Reaction of a Terminal Phosphinidene Complex with Azulenes: η^1-Complexes, C–H Bond Insertions, and 1,4-Adducts

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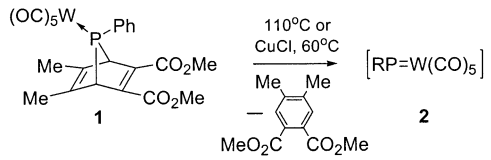
Abstract: Reaction of an in situ generated phosphinidene complex [PhPW(CO)$_5$] with the aromatic azulene and guaiazulene leads to unexpected 1,4-adducts of the seven-membered ring and to C–H bond insertion of the five-membered ring. A DFT analysis suggests that the reaction is initiated by formation of a η^1-complex between the phosphinidene and the five-membered ring of the aromatic substrate. Four conformations of this complex were identified. Two convert without barrier to the slightly more stable *syn*- and *anti*-1,2-adducts. These undergo pericyclic 1,7-sigmatropic rearrangements with remarkably low barriers to give 1,4-adducts, with an inverted configuration at the phosphorus center. An X-ray crystal structure is presented for one of the 1,4-adducts of guaiazulene. The other two η^1-complexes insert with modest barriers into a C–H bond of the five-membered ring.

Keywords: azulenes · density functional calculations · electrophilic substitution · phosphorus

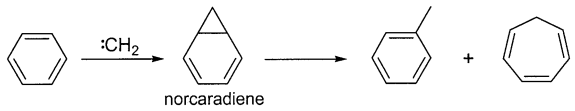
Introduction

Two decades ago, Mathey and Marinetti[1] reported on the generation of the terminal phosphinidene complex [RPW(CO)$_5$] (Scheme 1) and its carbene-like reactivity toward olefins. Numerous reactions with double and triple bonds, leading to a plethora of novel ring structures, have subsequently shown the applicability of this transient reagent with singlet electrophilic character.[2,3]

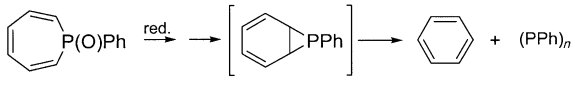


Scheme 1. Formation of phopshinidene complex **2** from a 7-phosphanorbornadiene complex.

A striking difference between carbenes and electrophilic phosphinidene complexes is their reactivity towards aromatic compounds. For example, it is well known that the parent carbene :CH$_2$ reacts with benzene to give mainly the [1+2] cycloadduct norcaradiene, which rearranges to both cycloheptatriene and toluene, (Scheme 2);[4,5] however, phosphinidene complexes do not give such reactions. In fact, [RPW(CO)$_5$] is generated in solvents like toluene by cheletropic elimination from **1**, with release of an aromatic substrate.[1] Also, the attempted synthesis of uncomplexed phosphepines is thwarted by expulsion of benzene from the presumed phosphanorcaradiene intermediates (Scheme 3).[6]



Scheme 2. Reaction of methylene with benzene.



Scheme 3. Formation and fragmentation of 7-phosphanorcaradiene.

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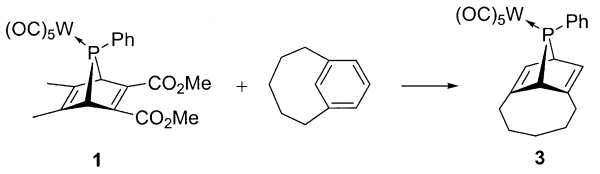
Nevertheless, [RPW(CO)$_5$] (**2**) reacts with selected aromatic compounds; an example is the C–H insertion into the cyclopentadienyl ring of ferrocene.[7] The nucleophilic hydrocarbon ring is an attractive target for the electrophilic phosphinidene. Another rare example is the unique [1+4] cycloaddition to [5]metacyclophane (Scheme 4), because it



1 3

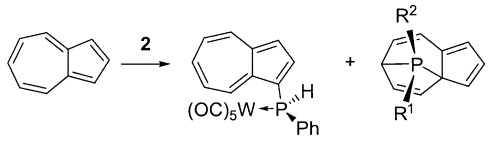
Scheme 4. Transfer of [RPW(CO)$_5$] from **1** to [5]metacyclophane.

is in fact, the reverse of the cheletropic elimination of **2** (Scheme 1);[8] the formation of **3** is thermodynamically favored, because the 1,4-addition releases much strain from the highly bent benzene ring of the cyclophane.

Here we report on the remarkable reaction of [PhPW(CO)$_5$] with the aromatic azulene and its derivative guaiazulene. Because of the large dipole moment of the hydrocarbon frame (azulene: 0.796 D), the electrophilic phosphinidene is expected to interact with the negatively charged five-membered ring. Using density functional theory we will show that the first step is the exceptional aromatic η^1-complexation to this five-membered ring from which insertion into one of its C–H bonds occurs, as well as a very rare 1,7-shift to give 1,4-adducts of the seven-membered ring.

Results and Discussion

Reaction of phosphinidene precursor **1** with azulene (**4**) in the presence of CuCl at 60 °C leads to C–H insertion product **5** (55 %) and the formal 1,4-adducts **6** and **7** (45 %) (Scheme 5). The analogous products result in different

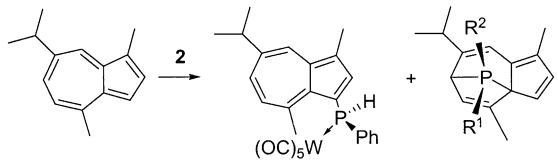


4 5 55% 6 15% 7 30%

6 R^1 = Ph, R^2 = W(CO)$_5$ 7 R^1 = W(CO)$_5$, R^2 = Ph

Scheme 5. Reaction of phosphinidene complex **2** with azulene with relative product yields.

ratios with the substituted derivative guaiazulene (**8**), favoring the 1,4-adducts (77 %) (Scheme 6). All products were fully characterized by NMR spectroscopy (see Experimental Section). Most diagnostic for the C–H insertion products are the ^{31}P NMR resonances of the phosphine group (**5**: −48.8 ppm, **9**: −31.8 ppm) with their large ^1J(H,P) coupling constants (**5**: 343.3 Hz, **9**: 348.3 Hz) and the aromatic patterns in the ^{1}H and ^{13}C NMR spectra. The 1,4-adducts have



8 9 22% 10 50% 11 27%

10 R^1 = Ph, R^2 = W(CO)$_5$ 11 R^1 = W(CO)$_5$, R^2 = Ph

Scheme 6. Reaction of phosphinidene complex **2** with guaiazulene with relative product yields.

much more deshielded δ(^{31}P) resonances (**6**: 150.3 ppm, **7**: 106.7 ppm, **10**: 135.5 ppm, **11**: 85.2 ppm) than are common for 5/6-membered phosphorus rings,[9] while both the ^{1}H and ^{13}C NMR spectra show the expected olefinic resonances and coupling constants. An X-ray structure determination ascertained the assignment of **10** (Figure 1). The similarity with the NMR characteristics of **10** (and **11**) was used to distinguish between compounds **6** and **7**.

