

## C–C Bond Insertion of a Complexed Phosphinidene into 1,6-Methano[10]annulene

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**Abstract:** Reaction of electrophilic phosphinidene complex [MePW(CO)<sub>5</sub>] with 1,6-methano-[10]annulene results in the sole formation of the isomeric C–C insertion products **6c** (main) and **6d** (minor). The single-crystal X-ray structure of the complexed 1,7-methano-3-phospha[11]annulene (**6c**) shows a *syn*-W(CO)<sub>5</sub> group at the *exo* bent phosphorus. The structure displays C–

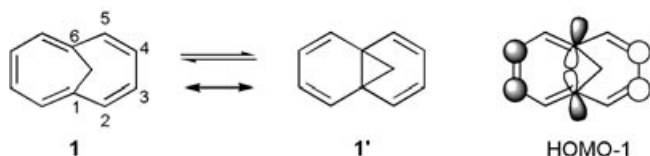
C bond alternation without bonding between the bridgehead carbon atoms. Density functional theory calculations indicate **6c** to result from a concerted

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disrotatory ring opening of an undetected tricyclic *exo-syn* phosphirane intermediate. The *endo-anti* phosphirane cannot undergo ring expansion, due to the high barrier that is associated with an intramolecular *antara-antara* retro Diels–Alder reaction. The stabilizing effect of transition-metal coordination is discussed.

### Introduction

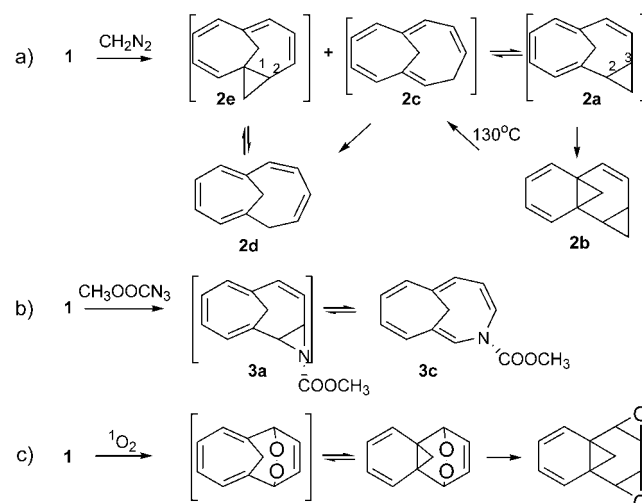
The intriguing properties of the 10π-aromatic compound 1,6-methano[10]annulene (**1**) have attracted considerable attention over the past decades,<sup>[1]</sup> particularly the alleged valence tautomerism between the delocalized aromatic (**1**) and localized bisnorcaradiene (**1'**) forms.<sup>[2]</sup> There are two possi-



bilities. Either the two forms are in equilibrium or only a single structure exists. The latter may have nonclassical properties with a C1–C6 bond length intermediate to those of **1** and **1'**. There are X-ray structures of both localized and delocalized forms, the nature of which depends on the substituents at the methano bridge.<sup>[3]</sup> The most recent theoretic-

cal study (B3LYP and MP2) on the parent molecule gives a single energy minimum with a structure that has a long C1–C6 distance (2.23 Å), which suggests a delocalized form. It has a HOMO–1 that indicates homoaromatic stabilization.<sup>[4]</sup>

The aromatic↔olefinic character of **1** has stimulated many reactivity studies, including those with reactive intermediates like carbenes, nitrenes, and singlet oxygen with varying results. Singlet methylene gives **2d** (major) and **2b** (minor) as products (Scheme 1a).<sup>[5]</sup> The formation of **2d** was thought to occur by <sup>1</sup>CH<sub>2</sub> addition to the C1–C2 bond (**2e**),



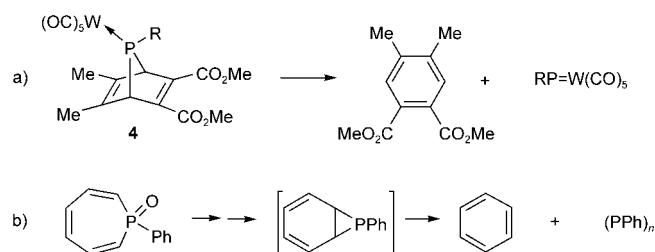
Scheme 1. Reaction of a) a carbene, b) a nitrene, and c) <sup>1</sup>O<sub>2</sub> with **1**.

