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Carbon-free D_{3d} $[E_3ME_3]^{2-}$ (E=P, As; M=Ni, Pd, Pt): The smallest inorganic sandwich complexes with aromatic η^3-P_3^- and η^3-As_3^- ligands

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A density functional theory and wave function theory investigation on the possibility of carbon-free phosphametallocenes $[P_3MP_3]^{2-}$ and arsenametallocenes $[As_3MAs_3]^{2-}$ (M=Ni, Pd, Pt) is presented in this work. Staggered singlet D_{3d} $[E_3ME_3]^{2-}$ (E=P, As)–the smallest inorganic metallocenes possible to construct-proved to be the global minima of the heptaatomic systems and may be targeted in future experiments. Cyclo-P_3^- and cyclo-As_3^- turned out to possess similar aromaticity to cyclo-P_5^- and cyclo-As_5^- and may serve as effective ligands to sandwich a wide range of transition metals. The first vertical electron detachment energies of C_s $[E_3ME_3]Li^-$ monoanions with a staggered $[E_3ME_3]^{2-}$ sandwich core were predicted to be between 2.7 and 2.9 eV; the extent of stabilization by Li^+ suggests that such materials be viable targets for experimental characterization.

phosphorus, arsenic, sandwich complexes, density functional theory, geometries, electronic structures.

1 Introduction

Being in a diagonal relationship with C in the periodic table, P is electronically equivalent (isolobal) to a CH group and can form various complexes with substituent-free cyclic and acyclic phosphorus ligands [1–13]. Other group 15 elements, especially the immediate follower As, possess certain similarities to P. The successful coordinative stabilization of cyclo-E_3^-, cyclo-E_4^{2-}, cyclo-E_5^-, and cyclo-E_6 (E=P, As) – all-phosphorus and all-arsenic analogues of $C_3H_3^-$, $C_4H_4^{2-}$, $C_5H_5^-$ (Cp), and C_6H_6 – in sandwich and double sandwich complexes [1–13] well supports the P(As)-CH isolobal relationship and greatly enriches the chemistry of phosphorus and arsenic [1]. However, most of the sandwich complexes reported so far contain mixed ligands, with only one cyclic η^n-E_n as a terminal or middle deck. Typical examples include the sandwich Cp^*NiP_3 [1–4] with a terminal η^3-P_3^-, $CpFeP_5$ with a terminal η^5-P_5^-, and the double sandwich $[CpMP_nMCp]$ (M = transition metals) [1–7] with a cyclo-P_n (n = 3–6) middle deck. The first totally carbon-free inorganic metallocene $[Ti(P_5)_2]^{2-}$ containing two aromatic η^5-P_5^- ligands was successfully synthesized and characterized in 2002, in which cyclo-P_5^- serves as an acceptor [14]. Carbon-free $[P_4MP_4]^{n-}$ with two aromatic η^4-P_4^{2-} ligands were recently proposed based on density functional theory (DFT) level calculations [15], but most of the predicted structures prove to be local minima on the potential surface of the systems and unlikely to be observed experimentally. To the best of our knowledge, there have been no carbon-free transition metal sandwich complexes with two η^3-P_3^- or η^3-A_3^- ligands reported to date. Various *ab initio* theory investigations have indicated that P_3^- anion possesses two almost isoenergetic low-lying isomers, an equilateral triangle triplet (D_{3h}, $^3A_2'$) and a linear singlet ($D_{\infty h}$, $^1\Sigma_g^+$), while the third one – a triplet bent C_{2v} lies about 3–6 kcal/mol higher in energy [16–19]. D_{3h} P_3^- and $D_{\infty h}$ P_3^- proved to be too close in

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*Corresponding author (email: lisidian@yahoo.com) energy to allow a definitive theoretical prediction of the ground state [16–19]. For example, at the multi-reference MR-CISD level, D_{3h} P_3^- lies 2.3–0.9 kcal/mol more stable than $D_{\infty h}$ P_3^- [17, 19] and at the MD/DF level with non-local modifications to the density functional, the energy difference is 1.84 kcal/mol [19]. In experiments, P_3^- did appear as a major peak in the mass spectroscopy of P_n^- anions and photoelectron spectroscopy (PES) measurement indicated that either (or both) of D_{3h} P_3^- and C_{2v} P_3^- together with the linear $D_{\infty h}$ P_3^- coexisted in the gas phases [19]. Keeping in mind the fact that, similar to cyclo-P_5^- and cyclo-P_4^{2-}, equilateral triplet D_{3h} P_3^- and D_{3h} As_3^- are π-aromatic in nature – they possess 4π electrons to conform to the 4n aromatic rule for open shell cyclic systems [16–19] and therefore may serve as effective ligands to coordinate transition metal centers, in this work, we investigate the possibility of carbon-free phosphametallocenes $[P_3MP_3]^{2-}$ and arsenametallocenes $[As_3MAs_3]^{2-}$ (M=Ni, Pd, Pt) at both density functional theory (DFT) and wave function theory levels. Staggered singlet D_{3d} $[E_3ME_3]^{2-}$ – the smallest inorganic metallocenes possible to construct, proved to be the global minima of the heptaatomic systems and may be targeted in future experiments. Cyclo-P_3^- and cyclo-As_3^- turned out to possess similar aromaticity to cyclo-P_5^- and cyclo-As_5^- and may serve as effective ligands to sandwich a wide range of transition metals.

2 Theoretical approaches

Structural optimizations, frequency analyses, and natural bonding orbital (NBO) analyses were performed using both the hybrid B3LYP [20, 21] and B3PW91 [22, 23] methods implemented in Gaussian 03 program [24]. The two DFT approaches produced essentially the same geometries with only minor bond length differences. Energy refinements were carried out using the more accurate coupled cluster method including triple excitations (CCSD(T)) [25] at the lowest-lying D_{3d} $[E_3ME_3]^{2-}$ and D_{3h} $[E_3ME_3]^{2-}$ structures to compare their relative stabilities. To assess the π aromaticity of the relevant molecules, the nucleus independent chemical shifts (NICS) [26] were evaluated with the ghost atoms lying 1.0 Å above the cyclo-E_3^- ligand planes (NICS(1)). The standard Gaussian basis of 6-311+G(3df) was employed for P, As, Li, and Ni and Stuttgart RSC 1997 ECP [27] augmented with 2 f and 1 g functions [28] for Pd and Pt. According to our CCSD(T) results, the equilateral triplet D_{3h} P_3^- and D_{3h} As_3^- lie 0.81 kcal/mol and 13.31 kcal/mol more stable than their linear singlet counterparts $D_{\infty h}$ P_3^- and $D_{\infty h}$ As_3^-, respectively. The calculated NICS(1) values of −15.3 ppm for cyclo-P_3^- (**1**) and −16.4 ppm for cyclo-As_3^- are comparable to the corresponding values for cyclo-P_5^- (−15.0 ppm) and cyclo-As_5^- (−15.2 ppm), indicating that cyclo-P_3^- and cyclo-As_3^- possess similar π-aromaticity to the well-known cyclo-P_5^- and cyclo-As_5^- ligands. This strongly supports our choice of D_{3h} cyclo-P_3^- and cyclo-As_3^- as potential η^3-ligands to sandwich transition metal centers. Figure 1(a) depicts the optimized structures of D_{3h} P_3^-, D_{3d} $[P_3NiP_3]^{2-}$, D_{3h} $[P_3NiP_3]^{2-}$, and D_{3h} $[P_3NiP_3]$, Figure 1(b) features the structural patterns of C_s $[P_3NiP_3]Li^-$, C_{2h} $[P_3NiP_3]Li_2$, and C_s $[CpNiP_3]$, and Figure 2 shows the pictures of the molecular orbitals (MOs) contributing to the aromaticities of D_{3h} P_3^- and D_{3d} $[P_3NiP_3]^{2-}$. The geometrical and electronic properties of singlet D_{3d} $[E_3ME_3]^{2-}$ and singlet D_{3h} $[E_3ME_3]^{2-}$ (E=P, As; M=Ni, Pd, Pt) are compared in Table 1. Other important low-lying isomers of $[P_3NiP_3]^{2-}$ (Figure 1S, see Supporting Information) and $[P_3NiP_3]$ (Figure 2S) and the detailed molecular orbital pictures of triplet D_{3h} P_3^- and singlet D_{3d} $[P_3NiP_3]^{2-}$ (Figure 3S) have been summarized in the Supporting Information. More extensive searches using the gradient embedded genetic algorithm (GEGA) [29] technique at the B3LYP/3-21G level produced no isomers with lower energies than those shown in Figure 1S and Figure 2S. Similar results were obtained for cyclo-As_3-containing complexes.

3 Results and discussion

Sandwiching a Ni center with two cyclo-P_3^- ligands along the three-fold axis of the complex forms the staggered singlet D_{3d} $[P_3NiP_3]^{2-}$ (**2**) and eclipsed singlet D_{3h} $[P_3NiP_3]^{2-}$ (**3**) which conform to the 18 valence electron (VE) rule and prove to be the two lowest-lying isomers of the dianion. D_{3d} $[P_3NiP_3]^{2-}$ (**2**) appears to be the ground state of the system, while the transition state of D_{3h} $[P_3NiP_3]^{2-}$ (**3**) with an imaginary frequency at −49 cm^{-1} (a_1" rotary mode) lies slightly higher in energy (1.98 kcal/mol). All the other 2D and 3D low-lying isomers are at least 24.21 kcal/mol less stable than D_{3d} **2** (see Figure 1S). D_{3d} $[P_3NiP_3]^{2-}$ (**2**) contains two almost intact cyclo-P_3^- ligands with $r_{P-P} = 2.195$ Å which is 0.026 Å longer than $r_{P-P} = 2.169$ Å in free cyclo-P_3^- (**1**) and 0.041 Å longer than the measured $r_{P-P} = 2.154$ Å in the experimentally known $[P_5TiP_5]^{2-}$ [14]. