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Nonbenzenoid aromaticity of 1-phosphafulvenes: synthesis of phosphacymantrenes†

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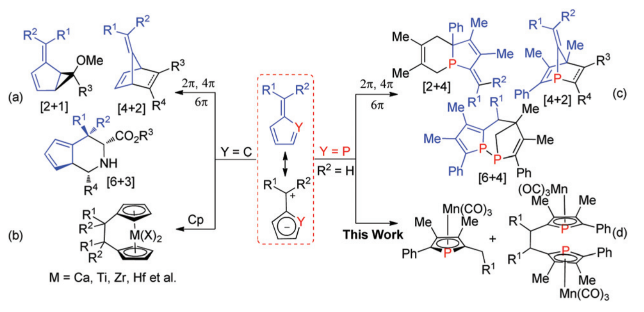
The coordination chemistry of 1-phosphafulvenes was investigated by employing their [6 + 4] adducts or α-C_2-bridged biphospholes as a precursor. Unbridged phosphacymantrenes arise from 1-phosphafulvenes *via* proton abstraction. α-C_2-bridged biphosphacymantrenes are probably yielded by the reductive coupling of 1-phosphafulvene with $Mn_2(CO)_{10}$. The coordination behavior of 1-phosphafulvenes is comparable to that of pentafulvenes, which again demonstrates the phosphorus-carbon analogy in low-coordinate organophosphorus chemistry.

Pentafulvenes are cyclic isomers of benzene with nonbenzenoid aromaticity and are unique in their rich and varied cycloaddition chemistry as well as organometallic chemistry.[1] Pentafulvenes can act as 2π, 4π, or 6π systems in cycloaddition and have been recognized as valuable synthons for the construction of polycycles and natural products[1b,2] (Scheme 1a). Another remarkable feature of pentafulvenes is the π electron shift from the exocyclic olefin to the endocyclic aromatic Cp ring,[3] which displays a wide array of coordination modes to metals. In particular, the reductive dimerization of fulvenes readily gives access to *ansa*-metallocene derivatives of Ca for transmetalation to numerous transition metals[1c,4] (Scheme 1b).

However, the chemistry of phosphafulvenes, the phospha-analogues of pentafulvenes, has been virtually unexplored. This is probably because of the high reactivity of the C═P bond that stems from weak π-bond strength (45 kcal mol^{-1} in $HP{=}CH_2$ *vs.* 65 kcal mol^{-1} for $CH_2{=}CH_2$).[5] With kinetic stabilization by the bulky 2,4,6-tri-*tert*-butylphenyl group (Mes*), Yoshifuji prepared the first isolable 1,3,6-triphosphafulvene.[6] However, the bulky Mes* group hampered the investigation of phosphafulvene chemistry. We have demonstrated that *in situ* generated unhindered 1-phosphafulvenes can act as 2π, 4π, or 6π precursors in cycloaddition chemistry[7] (Scheme 1c). The unusual addition of 1-phosphafulvene to benzoquinone was discovered by the same *in situ* generation strategy,[8] but the formation of phosphametallocenes by coordination of 1-phosphafulvene with transition metals has never been explored.

Phosphametallocene, the η^5 coordination of phospholide[9] with a transition metal cation, behaves as a strong π acceptor and weak σ donor, closer in behavior to CO than to ordinary phosphines.[10] The coordination chemistry of phosphaferrocenes has been widely explored and has been successfully applied in homogeneous catalysis.[11] In comparison, less attention has been paid to phosphacymantrene (phospholylmanganese tricarbonyls) derivatives, which are more stable as compared to phosphaferrocenes in air. Notably, methylcymantrene is stable enough to be used as a lead-free antiknock derivative in gasoline and related fuels.[12] Thus, it is interesting to prepare phosphacymantrene from 1-phosphafulvene.

It is known that 1-phosphafulvene **1** reacts with 2*H*-phosphole to give a [6 + 4] cycloadduct **2** in low yield due to the dissociation of the adduct.[7] The easy dissociation of **2** suggests that it can be used as a precursor of phosphafulvene.



Scheme 1 The cycloaddition and coordination chemistry of pentafulvenes and 1-phosphafulvenes.