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although addition to the C2–C3 bond (**2a**⇌**2c**)<sup>[6]</sup> followed by a 1,9-H shift could be an alternative. Direct addition at C2–C3 gives the minor product, which rearranges at higher temperatures to the major product presumably via **2c**. Also methoxycarbonylnitrene inserts into the C2–C3 bond (besides adding to the C1–C2 and C3–C4 bonds) to give **3c**, likely via the aziridine intermediate **3a** (Scheme 1b).<sup>[7]</sup> Addition of <sup>1</sup>O<sub>2</sub> gives a 1,4-endoperoxide, which upon further heating rearranges to a diepoxide (Scheme 1c).<sup>[8]</sup> Stimulated by the diagonal P/C-relationship<sup>[9]</sup> we were intrigued to explore the reactivity of phosphinidene complex [MePW(CO)<sub>5</sub>], which is another low-valent reactive intermediate.

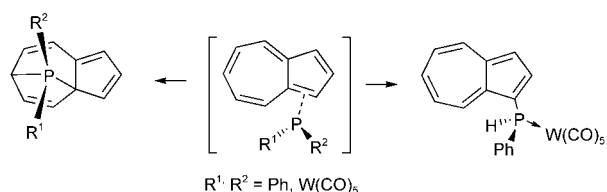
Electrophilic phosphinidene complexes, like carbenes, add to double bonds to give stable three-membered phosphiranes,<sup>[10,11]</sup> but unlike the carbenes they hardly react with aromatic compounds. In fact, transient [RPW(CO)<sub>5</sub>] is generated in aromatic solvents (toluene) by cheletropic elimination from **4** with release of a benzene derivative (Scheme 2a).



Scheme 2. Generation of a) a complexed and b) a free phosphinidene, facilitated by formation of aromatic byproducts.

Moreover, phosphepines even decompose rapidly, presumably via an intermediate phosphanorcaradiene that expels benzene (Scheme 2b), which sharply contrasts the behavior of the nitrogen and carbon homologues.<sup>[12]</sup>

Still, reactions occur with some aromatics, but the products are less common. For example, [RPW(CO)<sub>5</sub>] inserts into the C–H bond of a cyclopentadienyl ring of ferrocene,<sup>[13]</sup> and a 1,4-adduct is obtained that contains the highly strained benzene ring of [5]metacyclophane.<sup>[14]</sup> Reaction with azulene also gives C–H insertion (five-membered ring) and 1,4-addition (seven-membered ring) products via intermediate 1,2-complexes (Scheme 3).<sup>[15]</sup> Theoretical calculations suggest the aromatic stabilization of **1** to resemble that of azulene; both having comparable nucleus-independent chemical shifts (NICS) in spite of their differences in polarity.<sup>[16]</sup> In light of this duality, that is, the decomposition of



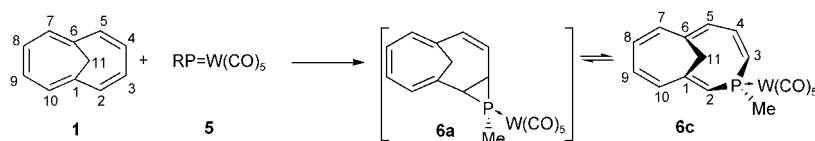
Scheme 3. Phosphinidene reaction products of azulene.

phosphepines versus the reactivity of azulene, we were intrigued to examine the behavior of **1** toward electrophilic phosphinidenes.

## Results and Discussion

Phosphanorbornadiene derivative **4** (R=Me), the precursor to phosphinidene [MePW(CO)<sub>5</sub>] (**5**), reacts with **1** at 90 °C or in the presence of a catalytic amount of CuCl at 55 °C in toluene to give *syn/anti* isomeric **6c** and **6d** as unexpected sole products in a 85:15 ratio (Scheme 4). Though these products probably result from the ring opening of intermediate **6a** (*syn/anti*), the C2C3 adduct; this tricyclic species, with cycloheptatriene and phosphirane rings, could not be detected by <sup>31</sup>P NMR monitoring of the reaction. The structure of the main product **6c** was fully characterized by the diagnostic <sup>1</sup>H and <sup>13</sup>C NMR resonances for the olefinic CH groups at C2 (H 4.93, C 114.4 ppm) and C3 (H 5.22, C 128.2 ppm), those of the CH<sub>2</sub> hydrogen atoms (3.67, 5.49 ppm), and the <sup>31</sup>P NMR chemical shift at –3.1 ppm; isomeric **6d** shows similar characteristics (see Experimental Section). The delocalized nature of the hydrocarbon frame of **6c** is further supported by the low field δ(<sup>13</sup>C) resonances of C1 (148.8 ppm) and C6 (141.3 ppm), which indicate that these atoms are not bound covalently. Variable temperature NMR experiments did not give any indication for an equilibrium between **6c** and **6a**.

