systems because the two “wheels” are covalently interlocked.

A phosphorus group, having longer and weaker P–C bonds connecting it to the hydrocarbon ring, should migrate more easily. This is the case for the *anti*-9-phenyl derivative of 9-phosphabicyclo[6.1.0]nona-2,4,6-triene (*a*-**1**), where P–Ph “walks” over the hydrocarbon frame below 50 °C (Figure 1).<sup>13</sup> For *functionality* of the gear, the motion of the phosphorus migrating over the eight-toothed hydrocarbon ring must be transferred, and this can be accomplished by attaching an axle to the smaller gear wheel.<sup>14</sup> Because of its convenient accessibility, we decided to use the W(CO)<sub>5</sub> transition metal group. Its preferred orientation in the transition state is rotated by 45° relative to the global minimum, resulting in a 90° rotation of

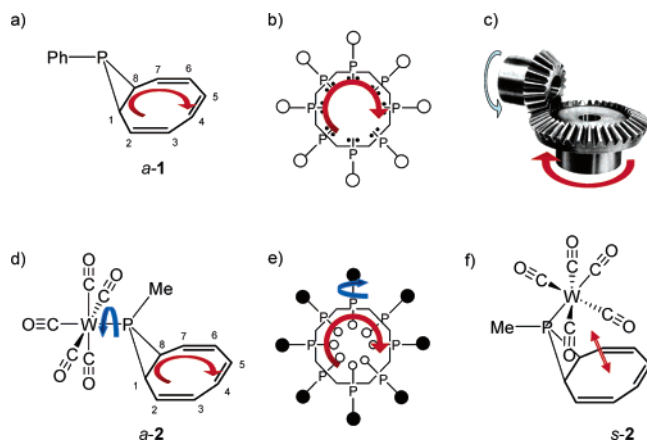
<sup>†</sup> ETH Zürich.

<sup>‡</sup> Vrije Universiteit.

<sup>§</sup> Utrecht University.

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- (14) We considered a phenyl group, but its correlated rotation is frustrated by an enthalpic preference for the same perpendicular orientation of the phenyl group in both the phosphirane and the transition state of respectively 0.3 and 2.5 kcal/mol at B3LYP/6-31G\*.



**Figure 1.** (a) *anti*-9-Phenyl-9-phosphabicyclo[6.1.0]nona-2,4,6-triene (*a-1*). (b) A representation of its successive [1,7]-sigmatropic shifts viewed down on the carbon ring with the phenyl group shown as a circle. (c) A macroscopic bevel gear. (d) *anti*-W(CO)<sub>5</sub>-9-phenyl-9-phosphabicyclo[6.1.0]-2,4,6-triene (*a-2*). (e) Its [1,7]- $\sigma$  shifts viewed on the carbon ring, with the W(CO)<sub>5</sub> shown as a filled circle and the methyl group as a small circle. (f) *s-2*, where the [1,7]-shift is prevented by steric interaction of the CO ligands with the carbon ring.

the axial carbonyl groups during each step that the phosphirane “walks” over the hydrocarbon ring.<sup>15</sup> A complication might be the small barrier for rotating the W(CO)<sub>5</sub> group from its preferred conformation, so that slippage of the axle might occur readily during the “walk”. Such slippage may be reduced with an asymmetric transition metal group to enhance the P=M double bond character. In the present study, we consider the merits of the W(CO)<sub>5</sub>-complexed system as a proof of principle.

## Results

Reaction of in-situ-generated phosphinidene [MePW(CO)<sub>5</sub>]<sup>16</sup> with cyclooctatetraene afforded *syn*- and *anti*-W(CO)<sub>5</sub>-complexed 9-methyl-9-phosphabicyclo[6.1.0]nona-2,4,6-triene (*s*- and *a-2*), which were fully characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectroscopy and by an X-ray crystal structure determination.<sup>17</sup> We focus on the *anti* isomer *a-2*, which has the W(CO)<sub>5</sub> group oriented away from the hydrocarbon ring. Its <sup>1</sup>H NMR spectrum displays no noticeable line broadening at 300 K, but selective inversion by a DPFGE excitation block of one of the ring protons ( $\delta(^1\text{H}) = 2.31$  (H1)), using a mixing time of 1 s, shows subsequent transfer of magnetization to all the other ring protons ( $\delta(^1\text{H}) = 6.01$  (H2), 6.23 (H3), 5.89 (H4)), thereby illustrating their interconversion and thus circumambulation. An activation enthalpy  $\Delta H^\ddagger$  of 17 kcal/mol was deduced for this dynamic process by <sup>1</sup>H NMR line shape analysis over a temperature range of 300–330 K. Without the transition metal group, the rearrangement barrier is slightly higher, that is, 20 kcal/mol for *a-1*.<sup>13</sup> Low-temperature <sup>13</sup>C NMR spectroscopy (−83 °C, C<sub>6</sub>D<sub>8</sub>) did not reveal splitting of the *cis*-CO resonance ( $\delta_{\text{av}} = 195.6$ ), indicating that in solution

exchange, i.e., rotation of the W(CO)<sub>5</sub>, is fast on the NMR time scale ( $\Delta E \leq 10$  kcal/mol).<sup>18</sup>

The relationship of the rotation of the eight-membered ring with that of the transition metal group, the axle, was analyzed with B3LYP/6-31G\* (and at other levels of theory, see Methods) for a model containing a H-substituted phosphorus and with tungsten replaced by chromium. The [1,7]-shift for this model is a normal pericyclic process with no diradical character in the transition state where the phosphorus atom inverts on the rim of a flat hydrocarbon ring (Figure 2). The calculated barrier of 13.4 kcal/mol is slightly lower than the experimentally observed one. An intrinsic reaction coordinate (IRC) analysis starting at the transition state for the “walk” reveals a correlated rotation with the Cr(CO)<sub>5</sub> group that can be followed for an 11° (out of 45°) rotation ( $\omega$ ) of the transition metal group, after which the reaction path bifurcates due to inversion of the near-planar hydrocarbon ring.<sup>19</sup>

The coupled rotation was confirmed with a Car–Parrinello Molecular Dynamics run using the PBE potential,<sup>20</sup> starting from the symmetric transition state at 50 K. The P–C bond closes within the first 100 fs, diminishing the potential energy (Figure 3) and increasing the temperature to 120 K, at which it remains for the remainder of the trajectory. After 300 fs, the flat ring bends into a more stable *exo* conformation. The simulation shows some fluctuation of the eight-membered ring until after 500 fs, when the Cr(CO)<sub>5</sub> group has completed the 45° rotation ( $\omega$ ) in the expected direction, confirming the correlation between the two motions. Repeating the procedure at 300 K showed the same correlation between the two movements. Within the run time, no free rotation of the metal group is observed. Simulation of the transition region renders a barrier of 15 kcal/mol at 120 K that is in excellent agreement with 13.5 kcal/mol obtained at B3LYP.

Whereas the rotation of W(CO)<sub>5</sub> is coupled to the “walk” of the phosphorus center, that of, e.g., a phenyl group is not, despite the anticipated resonance stabilization. P–C bond rotation is not evident from the quantum dynamics calculations that keep this group in a perpendicular orientation.<sup>14</sup>

Circumambulation of the parent *a-2* occurs within a limited temperature domain. Above about 100 °C, a competitive conversion sets in, giving *anti*-9-phosphabicyclo[4.2.1]nona-1,3,6-triene (*a-3*) as the main product in 22 h (Scheme 1). Evidently, the bevel gear flexes at higher temperatures, and when the angle between its components becomes too small, the teeth opposite to the gearing point connect and lock the entire system permanently. *a-3* is the thermodynamic sink, as it is 16.9 kcal/mol more stable than *a-2* at B3LYP/6-31G\*. The product was fully characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectroscopy and by an X-ray crystal structure determination.<sup>17</sup> The <sup>31</sup>P chemical shift of −56.8 ppm is very shielded for a phospholene, but the P–W coupling of 236.7 Hz is typical for an *anti* isomer. The conversion suggests a Woodward–Hoffmann-forbidden [1,3]-

(15) B3LYP/6-31G\* calculations give a preference of 0.6 kcal/mol for an eclipsed W(CO)<sub>5</sub> orientation in the three-membered ring geometry, and 0.7 kcal/mol for the staggered orientation in the transition state.

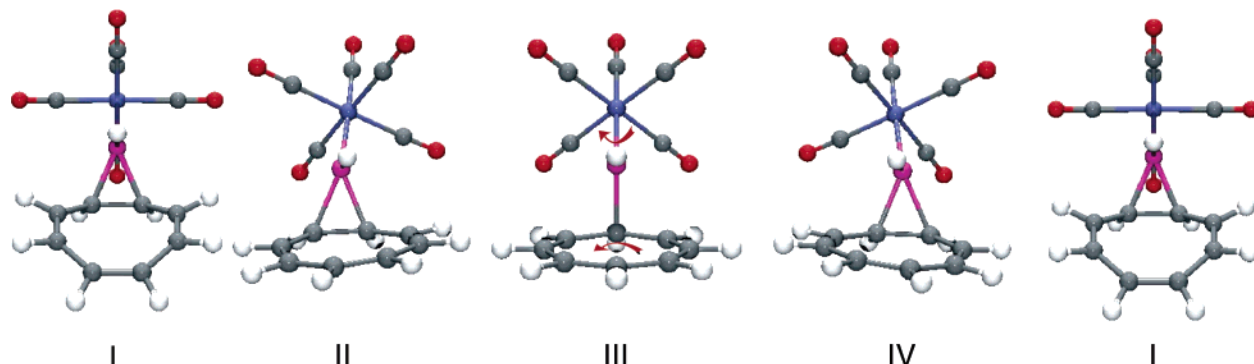
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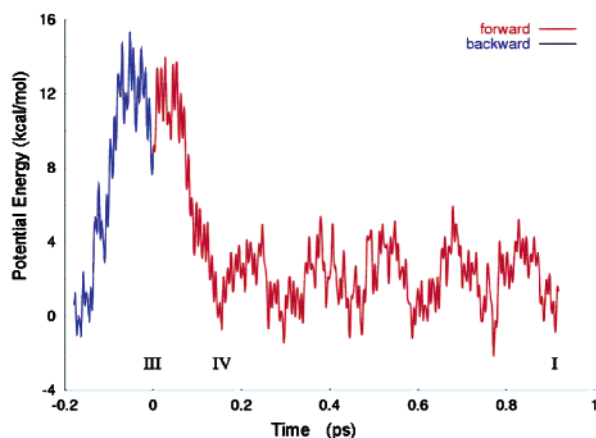
(18) (a) The observed line-broadening for the *cis*-CO resonance could not be distinguished from the low-temperature solvent effect. (b) For NMR studies on M–P bond rotations see, for example: DiMeglio, C. M.; Ahmed, K. J.; Luck, L. A.; Weltin, E. E.; Rheingold, A. L.; Bushweller, C. H. *J. Phys. Chem.* **1992**, *96*, 8765–8777. Mastroianni, P.; Nobile, C. F.; Latronico, M.; Gallo, V.; Englert, U.; Fanizzi, F.; Sciacovelli, O. *Inorg. Chem.* **2005**, *44*, 9097–9104.

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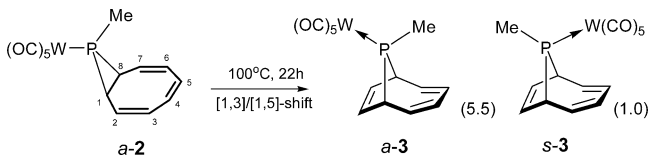


**Figure 2.** Selected B3LYP/6-31G\* structures and energies for the gearing process. **I** is the ground-state minimum ( $\omega = 0^\circ$ ), **III** the transition structure for the [1,7]-sigmatropic shift ( $\omega = 45^\circ$ ), and **II** ( $\omega = 60^\circ$ ) and **IV** ( $\omega = 30^\circ$ ) structures in between on the reaction coordinate.



**Figure 3.** Car-Parrinello Molecular Dynamics trajectory starting from transition structure **III** via **IV** to minimum energy structure **I** at 50 K and upon heating to 120 K.

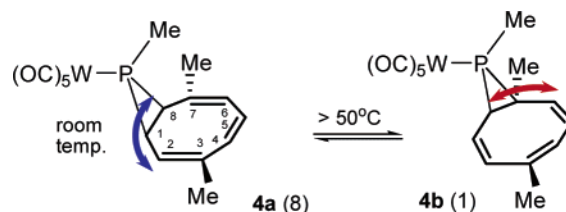
#### Scheme 1. Symmetry-Forbidden Rearrangement of *s*-2



shift with retention (or a [1,5]-shift with inversion) at the phosphorus center. B3LYP/6-31G\* estimates for the model compound two diradical transition states with barriers of 21.3 and 19.6 kcal/mol. The preference for the symmetry-forbidden product (*a*-3) differs from the concerted rearrangement of uncomplexed *a*-1<sup>13</sup> but relates to that of the hydrocarbon analogue bicyclo[6.1.0]nona-2,4,6-triene, for which the rearranged product distribution was attributed to *dynamic matching*.<sup>19</sup>

No gearing is evident in the NMR spectra of *s*-2, which concurs with the B3LYP/6-31G\* calculations on the model that give a 4.8 kcal/mol higher “walk” barrier than for the *anti* isomer. Steric repulsion between the W(CO)<sub>5</sub> entity and the carbon ring causes the energy difference. In other words, the bulky axle of the small gear hangs over the carbon gear to interfere with its rotation. Competing [1,5]-shifts occur at 100 °C, forming both the *syn* and *anti* isomers of W-MPNT in a ratio of 1.3:1.0, respectively. The mechanism likely involves the same two diradical transition states as that of the more stable *a*-2 isomer. Their barriers are similar in magnitude to that for the “walk” and thereby effectively eliminate observation of the latter.

#### Scheme 2. The “Walk”-Process of *a*-4<sup>a</sup>



<sup>a</sup> The blue arrow indicates the process at room temperature and the red arrow the additional rearrangement above 50 °C.

The sensitivity of the gearing motion becomes evident on introducing methyl groups at the carbon ring. Reacting [MePW(CO)<sub>5</sub>] with 1,5-dimethylcyclooctatetraene resulted in an 8:1 ratio of *anti* products *a*-4a and *a*-4b (Scheme 2) that equilibrate at room temperature with a 1.25 kcal/mol preference, as determined by <sup>1</sup>H NMR, for isomer *a*-4a, which has no bridgehead methyl group. Rotation past this substituent requires a temperature above 50 °C. Evidently, the methyl groups retard the “walk”.

The circumambulatory rearrangement with characteristics of a covalent molecular bevel gear, which we present here as proof of principle, illustrates molecular machinery that is likely to have more cases embedded in covalent chemistry. It complements the heavily researched noncovalent molecular bevel gears. While fully supported by theoretical DFT and MD calculations in the picosecond range, the presented system is not ideal because in solution it suffers from slippage of the P=W axle, being the transition metal group. Under experimental conditions, this slippage obscures synchronization of the two motions. For better transfer of the circumambulatory motion, the transition metal group must be anchored more tightly by diminishing the independent M=P double bond rotation, for example, by reducing the number of transition metal ligands. Currently, we are attempting to improve this mechanical aspect using new synthetic strategies.<sup>21</sup>

#### Experimental Section

**Methods.** All geometry optimizations, zero-point energies (ZPEs), and IRC calculations were computed with the Gaussian98 program package,<sup>22</sup> using the hybrid (U)B3LYP exchange-correlation potentials

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and the LANL2DZ basis set for chromium and 6-31G\* for all other elements. Minima were confirmed to have only positive force constants and transition structures (TS) to have only one imaginary value. To extract the open-shell singlet energies from the mixture of singlet and triplet states that are obtained on calculating open-shell singlet energies with spin UB3LYP, we use a spin projection method introduced by Houk and co-workers.<sup>23</sup> Similar energy differences between the stationary points<sup>15</sup> were obtained with BP86/TZP<sup>24</sup> and with B3PW91/63111+G\*\* + LACVP3P. The Car–Parrinello Molecular Dynamics simulations<sup>25</sup> were performed using the CPMD package.<sup>26</sup> We employed the PBE exchange-correlation functional.<sup>27</sup> The simulation system is a periodically repeated cubic box containing one molecule. The size of the box is 25.0 × 25.0 × 25.0 Å<sup>3</sup>. A plain wave basis set with an energy cutoff of 40 Ry was employed. The interactions of the core and valence electrons were described with norm-conserving pseudo-potentials for phosphorus (revPBE), carbon (PBE), and hydrogen (PBE)<sup>28</sup> and ultrasoft ones for chromium (PW) and oxygen (PBE). All results were obtained applying a spin-unrestricted formalism. In the MD simulation, we used a 0.120 fs time step and 800 au for the electron mass.

**Synthesis of *a*- and *s*-2.** Phosphinidene MePW(CO)<sub>5</sub> was generated *in situ* from 0.59 g (1 mmol) of 2,3-dimethyl-5,6-dimethyldicarboxylate-7-pentacarbonylungsten-7-methyl-7-phoshanorbornadiene (**5**)<sup>16</sup> in the presence of 0.56 mL (5 mmol) of cyclooctatetraene and 10% CuCl, and the mixture was stirred at 60 °C under nitrogen for 11 h in 20 mL of dry toluene. The reaction was monitored by <sup>31</sup>P NMR for disappearance of the precursor (202 ppm). After solvent evaporation, the reaction mixture was chromatographed on activated silica with a pentane/toluene (4:1) mixture as eluent to give two fractions. *a*-2 was obtained from the first fraction as white needles (32%) after crystallization from pentane. After concentration and crystallization from pentane, the second fraction yielded *s*-2 as yellow needles (13%).

NMR spectra were recorded on Bruker Avance 250 and MSL 400 spectrometers (<sup>31</sup>P, 85% H<sub>3</sub>PO<sub>4</sub>; <sup>1</sup>H and <sup>13</sup>C, TMS). IR spectra were recorded on a Mattson-6030 Galaxy FT-IR spectrophotometer, and high-resolution mass spectra (HR-MS) were recorded on a Finnigan Mat 900 spectrometer.

*a*-2 was obtained from the first fraction as white needles (32%) after crystallization from pentane: <sup>31</sup>P NMR (250 MHz, CDCl<sub>3</sub>) δ = −150.0 (<sup>1</sup>J(P,W) = 254 Hz); <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ = 197.8 (d, <sup>2</sup>J(C,P) = 30.3 Hz, *trans*-CO), 195.6 (d, <sup>2</sup>J(C,P) = 8.3 Hz, *cis*-CO), 130.7 (d, <sup>3</sup>J(C,P) = 7.8 Hz, 2CH=, C3), 124.4 (s, 2CH=, C4), 122.5 (s, 2CH=, C2), 28.3 (d, <sup>1</sup>J(C,P) = 9.6 Hz, 2CHP, C1), 8.8 (d, <sup>1</sup>J(C,P) = 15.4 Hz, Me); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 6.23 (d, <sup>3</sup>J(H,H) = 11.7 Hz, 2CH=, H3), 6.01 (dd, <sup>3</sup>J(H,P) = 9.1 Hz, <sup>3</sup>J(H,H) = 11.7 Hz, 2CH=, H2), 5.89 (s, 2CH=, H4), 2.31 (s, 2CHP, H1), 1.18 (d, <sup>2</sup>J(H,P) = 6.5 Hz, Me); HRMS calcd for C<sub>14</sub>H<sub>11</sub>WPO<sub>5</sub> 473.98541, found 473.98346 (δ = 2.0 × 10<sup>−3</sup>).

*s*-2: <sup>31</sup>P NMR (250 MHz, CDCl<sub>3</sub>) δ = −150.1 (<sup>1</sup>J(P,W) = 265 Hz); <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ = 197.4 (d, <sup>2</sup>J(C,P) = 30.2 Hz, *trans*-CO), 195.2 (d, <sup>2</sup>J(C,P) = 8.1 Hz, *cis*-CO), 130.6 (d, <sup>3</sup>J(C,P) = 13.0 Hz, 2CH=, C3), 124.9 (d, <sup>2</sup>J(C,P) = 1.2 Hz, 2CH=, C2), 124.8 (d, <sup>4</sup>J(C,P) = 0.8 Hz, 2CH=, C4), 29.9 (d, <sup>1</sup>J(C,P) = 9.4 Hz, 2CHP, C1), 18.6 (d, <sup>1</sup>J(C,P) = 13.9 Hz, Me); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 6.18 (d, <sup>3</sup>J(H,H) = 11.6 Hz, 2CH=, H3), 6.07 (dd, <sup>3</sup>J(H,P) = 12.5 Hz, <sup>3</sup>J(H,H) = 11.6 Hz, 2CH=, H2), 5.90 (s, 2CH=, H4), 2.45 (d, <sup>2</sup>J(H,P) = 9.9 Hz, 2CHP, H1), 1.55 (d, <sup>2</sup>J(H,P) = 7.0 Hz, Me); HRMS calcd for C<sub>14</sub>H<sub>11</sub>WPO<sub>5</sub> 473.98541, found 473.98437 (δ = 1.0 × 10<sup>−3</sup>).

**Synthesis of *a*-4.** A 0.335 g (0.48 mmol) sample of **5**,<sup>16</sup> 0.323 g (2.45 mmol) of 1,4-dimethylcyclooctatetraene,<sup>29</sup> and 10% CuCl were stirred at 55 °C under nitrogen for 9 h in 20 mL of dry toluene. The reaction was monitored by <sup>31</sup>P NMR for disappearance of the precursor (202 ppm). The solvent was evaporated, and the reaction mixture was chromatographed on activated silica with a pentane/toluene (9:1) mixture as eluent. Crystallization from hexane afforded a mixture of the two interconverting isomers, *a*-4a and *a*-4b (Scheme 1), in an 8:1 ratio, as small, colorless needles (10%). The NMR data were obtained from the mixture.

*a*-4a: <sup>31</sup>P NMR (250 MHz, toluene-*d*<sub>8</sub>) δ = −170.2 (<sup>1</sup>J(P,W) = 254.0 Hz); <sup>13</sup>C NMR (400 MHz, toluene-*d*<sub>8</sub>) δ = 139.3 (d, <sup>3</sup>J(C,P) = 8.0 Hz, CMe3), 131.8 (d, <sup>2</sup>J(C,P) = 5.0 Hz, CMe7), 127.7 (d, <sup>3</sup>J(C,P) = 6.3 Hz, C6), 127.2 (s, C5), 124.6 (s, C5), 123.1 (d, <sup>2</sup>J(C,P) = 4.3 Hz, C2), 34.2 (d, <sup>1</sup>J(C,P) = 10.1 Hz, C8), 27.9 (d, <sup>1</sup>J(C,P) = 7.9 Hz, C1), 25.4 (d, <sup>3</sup>J(C,P) = 4.2 Hz, Me7), 23.9 (s, Me3), 8.9 (d, <sup>1</sup>J(C,P) = 14.6 Hz, MeP); <sup>1</sup>H NMR (400 MHz, toluene-*d*<sub>8</sub>) δ = 5.64 (m, CH=, H6), 5.53 (m, <sup>3</sup>J(H,H) = 13.2 Hz, CH=, H5), 5.45 (d, <sup>3</sup>J(H,H) = 13.2 Hz, CH=, H4), 5.17 (d, <sup>3</sup>J(H,P) = 10.5 Hz, CH=, H2), 2.03 (d, <sup>3</sup>J(H,H) = 9.7 Hz, CHP, H1), 1.85 (d, <sup>3</sup>J(H,H) = 9.7 Hz, CHP, H8), 1.64 (s, Me7), 1.57 (s, Me3), 0.82 (d, <sup>2</sup>J(P,H) = 6.6 Hz, MeP); IR (KBr) ν (CO) 2072 (w), 1987 (w), 1929 (s).

*a*-4b: <sup>31</sup>P NMR (250 MHz, CDCl<sub>3</sub>) δ = −151.4 (<sup>1</sup>J(P,W) = 254.0 Hz); <sup>13</sup>C NMR (400 MHz, toluene-*d*<sub>8</sub>) δ = 135.5 (CMe4), 134.0 (C3), 127.2 (C7), 124.6 (C6), 121.7 (C2), 121.0 (C5), 33.8 (C1), 31.4 (C8), 25.4 (d, <sup>2</sup>J(C,P) = 5.1 Hz, Me8), 23.2 (s, Me4), 10.8 (d, <sup>1</sup>J(C,P) = 15.1 Hz, MeP); <sup>1</sup>H NMR (400 MHz, toluene-*d*<sub>8</sub>) δ = 5.73 (d, <sup>3</sup>J(H,H) = 11.3 Hz, CH=, H3), 5.69 (dd, <sup>3</sup>J(H,H) = 4.0 Hz, <sup>3</sup>J(H,H) = 12.1 Hz, CH=, C6), 5.36 (d, <sup>3</sup>J(H,H) = 4.0 Hz, CH=, C5), 5.29 (dd, <sup>3</sup>J(H,P) = 10.8 Hz, <sup>3</sup>J(H,H) = 12.1 Hz, CH=, H7), 5.27 (dd, <sup>3</sup>J(H,P) = 11.2 Hz, <sup>3</sup>J(H,H) = 11.3 Hz, CH=, H2), 1.79 (s, HCP, H1), 1.64 (s, Me4), 1.12 (d, <sup>3</sup>J(H,P) = 18.9 Hz, Me8), 0.94 (d, <sup>2</sup>J(H,P) = 6.6 Hz, MeP).