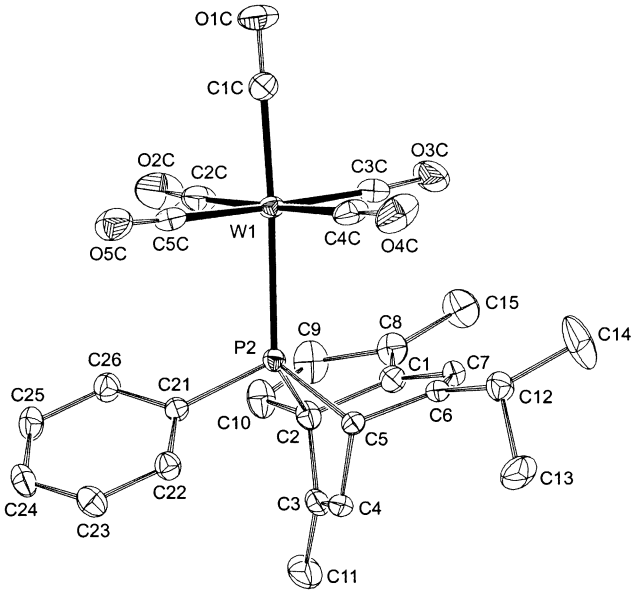


Figure 1. Displacement ellipsoid plot (50 % probability) of **10**. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å], angles and torsion angles [°]: P2–W1 2.5065(4), P2–C21 1.8224(16), P2–C2 1.8702(16), P2–C5 1.8644(16), C1–C2 1.517(2), C2–C3 1.527(2), C3–C4 1.318(2), C4–C5 1.521(2), C5–C6 1.519(2), C6–C7 1.344(2), C7–C1 1.442(2), C2-P2-C5 85.32(7), P2-C2-C1-C7 49.71(17), P2-C5-C6-C7 −44.80(17), C7-C1-C2-C3 −58.81(19), C7-C6-C5-C4 64.52(19).

To bring about an understanding into the unexpected formation of both these reaction products we resorted to density functional theory (see section on Computational Methods) by addressing the interaction of [HPCr(CO)$_5$] (**2′**), as a simplified model for the transition-metal-complexed phosphinidene, with azulene. Next, rearrangement pathways were evaluated and finally the influence of substituents was considered.

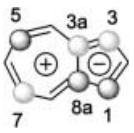


Figure 2. Frontier orbitals of azulene.

1,2-Addition: Azulene has a significantly negatively charged five-membered ring and large HOMO coefficients for C1–C8a (and C3–C3a; Figure 2) that should be attractive for initial 1,2-addition by the phosphinidene complex. If indeed this occurs would such 1,2-adducts lead to the final products and if so by what pathways?

To address this question, we first explored the kinetic pathway, as dictated by the charges and frontier orbitals, by bringing $[HPCr(CO)_5]$ in a stepwise manner close to the C1–C8a bond of azulene. This approach is expected to occur in an asynchronous manner with the phosphinidene tilted toward or away from C1, while its transition metal group can be oriented either *syn* or *anti* with respect to the five-membered ring. The asynchronous approach is well established for the addition of $^1CH_2$ to ethylene[10,11] and is governed by the overlap of the carbene's empty p orbital with the filled olefinic π orbital and by the carbene's lone pair with the empty π* orbital. Figure 3 shows these interactions for $CR^{1\prime}R^{2\prime}$ tilted toward the olefinic CR^3R^4 substituents.

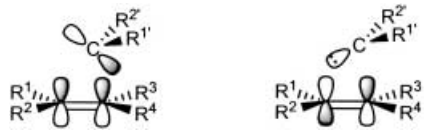
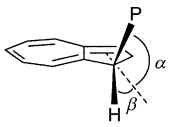


Figure 3. $^1CH_2$–ethylene frontier orbital interactions.

***syn* Intermediates**: The stepwise *syn* approach of $[HPCr(CO)_5]$ to azulene confirmed an asynchronous (tilted) pathway. We were surprised to locate two *syn* η^1-adducts, that is, **s12** and the 0.6 kcal mol^{-1} less stable **s13** (Figure 4, **s** indicates *syn*). Such η^1-adducts are not found along the reaction pathway of $[HPCr(CO)_5]$ and ethylene. Both intermediates are intermediate between aromatic π and σ complexes,[12] as reflected by the angles of the P–C1 (α) and C1–H (β) bonds with the five-membered ring (Scheme 7). Of the two η^1-adducts, **s12** ($\alpha = 79.7°$, $\beta = 26.4°$) exhibits slightly less σ character than **s13** ($\alpha = 64.7°$, $\beta = 36.1°$). In a regular σ complex, like the heptamethylbenzenium ion, α and β are the same (55°).[13] No or little bending of the C–H bond ($\beta \sim 0°$) occurs in π complexes such as those between NO^+ and arenes.[14] The much-debated silyl cations[15] can show σ character in their interaction with arenes,[16] as in the theoretically studied Et_3Si^+–benzene complex (α 76°).[17] The intermediate σ/π character in the phosphinidene η^1-adducts is also evident from the P–C1 bond length (**s12**: 2.093, **s13**: 2.080 Å), which is clearly elongated from a regular σ bond.



Scheme 7. Definition of the α and β angles for the C1 substituents.

