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Remarkable Metal-Complexed Phosphorus Analogues of the Cyclopropenylcarbene–Cyclobutadiene Rearrangement

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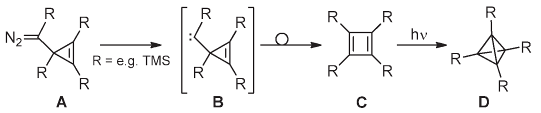
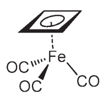
S *Supporting Information*

ABSTRACT: In situ-generated metal carbonyl-complexed cyclopropenylphosphinidenes undergo a sequence of structural changes leading to phosphorus analogues of Pettit's seminal (η^4-cyclobutadiene)iron tricarbonyl complex via multiple valence isomers along the reaction pathway and the elimination of one molecule of carbon monoxide.

Cyclobutadiene (CBD, **C**) has intrigued chemists for decades,[1] with landmarks such as the isolation of the parent C_4H_4 inside a hemicarcerand cage,[2] the photoisomerization of a derivative to the highly strained tetrahedrane **D**,[3] and the formation of the seminal (η^4-cyclobutadiene)iron tricarbonyl complex (**E**).[4] One effective route to CBD is ring expansion of the in situ-generated cyclopropenylcarbene **B** by N_2 elimination from cyclopropenyldiazomethane **A**.[5] This elegant rearrangement (**B** → **C**) has also been applied for sila[6] and aza analogues,[7,8] but detailed mechanistic insight is still lacking. In view of the diagonal C–P relationship, it is surprising that the phosphacyclobutadiene ring structure (P_1-CBD)[9] is known only as a rare transition-metal ligand (**F**) constructed from phosphaalkynes ($R_1C{\equiv}P$) and alkynes[10] and that no phosphatetrahedranes (P_1-**D**) have ever been synthesized.[11] Here we report on the application of the phosphorus analogue of the cyclopropenylcarbene–cyclobutadiene rearrangement for the selective formation of the P_1 analogues of Pettit's complex **E**. A detailed computational study has shown that the facile isomerization of the in situ-generated metal carbonyl-complexed cyclopropenylphosphinidenes P_1-**B**[12,13] comes with surprises and has highlighted for the first time the connection of P_1-**B** with the corresponding tetrahedranes P_1-**D**.





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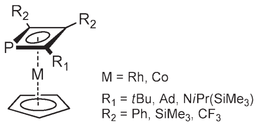

F

In this study, we focused on the rearrangement of the sterically shielded 1,2,3-tris(*tert*-butyl)cyclopropenyl-substituted phosphinidenes[14] **4** bearing the metal carbonyl (ML_n) fragments $Fe(CO)_4$ (**a**), $W(CO)_5$ (**b**), and $Mo(CO)_5$ (**c**) (Scheme 1). These transient intermediates can be generated by thermal fragmentation of the corresponding 3*H*-3-benzo[*d*]phosphepines **3**.[15] The starting material for **3**, bis(trimethylsilyl)-1,2,3-tris(*tert*-butyl)cyclopropenylphosphane (**1**) (^{31}P NMR: $\delta = -134.6$ ppm, $^1J_{PSi} = 47.6$ Hz) was prepared according to literature procedures[16] and converted quantitatively into its primary phosphane (^{31}P NMR: $\delta = -119.1$ ppm, $^1J_{PH} = 189.3$ Hz) using 2.4 equiv of MeOH. Subsequent complexation with the appropriate metal carbonyl source afforded the air- and moisture-stable complexes **2a**–**c** after purification by column chromatography (54–64%; Scheme 1). Subsequently, the base-catalyzed double hydrophosphination of 1,2-diethynylbenzene with the primary phosphane complexes **2** afforded phosphepines **3**, albeit in modest yields [12–41%; ^{31}P NMR: $\delta = 36.2$ (**3a**), -16.9 (**3b**), 1.5 ppm (**3c**)], which we ascribed to the bulky nature of the P substituent (see the Supporting Information).