**Synthesis of *a*-3.** A 39 mg sample of *a*-2 was dissolved in 2 mL of toluene. The conversion of *a*-2 to *a*-3 was monitored by <sup>31</sup>P NMR spectra, which were acquired at 60 min intervals. When the conversion was completed, *a*-3 was isolated on a silica column with pentane/toluene (1:9) as eluent. Crystallization from pentane yielded yellow crystals in 41% yield.

*a*-3: <sup>31</sup>P NMR (250 MHz, CDCl<sub>3</sub>) δ = −56.8 (<sup>1</sup>J(P,W) = 236.7 Hz); <sup>13</sup>C NMR (250 MHz, CDCl<sub>3</sub>) δ = 199.4 (d, <sup>2</sup>J(C,P) = 20.5 Hz, *trans*-CO), 197.3 (d, <sup>2</sup>J(C,P) = 7.2 Hz, *cis*-CO), 134.4 (d, <sup>2</sup>J(C,P) = 8.0 Hz, 2CH=, C2, C5), 127.3 (d, <sup>2</sup>J(C,P) = 2.9 Hz, 2CH=, C7, C8), 124.6 (d, <sup>3</sup>J(C,P) = 11 Hz, 2CH=, C3, C4), 46.5 (d, <sup>1</sup>J(C,P) = 22.5 Hz, 2CHP, C1, C6), 15.4 (d, <sup>1</sup>J(C,P) = 18.8 Hz, Me); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 6.13–6.03 (m, 4HC=, H2, H3, H4, H5), 5.59 (dd, <sup>3</sup>J(H,P) = 18.5 Hz, <sup>3</sup>J(H,H) = 2.6 Hz, 2HC=, H7, H8), 3.35 (ddd, <sup>2</sup>J(H,P) = 3.8 Hz, <sup>3</sup>J(H,H) = 2.8 Hz, <sup>3</sup>J(H,H) = 8.0 Hz, 2HCP, H1, H6), 1.49 (d, <sup>2</sup>J(H,P) = 6.4 Hz, Me).

**Synthesis of *s*-3.** In an NMR tube, 12 mg (0.03 mmol) of *s*-2 was dissolved in toluene and heated to 100 °C. The rearrangement was monitored by <sup>31</sup>P NMR spectroscopy. After 5 h, most of the starting material had disappeared, and a mixture of *s*-3 and *a*-3 remained in a 1.3:1 ratio.

*s*-3: <sup>31</sup>P NMR (250 MHz, toluene) δ = −14.4 (<sup>1</sup>J(P,W) = 241.8 Hz); <sup>13</sup>C NMR (250 MHz, CDCl<sub>3</sub>) δ = 199.7 (d, <sup>2</sup>J(C,P) = 20.4 Hz, *trans*-CO), 197.2 (d, <sup>2</sup>J(C,P) = 7.2 Hz, *cis*-CO), 133.3 (d, <sup>2</sup>J(C,P) = 4.6 Hz, 2CH=, C2, C5), 128.5 (d, <sup>2</sup>J(C,P) = 4.5 Hz, 2CH=, C7, C8), 122.8 (s, 2CH=, C3, C4), 47.5 (d, <sup>1</sup>J(C,P) = 19.5 Hz, 2CHP, C1, C6), 16.9 (d, <sup>1</sup>J(C,P) = 23.2 Hz, Me); <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ = 6.26–6.0 (m, 4HC=, H2, H3, H4, H5), 5.6 (dd, <sup>3</sup>J(H,P) = 14.1 Hz, <sup>3</sup>J(H,H) = 2.0 Hz, 2HC=, H7, H8), 3.2 (dd, <sup>3</sup>J(H,H) = 8.3 Hz, <sup>3</sup>J(H,H) = 2.0 Hz, 2HCP, C1, C6), 1.64 (d, <sup>2</sup>J(H,P) = 5.7 Hz, Me).

**Thermodynamic Measurements.** In an NMR tube, a small amount of the *a*-4a/*a*-4b mixture was dissolved in toluene. The equilibrium

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was monitored with  $^{31}\text{P}$  NMR spectra. After careful phasing of the NMR signals, their areas were accurately integrated. The equilibrium was studied at five temperatures in the range from  $-20$  to  $50$  °C. The Eyring plot ( $\ln(K/T)$  vs  $1/T$ ) shows an enthalpy difference of  $\Delta H = 1.25$  kcal/mol; errors are 95% confidence regions and correspond to two standard deviations.

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**Supporting Information Available:** Complete ref 22; details about the crystal structure determinations (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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