It is well established that entropy factors are important in carbine–olefin addition, as they tend to disfavor the intermediate π complex.[18] Entropy factors also influence the existence of the η^1-adducts **s12** and **s13**. Using ΔG eliminates the 12.7 kcal mol^{-1} complexation energy for **s12** and reduces that of **s13** to a marginal 0.1 kcal mol^{-1}.

If complex **s12** is not a viable species on the reaction coordinate, the 1,2-adduct may be. Indeed, *syn* phosphirane **s14** is 1.5 kcal mol^{-1} more stable with a 0.7 kcal mol^{-1} barrier for its formation (Figure 5). On including entropy factors this barrier disappears and **s14** is formed directly from its constituents ($\Delta G = 4.7$ kcal mol^{-1}). No pathway was found for conversion of **s13** to a phosphirane, probably because of steric congestion caused by the transition-metal group.

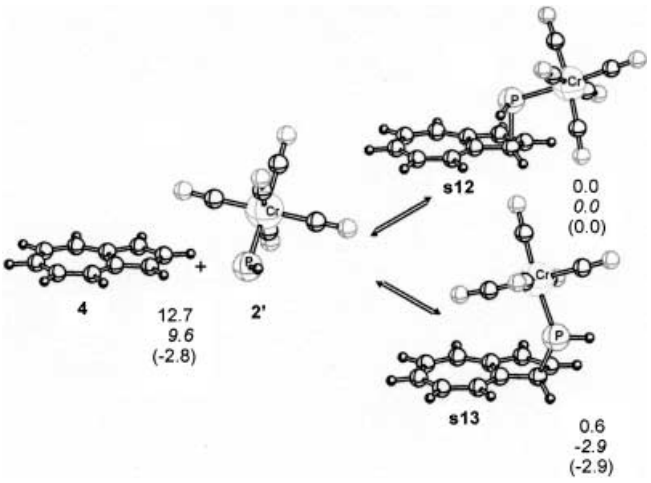


Figure 4. *syn* η^1-adducts from phosphinidene complex **2′** and azulene. BP/6-31G* energies, enthalpies (italic) and Gibbs energies (parenthesis) are in kcal mol^{-1}.

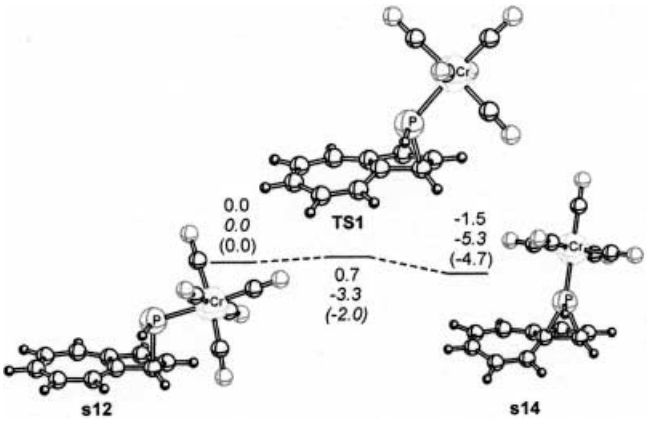


Figure 5. Conversion of complex **s12** to phosphirane **s14**. BP/6–31G* energies, enthalpies (italic) and Gibbs energies (parenthesis) are in kcal mol^{-1}.

C–H bond insertion: Complex **s13** with its long P–C8a distance of 2.964 Å, which reflects hardly any interaction of the phosphinidene group with C8a, is not likely to transfer this group to the seven-membered ring; it is instead a better candidate for C1–H bond insertion. This reaction channel

was confirmed. The insertion giving **15** is exothermic (25.6 kcal mol^{-1}) and has a sizeable barrier of 18.6 kcal mol^{-1} (**TS2** $\Delta G = 14.5$, Figure 6), because a CH bond must be cleaved. In the transition structure the transferring hydrogen atom has C1–H and P–H bond lengths of 1.329 and 1.627 Å, respectively.

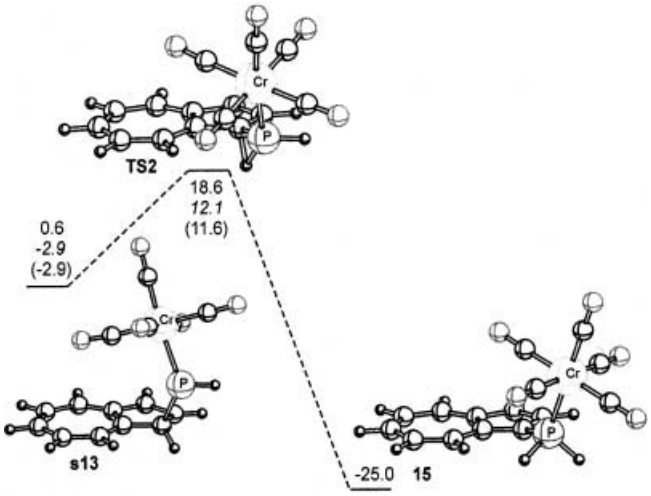


Figure 6. C–H bond insertion of [HPCr(CO)$_5$]. Calculated energies, enthalpies (italic) and Gibbs energies (parenthesis) are in kcal mol^{-1}.

1,7-Sigmatropic shift: If **s13** is the precursor for CH insertion, can **s14** rearrange to a 1,4-adduct by transferring the phosphorus group from the five- to the seven-membered ring?

Extremely little is known about such 1,7-σ sigmatropic shifts, but a recent example is the circumambulation of uncomplexed phenyl-9-phosphabicyclo[6.1.0]nona-2,4,6-triene, in which the phosphirane "walks" over the eight-membered hydrocarbon frame.[19] This concerted process occurs with inversion at the phosphorus center at each step and has an experimental barrier $\Delta H^{\neq}$ of 20 kcal mol^{-1}; at B3LYP/6–31G* $\Delta H^{\neq} = 16.1$ kcal mol^{-1} for the H-substituted system.

Likewise, we found the rearrangement of 1,2-adduct **s14** to 1,4-adduct **s16** to occur in a single step (Figure 7). The modestly exothermic reaction (7.0 kcal mol^{-1}) reflects that **s16** is less strained than **s14**; the strain energy of the parent phosphirane C_2PH_5 is 21.4 kcal mol^{-1} at G3.[20] This remarkable 1,7-σ shift has a barrier of only 12.0 kcal mol^{-1} and is hardly influenced by entropy factors. The rearrangement occurs with inversion of configuration at the phosphorus center, as expected for a pericyclic process. Transition state **TS3** does not exhibit any diradical behavior. This contrasts with the diradical character of the 1,3-σ shift of 2-vinylphosphirane, that requires 20.5 kcal mol^{-1} for the Cr(CO)$_5$-complexed parent.[21,22] The structure of **s16** compares well with the crystal structure of **10**, despite the difference in substituents at phosphorus. Naturally, the P–Cr bond (2.355 Å) is shorter than the P–W bond (2.507 Å). Accordingly, the P–C distances (P–C2 = 1.930 Å, P–C5 = 1.926 Å) are predicted to be slightly longer than the experimentally derived ones (P–C2 = 1.8702(16) Å, P–C5 = 1.8644(16) Å).

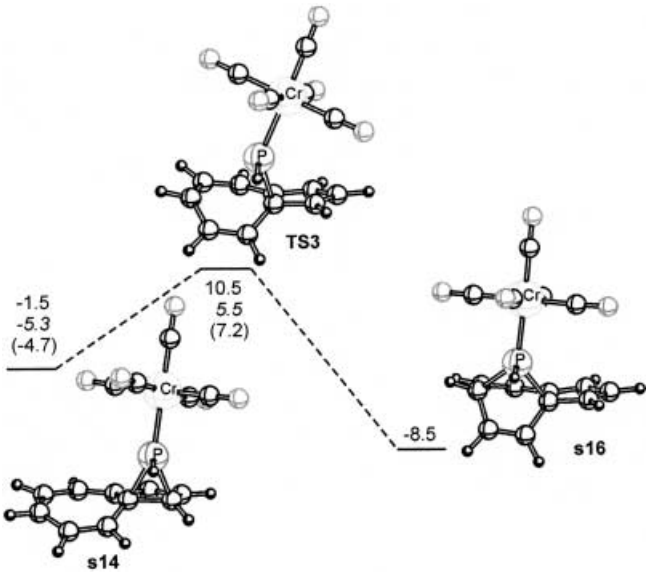


Figure 7. 1,7-Sigmatropic rearrangement giving the 1,4-adduct. Calculated energies, enthalpies (italic) and Gibbs energies (parenthesis) are in kcal mol^{-1}.

Products from *anti* addition: So far, we have discussed avenues for the approach of [HPCr(CO)$_5$] toward azulene in a *syn* manner. Of course, an *anti* (**a**) approach is equally feasible and likewise gives two η^1-adducts (Figure 8). These will not be discussed because their behavior is similar to the *syn* adducts. Thus, **a13** converts to the C–H insertion product **15**, while **a12** converts on inclusion of entropy factors to **a14** and subsequently to **a16** after a 1,7-σ shift. The $\Delta G^{\neq}$ barrier for this 7.1 kcal mol^{-1} exothermic process amounts to 10.6 kcal mol^{-1}, which is similar to that for the conversion of **s14** into **s16**.

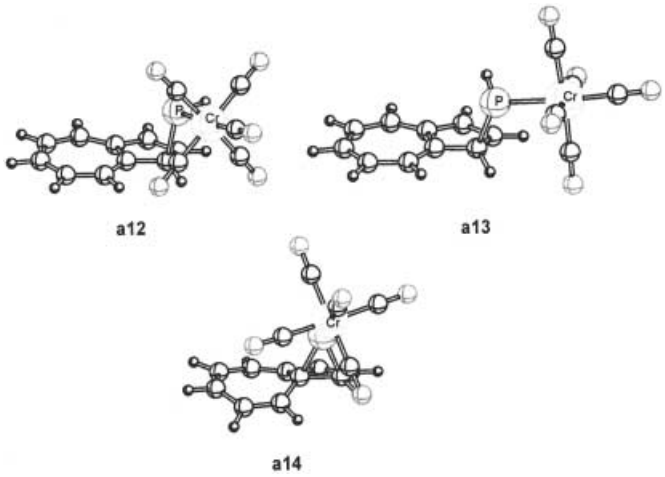


Figure 8. *anti* η^1-adducts **a12** and **a13** and *anti* phosphirane **a14**.

The described (*syn* and *anti*) reaction channels satisfactorily explain the observed C–H insertion and 1,4-addition products that result from the reaction of **1** with azulene, albeit that the calculated barrier heights do not properly reflect the observed product ratios. This is, in fact, not surpris-

ing given the different nature of the transition states and the limitations of DFT methods to accurately calculate barrier heights.[23] Dynamic effects may also contribute to the rapid interchange of the η^1-adducts.

Guaiazulene: The influence of the substituents on azulene is reflected in the more rapid reaction of **8** and its product ratio, which strongly favors the 1,4-adducts (77%). DFT calculations suggest that both steric and electronic reasons underlie these effects.

To establish whether the course of events is similar to that of azulene, calculations were performed with $[HPCr(CO)_5]$ approaching guaiazulene in a *syn* manner. Satisfyingly, although anticipated, again two η^1-adducts resulted, that is, **s17** and **s18** (Figure 9). Two aspects are noted. First, the preferred complexation is at the unsubstituted carbon atom (C3) of the five-membered ring, enabling insertion into the C3–H bond and rearrangement to the 1,4-adduct. Second, the exothermicity for formation of the η^1-adducts is larger than for azulene itself, which may explain the shorter reaction time for guaiazulene provided that their rearrangement barriers do not differ significantly. The apparently favored 1,7-shift may be due to the *peri*-methyl group (at C4), which sterically hinders the C–H insertion. We simulated this process by substituting transition structure **TS2** with three non-optimized methyl groups in positions 1, 4, and 7. Steric congestion with the *peri*-methyl group is evident as the distance between its hydrogen atom and the phosphorus atom is well within the sum of the van der Waals radii, that is, $r(P{-}H{-}(Me)) = 0.78\,(r_{VDW}(P) + r_{VDW}(H))$; this is also the case for the interaction with one of the carbonyl groups. Also the β-methyl group (at C7) of **8** electronically favors the 1,7-σ shift by enhancing the coefficient of C6 in the HOMO.