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† Electronic supplementary information (ESI) available: X-ray crystal structure analysis of compounds. CCDC 2009638 (**5a**); 2021606 (**5b**); 2009639 (**7b**), 2009640 (**8a**) and 2011029 (**9**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0dt03934a

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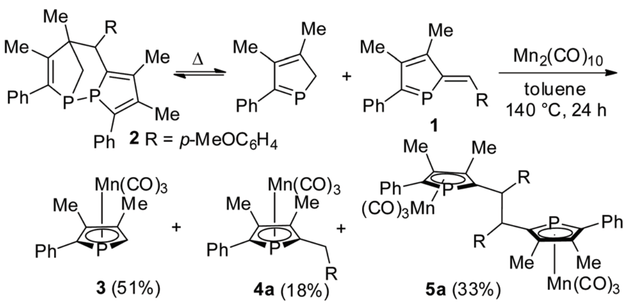
The reaction of **1** with 1 equivalent of decacarbonyldimanganese $Mn_2(CO)_{10}$ was carried out at 140 °C in a heavy wall pressure tube (Scheme 2). The ^{31}P NMR signals (δ −25.0, −29.5, and −35.8 ppm) of the crude reaction mixture show that the reaction gives three products, with a typical high-field position, similar to the reported examples of phosphacymantrenes.[13] The reaction of 2*H*-phosphole with $Mn_2(CO)_{10}$ gave 3,4-dimethyl-2-phenylphosphacymantrene **3**. The NMR data of **3** were consistent with the literature report.[14] The structure of **4a** was deduced from mass, ^1H, and ^{13}C NMR spectroscopy. Multiple peaks between 3.40 and 3.44 ppm in the ^1H NMR spectrum are assigned to CH_2. The ^{13}C NMR spectrum of **4a** shows a characteristic phospholyl carbon at 115.3, 116.1, 119.0, and 119.9 ppm with a very high $^1J_{C-P}$ coupling constant ($^1J_{C2-P}$ = 57.0 Hz, 60.8 Hz). α-C_2-bridged biphosphacymantrene **5a** was isolated in a 33% yield. The structure of **5a** was unambiguously established by X-ray crystallographic analysis (Fig. 1, left). The two phosphacymantrene rings are in a head-to-tail disposition with the two $Mn(CO)_3$ moieties having the same orientation and in the *para*-position of the C–C bridge in order to minimize steric crowding. The observation of products **3**, **4a** and **5a** implies a radical based mechanism. Phosphacymantrene **4a** originates from 1-phosphafulvene **1** and abstracts H· from 2*H*-phosphole during the reaction, along with the formation of **3**. A similar proton abstraction process was observed in the reductive coupling of dimethylfulvene.[15]

Since the reaction with **2** will give **3** as a co-product, the reaction was then explored with a facilely prepared α-C_2-bridged biphospholes **6**.[16] The versatile cycloaddition of 1-phosphafulvenes has been revealed by employing biphospholes **6** as precursors.[7] As shown in Scheme 3, the reaction of biphospholes **6a** with 1 equivalent of $Mn_2(CO)_{10}$ readily gave four phosphacymantrene derivatives. Besides the same products **4a** and **5a** from **1** as shown in Scheme 2, the reaction with **5a** offered additional C_2-bridged phosphacymantrenes **7a** and **8a**. The structure of **7a** was deduced by comparing the NMR data of **7a** and **7b**, as well as the X-ray crystal structure of **7b** (Fig. 2, right). The structure of **8a** was definitively established by performing an X-ray study (Fig. 1, right). In **7a** and **8a**, the phospholyl ligand acts not only as a six-electron η^5-ligand towards a single metal but also as an eight-electron η^5,η^1-ligand with the phosphorus lone pair providing additional two electrons. The incorporation of phosphorus into fulvene backbones provides an extra two-electron coordination site. The two phospholyl ligands are in a head-to-tail disposition for **7a** and a head-to-head disposition for **8a**. When p-$MeOC_6H_4$ was replaced by 2-pyridinyl, the reaction with **6b**[17] produced similar products. The X-ray structure of **5b** (Fig. 2, left) shows that the stereochemistry is different from



Scheme 2 Coordination chemistry of **2** with $Mn_2(CO)_{10}$.

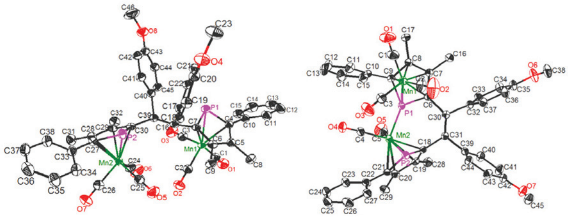
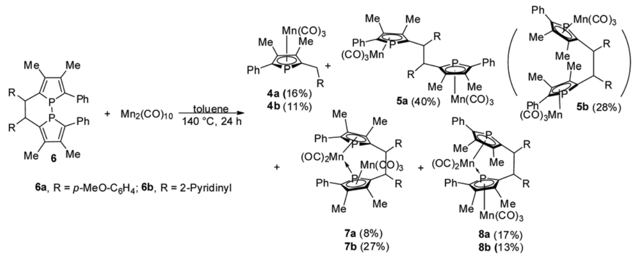


Fig. 1 X-ray crystal structures of **5a** (left) and **8a** (right). All hydrogen atoms are omitted for clarity; the level set for thermal ellipsoids of all atoms is 30%. Main bond lengths (Å) and angles (°): **5a**: Mn1–P1 2.3898(9), C4–P1 1.771(3), C7–P1 1.786(3), Mn1–phospholyl centroid 1.7800(5), Mn2–P2 2.3835(10), C27–P2 1.775(3), C30–P2 1.779(3), Mn2–phospholyl centroid 1.7742(5); C4–P1–C7 90.20(15), C16–C7–P1 125.4(2), C27–P2–C30 90.23(15), C39–C30–P2 126.0(2). **8a**: Mn1–P1 2.4025(13), Mn2–P1 2.1326(12), C6–P1 1.747(4), C9–P1 1.744(4), Mn1-phospholyl centroid 1.7781(7), Mn2–P2 2.3773(13), C18–P2 1.796(4), C21–P2 1.800(4), Mn2–phospholyl centroid 1.7584(6); Mn1–P1–Mn2 137.43(6), P1–Mn2–P2 93.84(4), C6–P1–C9 93.42(19), C18–P2–C21 89.54(19).



Scheme 3 Coordination chemistry of **6** with $Mn_2(CO)_{10}$.

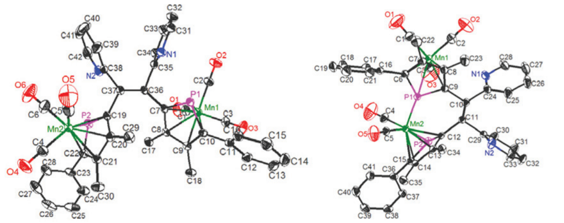


Fig. 2 X-ray crystal structures of **5b** (left) and **7b** (right). All hydrogen atoms are omitted for clarity; the level set for thermal ellipsoids of all atoms is 30%. Main bond lengths (Å) and angles (°): **5b**: Mn1–P1 2.3723(8), C7–P1 1.786(3), C10–P1 1.776(3), Mn1–phospholyl centroid 1.7834(4), Mn2–P2 2.3752(8), C19–P2 1.780(3), C22–P2 1.776(3), Mn2–phospholyl centroid 1.7771(4); C7–P1–C10 89.84(13), C36–C7–P1 123.50(19), C19–P2–C22 89.54(13), C37–C19–P2 123.8(2). **7b**: Mn1–P1 2.3989(8), Mn2–P1 2.1499(7), C6–P1 1.754(2), C9–P1 1.761(3), Mn1–phospholyl centroid 1.7952(5), Mn2–P2 2.3746(7), C12–P2 1.779(2), C15–P2 1.783(2), Mn2–phospholyl centroid 1.7651(4); C6–P1–C9 92.75(12), C12–P2–C15 89.31(11), P1–Mn2–P2 111.80(3).

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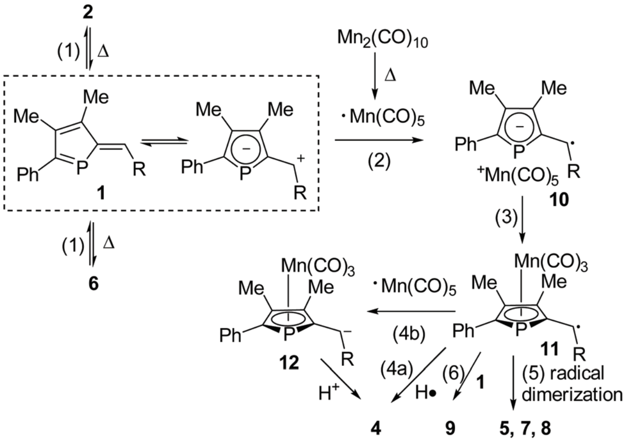
that of **5a**, which agrees with the NMR data. The X-ray crystal structure of **7b** (Fig. 2) demonstrates that the two phosphacymantrene rings are on the same side of the bridge and approximately parallel with a head-to-tail disposition. The two Mn(CO)$_3$ moieties are in opposite directions. The structure of **8b** was deduced from the *p*-MeOC$_6$H$_4$ analogy.