An X-ray structure determination ascertained the assignment of **6c** (Figure 1). The structure shows large separations



Scheme 4. Phosphinidene reaction with 1,6-methano[10]annulene (**1**). The same structure numbering is used for both product **6c** and **1** for simplicity of the discussion.

between C1 and C6 (2.413(3) Å) and between C2 and C3 (2.979(3) Å), but also bond length alternation along the carbon periphery ( $d(\text{C}=\text{C})$  1.338(3)–1.347(3) Å,  $d(\text{C}-\text{C})$

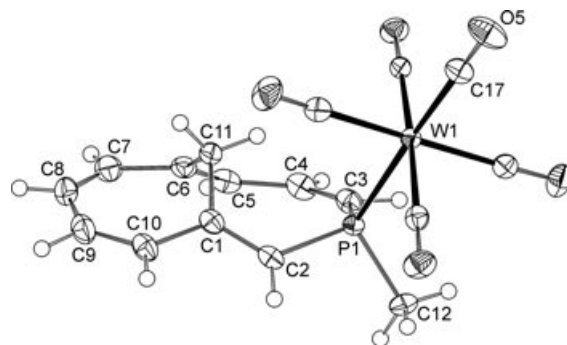


Figure 1. Displacement ellipsoid plot (50% probability level) of **6c**. Selected bond lengths [Å], and torsion angle [°]: C1–C2 1.343(3), C2–P1 1.805(2), P1–C3 1.823(2), C3–C4 1.347(3), C4–C5 1.461(3), C5–C6 1.338(3), C6–C7 1.466(3), C7–C8 1.342(4), C8–C9 1.455(4), C9–C10 1.344(3), C10–C1 1.458(3), C2–C3 2.979(3), C1–C6 2.413(3); C11–C1–C2–P1 4.8(3).

1.455(4)–1.466(3) Å). The Julg parameter<sup>[17]</sup> of 0.61 supports the conjugated olefinic nature of the frame of ten carbon atoms. Interestingly, the [MePW(CO)<sub>5</sub>] group is bent upwards with its transition-metal group directed toward the methylene bridge (*exo*), which is seemingly the more congested position.

The unexpected PCC-ring expansion on the one hand and the very formation of **6c** and **6d** as only products with their unique structure on the other hand prompted us to investigate the reaction pathway and the structural characteristics of the main product with theoretical methods. This leads to unexpected novel mechanistic insights.

**Formation of *syn-exo* phosphirane 6a:** Density functional theory calculations show a concentration of electron density at the *exo*-side of the C2–C3 bond of **1**. Therefore, attack by the electrophilic phosphinidene [MePW(CO)<sub>5</sub>] is expected to be more facile at this side, but we will also consider attack from the less congested *endo*-side. The minor role of *endo*-addition can be inferred from the olefin cycloadditions of carbenes and phosphinidenes. Those for halocarbenes have negative enthalpy barriers, and therefore their rate dependency indicates an entropy controlled process.<sup>[18]</sup> Likewise, it has been shown that [RPW(CO)<sub>5</sub>] adds without an enthalpy barrier, yet showing a preference for the more electron-rich olefin.<sup>[15,19,20]</sup> In view of this we expect addition to the less electron-rich site, that is, the *endo*-site, to play only a minor role.

For 1,6-methano[10]annulene the calculated energy difference of 0.1 kcal mol<sup>-1</sup> between the *syn* and *anti* adducts **6a** is very modest, but in line with the observed 85:15 *syn:anti* ratio of **6c** and **6d** and similar *syn:anti*-addition ratios for simple olefins.<sup>[20c,21]</sup> The clear preference for formation of the congested *syn-exo* adduct of norbornadiene may suggest a similar behavior for **1**.<sup>[22]</sup> For reasons of simplicity and computational cost, we explore only the *syn* adduct with Me substituted for H and W for Cr. These model structures are labeled with capital letters. In the text, relative  $\Delta H_{298}$  values are used;  $\Delta E$  values are given in addition in the figures and in the Supporting Information.

Structure **6A** represents the initial 1,2-adduct (Figure 2). The presence of a phosphirane ring is evident from the short C2–C3 distance of 1.557 Å. Like parent **1**,<sup>[3e]</sup> a Bader analysis<sup>[23]</sup> of the C1–C6 electron density provides no bond critical point. Yet, the nucleus-independent chemical shifts (NICS) value of –13.1 for the cycloheptatriene ring is indicative of homoaromatic stabilization. Further tightening of the structure with closure of the C1–C6 bond (2.280→

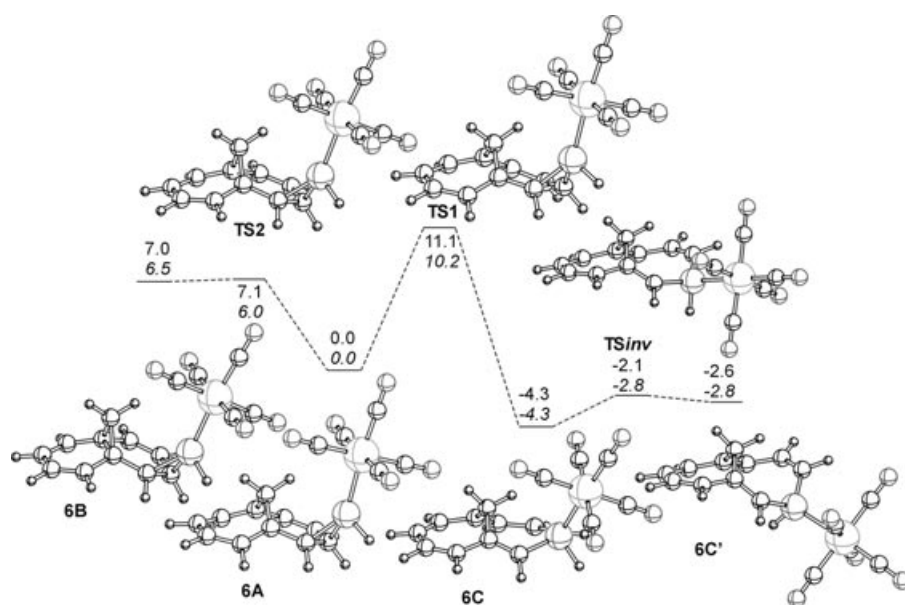


Figure 2. Relative BP/TZP energies (in kcal mol<sup>-1</sup>) for the rearrangements of **6A**.  $\Delta H_{298}$  values are in italics.

1.645 Å) results in the 6.5 kcal mol<sup>-1</sup> less stable localized structure **6B**. However, this structure converges back to **6A** without an enthalpy barrier.

**Formation of the W(CO)<sub>5</sub> complex of 3-methyl-1,7-methano-3-phospha[11]annulene (6c):** Phosphirane **6A** rearranges to the 4.3 kcal mol<sup>-1</sup> more stable **6C** by means of a concerted disrotatory ring opening with a low enthalpy barrier of 10.2 kcal mol<sup>-1</sup>. Apart from a slightly increased bond delocalization ( $d_{av}(\text{C}=\text{C})$  1.364 Å,  $d_{av}(\text{C}-\text{C})$  1.451 Å), its structure is in excellent agreement with the crystal structure of **6c** with similarly large C1–C6 (2.448 Å) and C2–C3 (3.016 Å) separations; the calculated NICS value of –0.3 for the cycloheptatriene ring shows that there is no homoaromatic stabilization in **6C**. The [HPCr(CO)<sub>5</sub>] group is likewise tilted toward the methylene bridge. Surprisingly, bending this group into the seemingly less congested conformation **6C'** is not only endothermic by 1.5 kcal mol<sup>-1</sup>, but has no an enthalpy minimum.

**The inaccessible *endo* route:** *Endo-anti* addition (labeled with ') of [HPCr(CO)<sub>5</sub>] to the C2C3 bond of **1** followed by ring opening of the phosphirane (Figure 3) and subsequent bending of the phosphorus group (Figure 2) would also explain the observed product formation. However, while *endo-anti* adduct **6A'** (favored over localized form **6B'** (C1–C6 1.590 Å)) is isoenergetic with *exo-syn* adduct **6A** (and has a similar NICS value (–19.5) for the cycloheptatriene unit), its barrier of 30.8 kcal mol<sup>-1</sup> for ring opening to **6C'** (2.8 kcal mol<sup>-1</sup>) requires an unexpected three times that of **6A**, making this an unlikely process to occur. To explain the apparent contrast, we focus on the weak C1–C6  $\pi$  interaction that is inherent to the homoaromatic character of **6A**. In so doing, we consider the **6A**–**6C** conversion as an intramolecular retro-Diels–Alder reaction instead of as an electrocyclic ring opening (Scheme 5).

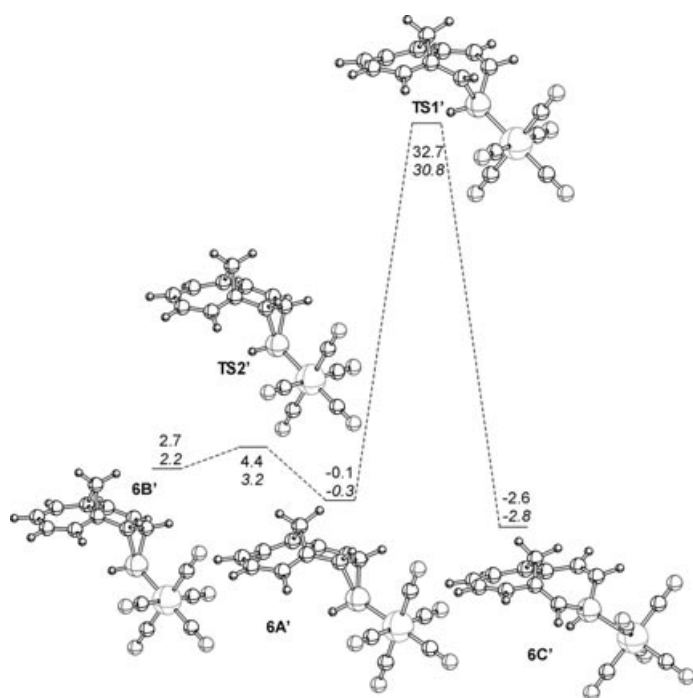
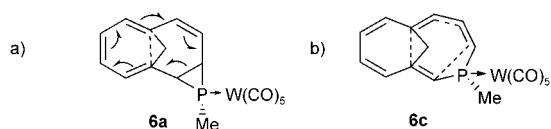


Figure 3. Relative BP/TZP energies (in kcal mol<sup>-1</sup>) for the rearrangement of **6A'** (referenced against **6A**).  $\Delta H_{298}$  values are in italics.



Scheme 5. a) Electrocyclic ring opening/closure and b) retro-Diels–Alder reactions.

The retro-Diels–Alder reaction is constrained by orbital symmetry rules that favor a *supra-supra*[2s+4s] pathway, but the *antara-antara*[2a+4a] path is formally also permitted. The rigid geometry of *syn-exo* isomer **6A** allows for a [2s+4s] process, which is evident from the HOMO–LUMO interactions of the fragments shown Figure 4a. With the [HPCr(CO)<sub>5</sub>] group tilted toward the *endo* site, this pathway is no longer feasible, and the structure becomes instead more amenable for *antara*-facial interactions between the diene and dienophile fragments, as shown in Figure 4b. The transition state for the **6A'**→**6C'** conversion indeed shows the characteristics for a [2a+4a] process. Within the con-

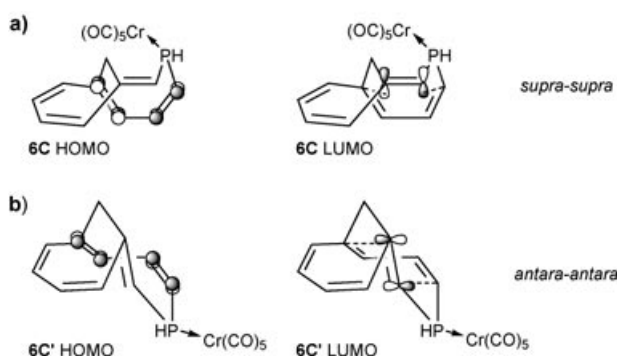


Figure 4. Orbital interactions leading to the respective *supra-supra* and *antara-antara* Diels–Alder reactions in **6C** and **6C'**.

finer ring structure, this process leads to significant geometrical distortions due to the required twisting of the dienophile fragment for proper orbital overlap (torsion in the transition structure), and thereby diminishes the  $\pi$  stabilization for the pericyclic process. It is then no surprise that the literature contains no examples of [2a+4a] Diels–Alder reactions; we are only aware of a theoretical study on a larger [4a+6a] cycloaddition.<sup>[24]</sup>

**Influence of the transition-metal group:** We have seen the unexpected, exclusive formation of the stable ring-expanded products **6c** and **6d** from the reaction of phosphinidene complex **5** with **1** to be supported by DFT calculation on the model structures **6A**–**6C**. This result is remarkable for two reasons. First, as noted, its formation contrasts the reactivity of all known phosphepines, which easily expel phosphinidenes to give aromatic hydrocarbons. Second, homoaromatic stabilization in the cycloheptatriene unit would be expected to stabilize phosphirane isomer **6a** over the complexed 1,7-methano-3-phospha[11]annulene.<sup>[6]</sup> We surmise that the transition-metal group reverses their stability; this fact is confirmed by calculations on the uncomplexed system of which the phosphirane-containing structure **7A** is 5.7 kcal mol<sup>-1</sup> more stable than the ring-opened structure **7C** (Figure 5).

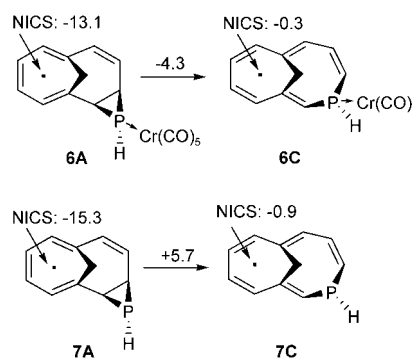


Figure 5. Relative BP/TZP energies (in kcal mol<sup>-1</sup>) for ring opening of **6A** and for uncomplexed **7A**.

The 4.3 kcal mol<sup>-1</sup> favorable ring opening of the Cr(CO)<sub>5</sub>-complexed system suggests that the transition-metal group weakens the C2–C3 bond of **6A** (1.557 Å), relative to that of uncomplexed **7A** (1.528 Å). This effect can be rationalized by using Walsh orbitals for the phosphirane ring in an analogous manner, by which the influence of substituents on the electrocyclic ring closure/opening of norcaradienes has been addressed.<sup>[25]</sup> Coordination of the transition-metal group involves  $\sigma$ -electron donation from the lone pair on phosphorus to the metal (Figure 6a) and  $\pi$  back-donation from the metal to the p orbital on phosphorus (Figure 6b). The  $\sigma$ -electron transfer to the metal reduces the C2–C3 bonding and  $\pi$ -electron transfer from the metal enhances the C2–C3 antibonding. The effect of both is in the same direction, namely coordination of the transition-metal group on phosphorus weakens its distal C2–C3 bond. A fragment-based analysis shows a 10 kcal mol<sup>-1</sup> stronger phosphorus–chromium interaction in **6C** (38.3 kcal mol<sup>-1</sup>) than in **6A**

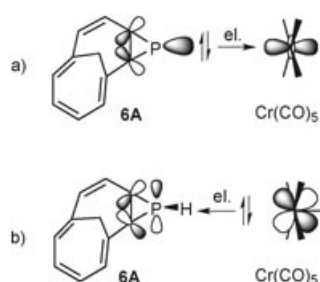


Figure 6. a)  $\sigma$ -donation and b)  $\pi$ -backdonation upon coordination of **7A** to  $\text{Cr}(\text{CO})_5$ .

(28.4 kcal mol<sup>-1</sup>), which is mainly due to the described orbital interactions ( $\Delta\Delta E_{\text{oi}} = 6$  kcal mol<sup>-1</sup>).

## Conclusions

Reaction of the transient phosphinidene complex  $[\text{MePW}(\text{CO})_5]$  with 1,6-methano[10]annulene results remarkably in the sole formation of the stable C–C insertion products **6c** and **6d**, which have the first phosphorus-containing 11-membered ring. A crystal structure analysis of the main isomer **6c** shows the tungsten pentacarbonyl moiety and the phosphorus atom to which it is coordinated positioned *cis* to the methylene bridge. The bicyclic compound results from a disrotatory ring opening of the undetected phosphinidene adduct **6a**, as confirmed by the modest barrier that is obtained by density functional calculations on a model system. The *trans* addition of the phosphinidene complex does not lead to observed product due to the high barrier for the electrocyclic ring opening, a process that mimics a concerted [4a+2a] retro-Diels–Alder reaction. The preference for the methano-bridged phospho[11]annulene structure **6c** over the localized phosphirane structure **6a** is due to the stabilizing effect of the transition-metal group, as the relative energy reverses sign without it. The stabilization results from the  $\sigma$ -electron withdrawing and  $\pi$ -electron backdonation of the metal group to the phosphorus atom, both of which destabilize the C2–C3 bond of the three-membered phosphirane ring.

## Experimental Section

**Computational methods:** All geometry optimizations were performed with the ADF program,<sup>[26]</sup> with a triple  $\zeta$  basis set with polarization functions, the local density approximation (LDA) in the Vosko–Wilk–Nusair parameterization<sup>[27]</sup> with nonlocal corrections for exchange (Becke88)<sup>[28]</sup> and correlation (Perdew86)<sup>[29]</sup> included in a selfconsistent manner, and the analytical gradient method of Versluis and Ziegler.<sup>[30]</sup>

Zero-point energies (ZPEs) were computed with the Gaussian 98 program package,<sup>[31]</sup> with geometries optimized with the BP86 exchange-correlation potentials 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.