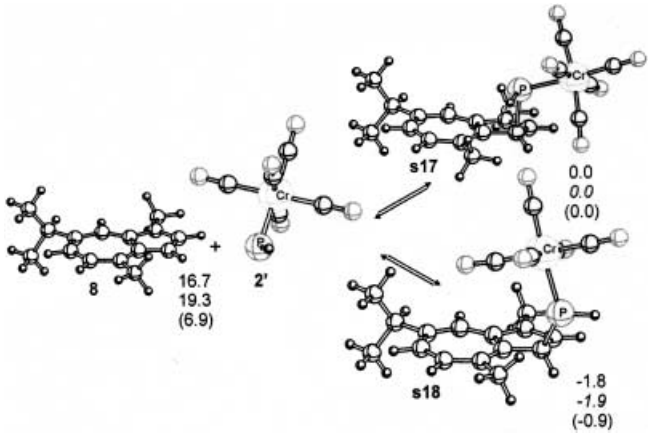


Figure 9. *syn* η^1-adducts **s17** and **s18** from phosphinidene complex **2'** and guaiazulene. Calculated energies, enthalpies (italic) and Gibbs energies (parenthesis) are in kcal mol^{-1}.

Conclusion

Reaction of in-situ generated phosphinidene complex $[PhPW(CO)_5]$ with aromatic azulene and guaiazulene gives unexpectedly 1,4-adducts with the seven-membered ring, as confirmed by an X-ray structure for one of them, and equally surprisingly C–H bond insertion of the five-membered ring.

Analysis of the reaction pathways with DFT theory, using $[HPCr(CO)_5]$ as model for the phosphinidene complex, shows several intriguing novel features.

1) The starting point of the reaction is the formation of an exceptional η^1-complex with the five-membered ring of the aromatic system of which there are four conformers with $[HPCr(CO)_5]$ tilted in outward or inward and oriented *syn* (**s**) or *anti* (**a**). The nature of the interaction is intermediate between σ and π bonding.
2) The outward tilted η^1-complexes converge on including entropy factors without barrier to slightly more stable 1,2-adducts of the five-membered ring.
3) These phosphiranes undergo a pericyclic 1,7-sigmatropic shift with inversion at the phosphorus center to give the more stable 1,4-adducts of the seven-membered ring.
4) The inward tilted η^1-complexes rearrange to give C–H insertion of the five-membered ring.
5) Alkyl substitution changes the product ratio from mainly CH insertion to favor formation of the 1,4-adducts for both steric and electronic reasons.

Computational Methods

All geometry optimizations were performed with the ADF program[24] by using a triple ζ basis set with polarization functions, the local density approximation (LDA) in the Vosko–Wilk–Nusair parameterization[25] with nonlocal corrections for exchange (Becke88)[26] and correlation (Perdew86)[27] included in a selfconsistent manner, and the analytical gradient method of Versluis and Ziegler.[28] BSSE corrections were calculated with the counterpoise method.[29]

Frequencies, zero-point energies (ZPEs), and thermal corrections were computed with the Gaussian 98 program package,[30] using 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.

Experimental Section

NMR spectra were recorded on Bruker Avance 250 (^{31}P; 85% H_3PO_4) and Avance 400 (^{1}H, ^{13}C; TMS) spectrometers. Assignments were made based on COSY, HMQC, and HMBC techniques. High-resolution mass spectra (HR-MS) were recorded on a Finnigan MAT 900 spectrometer. Elemental analyses were obtained from Microanalytisches Labor Pascher, Remagen-Bandorf (Germany).

***P*-Pentacarbonyltungsten-*P*-phenyl-1-phosphinoazulene (5)**: Compound **1** (0.521 g, 0.798 mmol),[1] azulene (0.078 g, 0.609 mmol), and a catalytic amount of CuCl (~10 mg) were stirred overnight at 60 °C under nitrogen in dry toluene (5 mL). Product ratios were determined from the crude reaction mixture by ^{31}P NMR spectroscopy, that is, **5**: 55%, **6**: 15%, **7**: 30%. Purification and partial separation by chromatography (activated silica, pentane/toluene 9:1) followed by fractional crystallization (pentane) afforded 157 mg of **5** (46%), and 6 mg of a mixture of **6** and **7**.

Data for compound 5: Purple crystals; m.p. 42–43 °C; ^{31}P NMR (101 MHz, $CDCl_3$): $\delta = -48.8$ ppm ($^1J(P,W) = 228.9$ Hz); ^{13}C NMR

(100 MHz, $CDCl_3$): $\delta = 199.8$ (d, $^2J(C,P) = 21.1$ Hz, *trans*-CO), 197.1 (d, $^2J(C,P) = 6.8$ Hz, *cis*-CO), 148.0 (s, C=, C3a), 145.3 (d, $^2J(C,P) = 21.2$ Hz, CH=, C2), 145.1 (d, $^2J(C,P) = 6.2$ Hz, C=, C8a), 139.2 (s, CH=, C6), 138.7 (s, CH=, C4), 136.2 (d, $^3J(C,P) = 3.1$ Hz, CH=, C8), 135.0 (d, $^1J(C,P) = 44.7$ Hz, ipso-Ph), 130.9 (d, $^2J(C,P) = 12.2$ Hz, *o*-Ph), 130.2 (s, *p*-Ph), 129.2 (d, $^3J(C,P) = 10.1$ Hz, *m*-Ph), 126.5 (s, CH=, C7), 125.6 (s, CH=, C5), 119.1 (d, $^3J(C,P) = 12.4$ Hz, CH=, C3), 114.5 ppm (d, $^1J(C,P) = 45.3$ Hz, CP=, C1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.23$ (d, $^1J(H,P) = 343.3$ Hz, 1H; HPC1), 7.1–7.3 (m, 7H; Ph, HC5, HC7), 7.35 (dd, $^4J(H,P) = 3.4$ Hz, $^3J(H,H) = 3.5$ Hz, 1H; HC3), 7.57 (t, $^3J(H,H) = 9.9$ Hz, 1H; HC6), 8.18 (dd, $^3J(H,P) = 4.0$ Hz, $^3J(H,H) = 3.5$ Hz, 1H; HC2), 8.26 (d, $^3J(H,H) = 9.5$ Hz, HC8), 8.30 ppm (d, $^3J(H,H) = 9.8$ Hz, HC4); HRMS: *m*/*z* calcd for $C_{21}H_{13}WPO_5$: 560.00104; found: 560.00155 ($\delta = 5.1 \times 10^{-4}$).

***syn*-11-Pentacarbonyltungsten-11-phenyl-11-phosphatricyclo[6.2.1.0^{1,5}]undeca-2,4,6,9-tetraene (6)**: ^{31}P NMR (101 MHz, $CDCl_3$): $\delta = 150.3$ ppm ($^1J(P,W) = 250.5$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 199.6$ (d, $^2J(C,P) = 25.2$ Hz, *trans*-CO), 196.5 (d, $^2J(C,P) = 7.0$ Hz, *cis*-CO), 144.4 (d, $^2J(C,P) = 5.2$ Hz, C=, C5), 139.1 (d, $^1J(C,P) = 25.0$ Hz, ipso-Ph), 138.7 (d, $^2J(C,P) = 7.5$ Hz, CH=, C2), 136.8 (d, $^3J(C,P) = 2.6$ Hz, CH=, C4), 132.2 (d, $^2J(C,P) = 1.8$ Hz, CH=, C10), 131.9 (d, $^2J(C,P) = 1.1$ Hz, CH=, C9), 131.5 (d, $^2J(C,P) = 8.7$ Hz, *o*-Ph), 129.9 (d, $^4J(C,P) = 1.6$ Hz, *p*-Ph), 129.0 (d, $^3J(C,P) = 2.9$, CH=, C3), 128.8 (d, $^3J(C,P) = 7.9$ Hz, *m*-Ph), 125.8 (d, $^3J(C,P) = 9.5$, CH=, C6), 125.3 (d, $^2J(C,P) = 6.0$ Hz, CH=, C7), 69.9 (d, $^1J(C,P) = 8.4$, CP, C1), 46.8 ppm (d, $^1J(C,P) = 16.5$, CHP, C8); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.07$ (ddddd, $^3J(H,H) = 4.2$ Hz, $^3J(H,H) = 7.7$ Hz, $^4J(H,H) = 0.8$ Hz, $^4J(H,H) = 0.8$ Hz, $^2J(H,P) = 2.6$ Hz, 1H; HC8), 5.56 (dd, $^3J(H,H) = 6.2$ Hz, $^3J(H,P) = 6.2$ Hz, 1H; HC10), 6.22 (dd, $^3J(H,H) = 6.2$ Hz, $^3J(H,H) = 4.2$ Hz, 1H; HC9), 6.46 (ddd, $^3J(H,H) = 9.4$ Hz, $^3J(H,P) = 12.7$ Hz, $^3J(H,H) = 7.7$ Hz, 1H; HC7), 6.67 (dd, $^3J(H,H) = 1.8$ Hz, $^3J(H,H) = 1.8$ Hz, 1H; HC3), 6.85 (dd, $^3J(H,H) = 9.4$ Hz, $^4J(H,P) = 5.7$ Hz, 1H; HC6), 7.06 (d, $^3J(H,H) = 1.8$ Hz, 2H; HC2), 7.06 (d, $^3J(H,H) = 1.8$ Hz, 2H; HC4), 7.35–7.54 ppm (m, 5H; Ph).

***anti*-11-Pentacarbonyltungsten-11-phenyl-11-phosphatricyclo[6.2.1.0^{1,5}]-undeca-2,4,6,9-tetraene (7)**: ^{31}P NMR (101 MHz, $CDCl_3$): $\delta = 106.7$ ppm ($^1J(P,W) = 245.1$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 199.3$ (d, $^2J(C,P) = 24.71$ Hz, *trans*-CO), 197.1 (d, $^2J(C,P) = 6.72$ Hz, *cis*-CO), 144.2 (d, $^2J(C,P) = 2.1$ Hz, C=, C5), 139.2 (s, CH=, C2), 139.1 (d, $^1J(C,P) = 23.2$ Hz, ipso-Ph), 137.0 (d, $^3J(C,P) = 9.6$ Hz, CH=, C3), 135.3 (d, $^2J(C,P) = 14.8$ Hz, CH=, C10), 129.8 (d, $^4J(C,P) = 1.8$ Hz, *p*-Ph), 129.3 (d, $^2J(C,P) = 15.9$ Hz,, CH=, C9), 128.6 (d, $^3J(C,P) = 8.0$ Hz, *m*-Ph), 128.0 (d, $^2J(C,P) = 8.3$ Hz, *o*-Ph), 126.5 (d, $^3J(C,P) = 1.3$ Hz, CH=, C4), 125.8 (d, $^2J(C,P) = 4.7$ Hz, CH=, C7), 123.0 (d, $^3J(C,P) = 5.6$ Hz, CH=, C6), 67.1 (d, $^1J(C,P) = 16.4$ Hz, CP, C1), 46.5 ppm (d, $^1J(C,P) = 18.8$, CHP, C8); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.01$ (ddddd, $^3J(H,H) = 7.2$ Hz, $^3J(H,H) = 4.8$ Hz, $^4J(H,H) = 0.9$ Hz, $^4J(H,H) = 0.9$ Hz, $^2J(H,P) = 0.8$ Hz, HC8), 5.99 (ddd, $^3J(H,H) = 6.2$ Hz, $^4J(H,H) = 0.9$ Hz, $^3J(H,P) = 9.2$ Hz, 1H; HC10), 6.17 (ddd, $^3J(H,H) = 9.5$ Hz, $^3J(H,H) = 7.2$ Hz, $^3J(H,P) = 9.5$ Hz, 1H; HC7), 6.25 (d, $^3J(H,H) = 2.4$ Hz, 1H; HC4), 6.32 (dd, $^3J(H,H) = 9.5$ Hz, $^4J(H,P) = 3.3$ Hz, 1H; HC6), 6.36 (ddd, $^3J(H,H) = 4.8$ Hz, $^3J(H,H) = 6.2$ Hz, $^3J(H,P) = 12.3$ Hz, 1H; HC9), 6.71 (m, 2H; *o*-Ph), 6.95 (ddd, $^3J(H,H) = 5.2$ Hz, $^3J(H,H) = 2.4$ Hz, $^4J(H,P) = 1.6$ Hz, 1H; HC3), 7.20 (m, 3H; *m*-Ph, *p*-Ph), 7.21 ppm (dd, $^3J(H,H) = 5.2$ Hz, $^4J(H,H) = 0.6$, 1H; HC2); HRMS: *m*/*z* calcd for $C_{21}H_{13}WPO_5$: 560.00104; found: 559.99988 ($\delta = 11.6 \times 10^{-4}$).