Thermal fragmentation of **3a**–**c** at 100 °C in toluene selectively generated the η^4-phosphacyclobutadiene complexes **5** (Scheme 1), which were isolated in 52–65% yield after subliming of naphthalene and filtration of the residue over Al_2O_3. No structural isomers of **5** could be detected by ^{31}P NMR spectroscopy during the reaction. The molecular structures of Fe complex **5a** and the W analogue **5b** were established unequivocally by single-crystal X-ray analyses (Figure 1)[17], which revealed an essentially planar P_1-CBD ring with delocalized P–C and C–C bonds [for **5b**: P1–C1, 1.8143(16); C1–C2, 1.468(2)]. The Fe–P and Fe–C separations in **5a** are comparable to those in the P_2 analogue [$Fe(\eta^4\text{-}P_2C_2R_2)(CO)_3$] (R = *t*Bu, Mes)[18] and the 16-electron complex [$Fe(\eta^4\text{-}P_2C_2tBu_2)_2$][19] and ~0.2 Å shorter than the W–P and W–C distances in **5b**.

The elegant conversion of **3** to **5** in which one CO ligand is eliminated to accommodate the change in coordination of the P ligand from η^1 to η^4 raises mechanistic questions, which we addressed with density functional theory (DFT) calculations at the B3PW91/6-311G(d,p) (LANL2DZ for Fe) level[20a] on Fe-containing model structures with Me instead of *t*Bu substituents (labeled **3a′**, **4a′**, etc.). The first reaction step concerns the thermally accessible electrocyclization of **3a′** ($\Delta E^{\ddagger} = 25.4$ kcal mol^{-1}, $\Delta E = 17.9$ kcal mol^{-1}), which is followed by fragmentation into naphthalene and cyclopropenylphosphinidene **4a′** ($\Delta\Delta E = -14.5$ kcal mol^{-1}).[15,20a] The **3a′** → **4a′** process is exergonically driven ($\Delta E = 3.4$ kcal mol^{-1}; $\Delta G = -9.8$ kcal mol^{-1} at 298.15 K).

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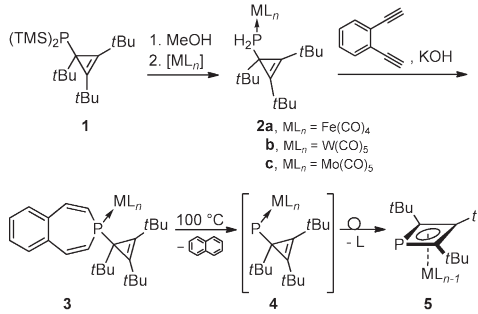
Scheme 1. Synthesis of Complexed Cyclopropenylphosphines 2, Benzophosphepines 3, and Phosphacyclobutadienes 5



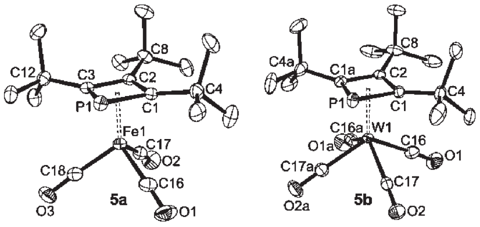


Figure 1. Displacement ellipsoid plots (50% probability) of **5a** (only one of two independent molecules is shown) and **5b**. All of the hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for **5a**: Fe1−P1, 2.2881(6); Fe1−C1/C2/C3, 2.0939(18)−2.1488(19); Fe1−C16/C17/C18, 1.784(2)−1.789(2); P1−C1, 1.816(2); P1−C3, 1.814(2); C1−C2, 1.460(3); C2−C3, 1.469(3); P1−C1−C2−C3, −6.03(13). For **5b**: W1−P1, 2.4972(5); W1−C1, 2.2872(15); W1−C2, 2.323(2); W1−C16, 2.0306(18); W1−C17, 2.0137(18); P1−C1, 1.8143(16); C1−C2, 1.468(2); P1−C1−C2−C1a, −6.77(15). Symmetry operation a: *x*, 0.5 − *y*, *z*.