The seven-membered rings in **7a** and **7b** were characterized by the nucleus-independent chemical shifts (NICS), a simple and efficient aromaticity probe.<sup>[32]</sup> NICS, the negative of the absolute magnetic shielding,

was computed at the ring centers by using gauge-including atomic orbitals (GIAO) in the stand alone utility program NMR<sup>[33]</sup> of the ADF program package. Negative NICS denote aromaticity ( $-7.5$  for benzene), and positive NICS denote antiaromaticity. Nonaromatics have negligible NICS values. An advantage of NICS over other aromaticity criteria is the relatively small dependence on ring size, and its ability to assess the aromaticity of individual rings in polycyclic systems.

**Synthetic methods:** NMR spectra were recorded on a Bruker Avance 250 and an MSL 400 spectrometer (<sup>31</sup>P; 85% H<sub>3</sub>PO<sub>4</sub>, <sup>1</sup>H, <sup>13</sup>C; TMS). High-resolution mass spectra (HR-MS) were recorded on a Finnigan Mat 900 spectrometer. Compound **1** was synthesized according to the literature.<sup>[34]</sup>

**Compounds 6c and 6d:** Compound **4b** (0.464 g, 0.78 mmol), compound **1** (0.088 g, 0.62 mmol), and CuCl<sub>2</sub> (0.01 g, 0.1 mmol) were stirred at 55 °C under nitrogen for 17 h in dry toluene (10 mL). The reaction was monitored by <sup>31</sup>P NMR spectroscopy, for disappearance of **4** (202 ppm). Besides **6c** and **6d**, only P,W-clusters and oxidation products were observed. After evaporation of the solvent, the reaction mixture was subjected to chromatography over activated silica with a hexane/dichloromethane (20:1) as eluents giving **6c** and **6d** (0.15 g 47.2% in total) in an 85:15 ratio as determined by <sup>31</sup>P NMR spectroscopy. Crystallization from pentane resulted in orange crystals of **6c**. M.p. 105–106 °C

**Data for 6c:** <sup>31</sup>P NMR (250 MHz, CDCl<sub>3</sub>):  $\delta = -3.1$  ppm (d, <sup>1</sup>J(P,W) = 231.7); <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 201.5$  (d, <sup>2</sup>J(C,P) = 18.88 Hz; *trans*-CO), 196.9 (d, <sup>2</sup>J(C,P) = 6.8 Hz; *cis*-CO), 148.8 (d, <sup>2</sup>J(C,P) = 2.74 Hz; C1), 141.3 (d, <sup>4</sup>J(C,P) = 1.72 Hz; C6), 134.3 (d, <sup>2</sup>J(C,P) = 10.89 Hz; C4), 133.2 (s; C7), 132.2 (d, <sup>3</sup>J(C,P) = 12.17 Hz; C10), 128.2 (d, <sup>1</sup>J(C,P) = 30.56 Hz; C3), 127.2 (s; C9), 125.6 (s; C8), 122.5 (d, <sup>3</sup>J(C,P) = 4.32 Hz; C5), 114.4 (d, <sup>1</sup>J(C,P) = 41.56 Hz; C2), 36.2 (d, <sup>3</sup>J(C,P) = 12.56 Hz; C11), 21.4 ppm (d, <sup>1</sup>J(C,P) = 36.36 Hz; MeP); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta = 1.94$  (d, <sup>2</sup>J(H,P) = 7.1 Hz; MeP), 3.67 (dd, <sup>4</sup>J(H,P) = 2.5 Hz, <sup>2</sup>J(H,H) = 11.4 Hz; *anti*-HC11), 4.93 (m, <sup>2</sup>J(H,P) = 21.9 Hz, <sup>4</sup>J(H,H) = 1.6 Hz; HC2), 5.22 (ddd, <sup>2</sup>J(H,P) = 26.8 Hz, <sup>3</sup>J(H,H) = 14.5 Hz, <sup>4</sup>J(H,H) = 1.8 Hz; HC3), 5.41 (d, <sup>3</sup>J(H,H) = 6.8 Hz; HC5), 5.49 (dd, <sup>4</sup>J(H,P) = 1.9 Hz, <sup>2</sup>J(H,H) = 11.4 Hz; *syn*-HC11), 5.74 (m, <sup>3</sup>J(H,H) = 11.1 Hz; HC8), 5.76 (m, <sup>3</sup>J(H,H) = 11.1 Hz; HC9), 6.13 (m; HC7), 6.21 (m; HC10), 6.21 ppm (ddd, <sup>3</sup>J(H,P) = 34.6 Hz, <sup>3</sup>J(H,H) = 6.8 Hz, <sup>3</sup>J(H,H) = 14.5 Hz; HC4); HRMS: *m/z* calcd for C<sub>16</sub>H<sub>11</sub>WPO<sub>5</sub>: 512.0000; found: 512.0010.