***syn*-11-Pentacarbonyltungsten-11-phenyl-4,10-dimethyl-7-isopropyl-11-phosphatricyclo-[6.2.1.0^{1,5}]undeca-2,4,6,9-tetraene (10)**: The reaction was executed and worked up in an analogous manner to that of **5**, but with **1** (0.624 g, 0.952 mmol), guaiazulene (0.118 g, 0.952 mmol), and CuCl (9.25 mg, 0.093 mmol) in dry toluene (5.5 mL), and required only 4 h until completion. Product ratios were determined from the crude reaction mixture by ^{31}P NMR spectroscopy, that is, **9**: 22%, **10**: 50%, **11**: 27%. Purification and partial separation by chromatography (activated silica, pentane/toluene 9:1) followed by fractional crystallization (pentane) afforded 317 mg of **10** (53%), 65 mg of **11** (10%) and 8 mg of **9** (1.3%).

Data for compound 10: Colorless crystals, m.p. 124–125 °C. ^{31}P NMR (101 MHz, $CDCl_3$): $\delta = 135.5$ ppm ($^1J(P,W) = 247.9$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 199.1$ (d, $^2J(C,P) = 24.3$ Hz, *trans*-CO), 196.1 (d, $^2J(C,P) = 6.8$ Hz, *cis*-CO), 143.7 (d, $^3J(C,P) = 7.8$ Hz, CH=, C3), 143.0 (d, $^2J(C,P) = 6.8$ Hz, C=, C7), 142.6 (d, $^2J(C,P) = 2.0$ Hz, C10), 140.1 (d, $^1J(C,P) = 26.2$ Hz, ipso-Ph), 137.2 (d, $^3J(C,P) = 5.6$ Hz, C=, C4), 135.2 (d, $^2J(C,P) = 3.5$ Hz, C=, C5), 133.7 (d, $^2J(C,P) = 1.9$ Hz, CH=, C2), 130.5 (d, $^2J(C,P) = 8.8$ Hz, *o*-Ph), 129.1 (s, *p*-Ph), 128.3 (d, $^3J(C,P) = 7.8$ Hz, *m*-Ph), 125.4 (s, CH=, C9), 115.3 (d, $^3J(C,P) = 8.7$ Hz, CH=, C6), 71.2 (d, $^1J(C,P) = 11.7$ Hz, CP, C1), 48.5 (d, $^1J(C,P) = 17.5$ Hz, CHP, C8), 35.8 (d, $^3J(C,P) = 5.8$ Hz, $(CHMe_2)$C7), 22.0 (s, CH_3, isopropyl), 20.4 (s, CH_3, isopropyl), 16.6 (d, $^3J(C,P) = 1.9$ Hz, MeC10), 12.7 ppm (s, MeC4); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.15$ (d, $^3J(H,H) = 6.8$ Hz, 3H; isopropyl), 1.19 (d, $^3J(H,H) = 6.8$ Hz, 3H; isopropyl), 1,20 (s, 3H; MeC10), 2.10 (d, 3H; $^5J(H,P) = 1.8$ Hz, MeC4), 2.64 (qq, $^3J(H,H) = 6.8$ Hz, $^3J(H,H) = 6.8$ Hz, $(HCMe_2)$C7), 3.68 (dd, $^2J(H,P) = 1.0$ Hz, $^3J(H,H) = 3.7$ Hz, CHP, HC8), 5.60 (dd, $^3J(H,P) = 10.5$ Hz, $^3J(H,H) = 3.7$ Hz, HC9), 6.45 (d, $^4J(H,P) = 5.5$ Hz, CH=, HC6), 6.87 (dd, $^4J(H,P) = 1.9$ Hz, $^3J(H,H) = 5.1$ Hz, HC3), 6.92 (dd, $^3J(H,P) = 2.4$ Hz, $^3J(H,H) = 5.1$ Hz, HC2), 7.28 (dt, $^5J(H,P) = 1.0$ Hz, $^3J(H,H) = 7.5$ Hz, *p*-Ph), 7.37 (dt, $^4J(H,P) = 2.0$ Hz, $^3J(H,H) = 7.5$ Hz, 2H; *m*-Ph), 7.47 ppm (m, $^3J(H,P) = 8.0$ Hz, 2H; *o*-Ph); HRMS: *m*/*z* calcd for $C_{26}H_{23}WPO_5$: 630.07928; found: 630.08342 ($\delta = 41.4 \times 10^{-4}$); elemental analysis calcd (%) for $C_{26}H_{23}O_5PW$: C 49.52, H 3.65; found: C 49.79, H 3.93.

***anti*-11-Pentacarbonyltungsten-11-phenyl-4,10-dimethyl-7-isopropyl-11-phosphatricyclo-[6.2.1.0^{1,5}]undeca-2,4,6,9-tetraene (11)**: Colorless crystals, m.p. 93–95 °C. ^{31}P NMR (101 MHz, $CDCl_3$): $\delta = 85.2$ ppm ($^1J(P,W) = 241.2$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 199.6$ (d, $^2J(C,P) = 25.3$ Hz, *trans*-CO), 197.2 (d, $^2J(C,P) = 6.9$ Hz, *cis*-CO), 145.5 (d, $^2J(C,P) = 25.3$ Hz, C=, C10), 143.7 (d, $^2J(C,P) = 6.9$ Hz, C=, C7), 141.6 (d, $^3J(C,P) = 9.2$ Hz, CH=, C3), 139.6 (d, $^1J(C,P) = 23.8$ Hz, ipso-Ph), 137.6 (d, $^2J(C,P) = 2.3$ Hz, C5), 136.8 (s, CH=, C2), 134.1 (d, $^3J(C,P) = 1.5$ Hz, C=, C4), 129.5 (d, $^4J(C,P) = 1.5$ Hz, *p*-Ph), 128.1 (d, $^2J(C,P) = 8.4$ Hz, *o*-Ph), 127.7 (d, $^3J(C,P) = 8.0$ Hz, *m*-Ph), 123.9 (d, $^2J(C,P) = 14.6$ Hz, CH=, C9), 112.8 (d, $^3J(C,P) = 4.6$ Hz, C6), 68.8 (d, $^1J(C,P) = 20.7$ Hz, C=, C1), 49.6 (d, $^1J(C,P) = 19.9$ Hz, CHP, C8), 36.8 (d, $^3J(C,P) = 3.8$ Hz, $(CHMe_2)$C7), 22.6 (s, CH_3, isopropyl), 21.0 (s, CH_3, isopropyl), 16.3 (d, $^3J(C,P) = 3.1$ Hz, 3H; MeC10), 12.5 ppm (s, 3H; MeC4); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.03$ (d, $^3J(H,H) = 6.72$ Hz, 3H; isopropyl), 1.13 (d, $^3J(H,H) = 6.72$ Hz, 3H; isopropyl), 1.54 (d, $^4J(H,H) = 1.61$ Hz, 3H; MeC10), 1.83 (s, 3H; MeC4), 2.47 (qq, $^3J(H,H) = 6.72$ Hz, $^3J(H,H) = 6.72$ Hz, 1H; $(HCMe_2)$C7), 3.78 (dd, $^3J(H,H) = 4.84$ Hz, $^2J(H,P) = 1.07$ Hz, CHP, HC8), 5.93 (ddq, $^3J(H,H) = 4.84$ Hz, $^4J(H,H) = 1.61$ Hz, $^3J(H,P) = 13.72$ Hz, HC9), 5.94 (d, $^4J(H,P) = 1.62$ Hz, HC6), 6.62 (m, 2H; *o*-Ph), 6.87 (dd, $^3J(H,H) = 5.18$ Hz, $^4J(H,P) = 1.44$ Hz, HC3), 7.08 (dd, $^3J(H,H) = 5.18$ Hz, $^3J(H,P) = 3.18$ Hz, HC2), 7.15 ppm (m, *m*-Ph, *p*-Ph); HRMS: *m*/*z* calcd for $C_{21}H_{13}WPO_5$: 630.07928; found: 630.08117 ($\delta = 18.9 \times 10^{-4}$).

***P*-Pentacarbonyltungsten-*P*-phenyl-1-phosphino-3,8-dimethyl-5-isopropylazulene (9)**: Blue crystals; ^{31}P NMR (101 MHz, $CDCl_3$): $\delta = -31.8$ ppm (d, $^1J(P,W) = 230.4$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 200.6$ (d, $^2J(C,P) = 20.87$ Hz, *trans*-CO), 197.3 (d, $^2J(C,P) = 6.24$ Hz, *cis*-CO), 147.1 (s, C=, C8a), 146.3 (d, $^2J(C,P) = 17.27$ Hz, CH=, C2), 143.4(s, C=, C5), 141.0 (s, C=, C3a), 138.7 (CP=, C1), 136.9 (s, CH=, C7), 135.0 (s, CH=, C4), 132.7 (d, $^3J(C,P) = 12.24$ Hz, *m*-Ph), 130.4 (d, $^4J(C,P) = 2.16$ Hz, *p*-Ph), 130.0 (s, CH=, C6), 129.6 (s, C=, C8), 125.8 (s, C=, C3), 129.2 (d, $^2J(C,P) = 10.08$ Hz, *o*-Ph), 38.5 (s, $(CHMe_2)$C5), 29.0 (d, $^4J(C,P) = 5.04$ Hz, MeC8), 25.0 (s, 2Me, isopropyl), 13.3 ppm (s, MeC3); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.36$ (d, $^3J(H,H) = 6.89$ Hz, 6H; isopropyl), 2.61 (s, 3H; MeC3), 2.96 (s, 3H; MeC8), 3.08 (sept, $^3J(H,H) = 6.89$ Hz, 1H; $(HCMe_2)$C5), 7.06 (d, $^3J(H,H) = 10.99$ Hz, 1H; HC6), 7.44 (dd, $^3J(H,H) = 10.99$ Hz, $^5J(H,P) = 1.85$ Hz, 1H; HC7), 7.3–7.6 (m, 5H; Ph), 7.59 (d, $^1J(H,P) = 348.30$ Hz, HP), 7.81 (d, $^3J(H,P) = 8.60$ Hz, 1H; HC2), 8.19 ppm (s, 1H; HC4); HRMS: *m*/*z* calcd for $C_{21}H_{13}WPO_5$: 630.07928; found: 630.07894 ($\delta = 3.4 \times 10^{-4}$).

Crystal structure determination of 10: $C_{26}H_{23}O_5PW$, $M_r = 630.26$, colorless block, $0.48 \times 0.26 \times 0.12$ mm^3, triclinic, $P\bar{1}$ (no. 2), $a = 8.9493(5)$, $b = 11.5213(8)$, $c = 13.3627(7)$ Å, $\alpha = 88.189(5)$, $\beta = 75.457(4)$, $\gamma = 67.258(5)$°, $V = 1226.65(14)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.706$ g cm^{-3}, $\mu = 4.808$ mm^{-1}; 43486 reflections were measured on a Nonius KappaCCD diffractometer with rotating anode ($\lambda = 0.71073$ Å) at a temperature of 150(2) K up to a resolution of $(\sin\theta/\lambda)_{max} = 0.65$ Å^{-1}; 5626 reflections were unique ($R_{int} = 0.024$). An absorption correction based on multiple measured reflections was applied (0.28–0.56 transmission). The structure was solved with automated Patterson methods (DIRDIF-99)[31] and refined with SHELXL-97[32] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters; methyl and phenyl hydrogen atoms were refined as rigid groups; all other hydrogen atoms were refined freely with isotropic displacement parameters. 322 refined parameters, no

restraints. R values [$I > 2\sigma(I)$]: $R1 = 0.0125$, $wR2 = 0.0278$. R values (all data): $R1 = 0.0150$, $wR2 = 0.0284$. GoF = 1.086. Residual electron density between -0.58 and $0.33\ e\ Å^{-3}$. Molecular illustration, structure checking and calculations were performed with the PLATON package.[33] CCDC 228857 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html, by emailing data request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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