The distances between Mn and the η^5-phospholyl centroid in **7** and **8** are in the range of 1.758–1.795 Å, which are similar to those in the phosphacymantrenes[18] and bridged cymantrene derivatives.[19] In the case of **7b**, the distances between Mn and the η^5-phospholyl centroid are quite different (Mn1–phospholyl centroid = 1.795 Å, Mn2–phospholyl centroid = 1.765 Å). The η^1-coordination of P1 to Mn2 reduces the electron density of the phospholide ring of P1 which weakens the η^5-coordination with Mn1 and shows a longer distance (1.795 Å) than that of **5b** (1.783 Å). Meanwhile, the η^1-coordination of P1 to Mn2 increases the back donation from Mn2 to the phospholide ring of P2 and reinforces the coordination effect, reflecting the short distance between Mn2 and the phospholyl centroid (1.765 Å). The IR spectra of all products were collected. The infrared CO stretching frequencies of the products are comparable to those of the known phosphacymantrenes.[20]

Furthermore, we obtained a single crystal of **9** occasionally, which contains three 1-phosphafulvene moieties. The structure of **9** also suggests the reaction of **6** with Mn$_2$(CO)$_{10}$ *via* 1-phosphafulvenes. Unfortunately, we did not observe the ^{31}P NMR signals corresponding to **9** in the crude reaction mixture, and no other data are available at present for **9** except the X-ray analysis results (Fig. 3).

It was known that the reductive coupling of pentafulvenes with metals afforded *ansa*-metallocene complexes.[4,21] The formation of proton abstraction product **4** and the formation of **9** suggest a mechanism involving 1-phosphafulvene. A plausible mechanism was proposed (Scheme 4) on the basis of experimental results and literature reports on the reductive dimerization of pentafulvenes. (1) Upon heating, 1-phosphafulvene **1** is obtained by either retro-[6 + 4] cycloaddition of **2** or the dissociation of biphosphole **6**. (2) A radical anion intermediate **10** is formed by transferring an electron from ·Mn(CO)$_5$ to 1-phosphafulvene. (3) The coordination with Mn(CO)$_3$ gives phosphacymantrene radical **11**. (4) There are two possible routes to afford the unbridged product **4**: (a) a H· abstraction from **11** affords unbridged product **4** or (b) **11** reacts with the ·Mn(CO)$_5$ species to give anionic phosphacymantrene intermediate **12** which is converted into **4** after the H$^+$ abstraction. (5) The radical dimerization of **11** provides bridged products **5**, **7**, and **8**. However, we cannot exclude the formation of **5**, **7**, and **8** by the P–P bond cleavage of **2** or **6** with Mn$_2$(CO)$_{10}$. (6) The 1,6-radical addition of **11** to 1-phosphafulvene **1** yields the unexpected product **9**.



Scheme 4 Plausible mechanism.

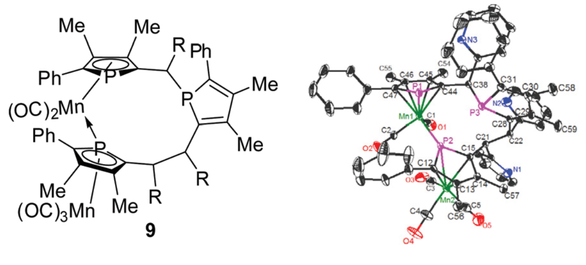


Fig. 3 Molecular structure of **9**. All hydrogen atoms are omitted for clarity; the level set for thermal ellipsoids of all atoms is 30%. Main bond lengths (Å) and angles (°): Mn1–P1 2.3886(14), C44–P1 1.781(4), C47–P1 1.786(4), Mn1–phospholyl centroid 1.7874(8), Mn1–P2 2.1809(11), Mn2–P2 2.4099(12), C12–P2 1.759(4), C15–P2 1.765(4), Mn2–phospholyl centroid 1.7866(9), C31–P3 1.800(4); P1–Mn1–P2 90.58(5), C44–P1–C47 89.0(2), C12–P2–C15 91.99(19).

In conclusion, we have demonstrated the remarkable coordination chemistry of manganese carbonyls with 1-phosphafulvene which was generated *in situ*. α-C$_2$-bridged biphosphacymantrenes were obtained probably *via* the reductive coupling of 1-phosphafulvenes. Unbridged phosphacymantrenes **4** were formed by the abstraction H· or H$^+$. This is the first illustration of nonbenzenoid aromaticity of 1-phosphafulvenes. The coordination chemistry of fulvenes was replicated in their phospha-analogues successfully, which highlighted the analogy between phosphorus and carbon in low-coordinate "phosha-organic" chemistry.[22] Finally, we believe that these phosphacymantrenes have potential applications in coordination and catalytic reactions based on their good stability and π-acceptor property.

Conflicts of interest

There are no conflicts to declare.

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