We found that the unimolecular rearrangement of the complexed singlet cyclopropenylphosphinidene **4a′** into the corresponding phosphacyclobutadiene can occur by two competitive torque-dependent motions that differ in the degree of rotation of the $Fe(CO)_4$ group around the P1−C1 bond (Figure 2). In the most facile one, a slight counterclockwise rotation around the P1−C1 axis enables P1−C2 bond formation to give zwitterionic 2-phosphabicyclo[1.1.0]butane *exo*-**6a′** ($\Delta E^{\ddagger}$ = 1.6 kcal mol^{-1}, ΔE = −12.3 kcal mol^{-1}),[21] which subsequently undergoes a barrierless transannular C−C bond stretching[22] to afford zwitterionic four-membered *exo*-**7a′** ($\Delta\Delta E$ = −1.9 kcal mol^{-1}) (Scheme 2). In the less favorable path, $Fe(CO)_4$ rotates further in the same direction, enabling P1−C3 bond formation ($\Delta E^{\ddagger}$ = 5.3 kcal mol^{-1} (**TS1*endo***), ΔE = 2.7 kcal mol^{-1}) to generate the puckered species *endo*-**6a′**$_{eq}$ having the P ligand at the equatorial site; *endo*-**6a′**$_{eq}$ then readily undergoes a Berry pseudorotation[23] to the more stable structure *endo*-**6a′**$_{ax}$ ($\Delta\Delta E$ = −2.1 kcal mol^{-1}) in which the P-ligand is at the axial site. Notably, the charge recombination in *endo*-**6a′**$_{ax}$ by P1−C2 bond formation to form phosphatetrahedrane **8a′** is *endo*thermic ($\Delta\Delta E$ = 8.2 kcal mol^{-1}; Figure 2), and thus, bond-stretching isomerization to give *exo*-**7a′** ($\Delta\Delta E^{\ddagger}$ = 0.7 kcal mol^{-1}, $\Delta\Delta E$ = −14.8 kcal mol^{-1}; Figure 2) is preferred.[24] This puckered structure is favored by a remarkable 3.6 kcal mol^{-1} over the planar η^1-phosphacyclobutadiene complex **9a′** (Scheme 2).[25]

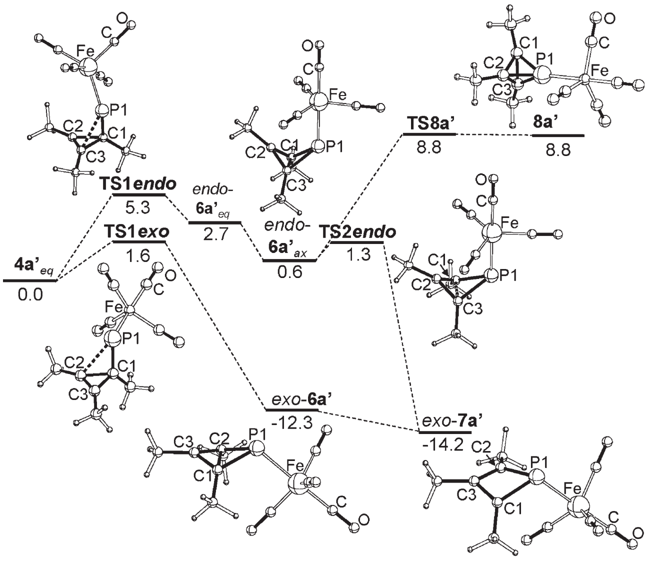
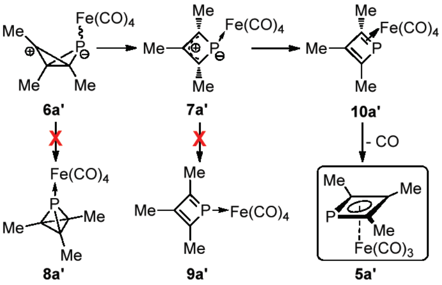


Figure 2. Relative B3PW91/6-311G(d,p) (LANL2DZ for Fe) energies [zero-point energy (ZPE)-corrected, in kcal mol^{-1}] for the rearrangement of **4a′** to **7a′**.

Scheme 2. Relevant Valence Isomers of Phosphinidene 4a′ and their Connectivities



Further stabilization occurs when the zwitterionic nature of η^1-complexed P_1-CBD **7a′** is removed through η^2 coordination of $Fe(CO)_4$, thereby giving **10a′** ($\Delta\Delta E$ = −10.3 kcal mol^{-1}; Scheme 2). The final step of the reaction pathway concerns the elimination of CO ($\Delta\Delta E^{\ddagger}$ = 18.0 kcal mol^{-1}, **TS10a′-5a′**) to give the experimentally ascertained η^4-complexed phosphacyclobutadiene **5a′** ($\Delta\Delta E$ = −6.4 kcal mol^{-1}; Figure 3).

While the experimental findings are fully supported by the DFT calculations, a question remains: why does the $Fe(CO)_4$-complexed phosphatetrahedrane **8a′** isomerize so easily? After all, carbon tetrahedrane **D** is kinetically stable (see the Supporting Information). Likewise, calculations on the similarly substituted metal-free system (labeled ″) showed that phosphatetrahedrane **8a″** is favored over *endo*- and *exo*-**6a″** (ΔE = 13.6 and 11.7 kcal mol^{-1}, respectively) and only slightly less stable than phosphacyclobutadiene **9a″** (ΔE = 4.1 kcal mol^{-1}). The effect of metal complexation became evident from an extended transition state−natural orbitals for chemical valence (ETS−NOCV) analysis[20b] of the $(OC)_4Fe$−P bond in these species, which revealed normal iron−phosphine interactions for **8a′** (σ-donation: −37.6 kcal mol^{-1}, 0.56e$^-$; π back-donation: −14.6 kcal mol^{-1}, 0.2e$^-$),[26] but an exceptionally strong Fe−P σ bond for *endo*-**6a′** (σ donation: −68.7 kcal mol^{-1}, 0.78e$^-$; π back-donation: −15.5 kcal mol^{-1}, 0.18e$^-$), as the metal

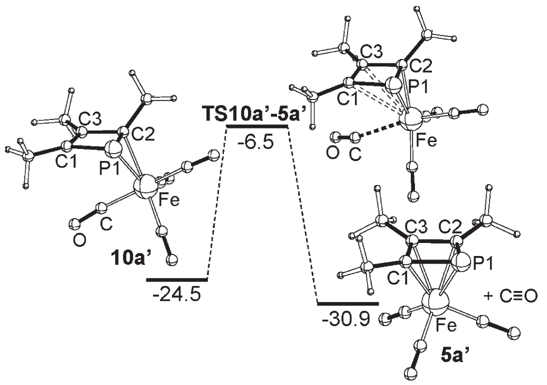


Figure 3. Relative B3PW91/6-311G(d,p) (LANL2DZ for Fe) energies (ZPE-corrected, in kcal mol^{-1}) for the rearrangement of **10a′** to **5a′**.

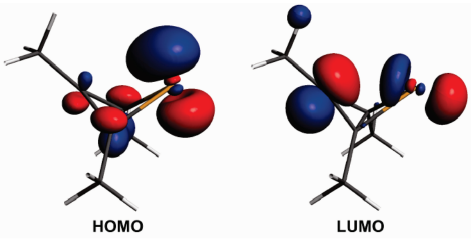


Figure 4. Frontier orbitals of *endo*-**6a″** (HOMO, doubly occupied p_z orbital on P; LUMO, mainly empty p_z orbital on C) at an isosurface value of 0.08.

group does not bind to the phosphorus lone pair but instead to the higher-lying (−3.4 eV) doubly occupied p_z orbital (Figure 4). Thus, the added stabilization of the negatively charged phosphorus atom by metal complexation is the reason that zwitterionic *endo*-**6a′** is more stable than tetrahedrane **8a′**. Planar η^1-phosphacyclobutadiene **9a′** (σ donation: −40.3 kcal mol^{-1}, 0.71e$^-$; π back-donation: −24.1 kcal mol^{-1}, 0.32e$^-$) is for the same reason less stable than zwitterionic *exo*-**7a′** (σ donation: −71.2 kcal mol^{-1}, 0.83e$^-$; π back-donation: −13.2 kcal mol^{-1}, 0.16e$^-$).

In conclusion, we have shown that the phosphorus analogue of the cyclopropenylcarbene−cyclobutadiene rearrangement provides a simple protocol for generating η^4-phosphacyclobutadiene complexes. The influence of the transition metal carbonyl fragment in the zwitterionic η^1 intermediate, as revealed by theoretical calculations, prohibits the formation of a complexed P_1-tetrahedrane, but our theoretical analysis indicates that the metal-free P_1-tetrahedrane is a viable synthetic target.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Cartesian coordinates and energies of all stationary points, crystallographic data (CIF), copies of the NMR spectra of all new compounds, and complete ref 20a (as SI ref 8). This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) CCDC 796777 (**5a**) and 796778 (**5b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. For the experimental details of the X-ray crystal structure determinations, see the Supporting Information.

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(21) The iron fragment in **TS1*exo*** has a distorted trigonal pyrimidal geometry, which indicates a Berry pseudorotation during the $\mathbf{4a}'_{eq}$ → *exo*-$\mathbf{6a}'_{ax}$ conversion. *exo*-**6a**′ is a saddle point on the PES for the rearrangement of **4a**′ into *exo*-**7a**′.

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