**Data for 6d:** <sup>31</sup>P NMR (250 MHz, CDCl<sub>3</sub>):  $\delta = -19.6$  ppm (d, <sup>1</sup>J(P,W) = 237.5 Hz); <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 200.7$  (d, <sup>2</sup>J(C,P) = 19.6 Hz; *trans*-CO), 197.2 (d, <sup>2</sup>J(C,P) = 7.0 Hz; *cis*-CO), 147.7 (d, <sup>2</sup>J(C,P) = 5.2 Hz; C10), 142.9 (d, <sup>4</sup>J(C,P) = 2.9 Hz; C5), 135.3 (d, <sup>2</sup>J(C,P) = 5.1 Hz; C3), 133.1 (s; C6), 132.7 (d, <sup>3</sup>J(C,P) = 12.4 Hz; C9), 132.0 (d, <sup>1</sup>J(C,P) = 32.3 Hz; C1), 128.1 (d, <sup>1</sup>J(C,P) = 31.9 Hz; C2), 127.1 (d, <sup>3</sup>J(C,P) = 6.3 Hz; C4), 126.5 (s; C7), 126.2 (s; C8), 34.2 (d, <sup>3</sup>J(C,P) = 7.8 Hz; C11), 23.1 ppm (d, <sup>1</sup>J(C,P) = 30.8 Hz; CH<sub>3</sub>P); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 6.34$ – $6.28$  (m; HC6, HC9), 6.27 (ddd, <sup>3</sup>J(H,P) = 36.3 Hz, <sup>3</sup>J(H,H) = 13.6 Hz, <sup>3</sup>J(H,H) = 5.5 Hz; HC3), 6.13 (d, <sup>2</sup>J(H,P) = 37.3 Hz; HC1), 5.92–5.83 (m; HC4, HC7, HC8), 5.58 (ddd, <sup>2</sup>J(H,P) = 24.9 Hz, <sup>3</sup>J(H,H) = 13.6 Hz, <sup>4</sup>J(H,H) = 1.7 Hz; HC2), 4.72 (d, <sup>2</sup>J(H,H) = 10.9 Hz; *cis*-HC11), 3.20 (d, <sup>2</sup>J(H,H) = 10.9 Hz; *trans*-HC11), 2.01 ppm (d, <sup>2</sup>J(H,H) = 7.1 Hz; CH<sub>3</sub>P).

**Crystal data for 6c:** C<sub>17</sub>H<sub>13</sub>O<sub>5</sub>PW, *M*<sub>r</sub> = 512.09, orange plate, 0.30 × 0.24 × 0.15 mm<sup>3</sup>, monoclinic, *P*2<sub>1</sub>/*c* (no. 14), *a* = 10.6574(1), *b* = 7.0617(1), *c* = 24.1276(3) Å,  $\beta = 109.3751(8)^\circ$ , *V* = 1712.99(4) Å<sup>3</sup>, *Z* = 4,  $\rho_{\text{calcd}} = 1.986$  g cm<sup>-3</sup>,  $\mu = 6.860$  mm<sup>-1</sup>. 18905 Reflections were measured on a Nonius Kappa CCD diffractometer with rotating anode ( $\lambda = 0.71073$  Å) at a temperature of 150(2) K up to a resolution of  $(\sin\theta/\lambda)_{\text{max}} = 0.65$  Å<sup>-1</sup>; 3921 reflections were unique (*R*<sub>int</sub> = 0.040). An analytical absorption correction was applied (0.21–0.56 transmission). The structure was solved with automated Patterson methods (DIRDIF-99)<sup>[35]</sup> and refined with SHELXL-97<sup>[36]</sup> against *F*<sup>2</sup> of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters; H atoms were refined freely with isotropic displacement parameters. 269 refined parameters, no restraints. *R* values [*I* > 2 $\sigma$ (*I*): *R*1 = 0.0167, *wR*2 = 0.0373. *R* values (all data): *R*1 = 0.0191, *wR*2 = 0.0381. GoF = 1.054. Residual electron density between  $-1.08$  and  $0.80$  e Å<sup>-3</sup>. Molecular illustration, structure checking and calculations were performed with the PLATON package.<sup>[37]</sup>

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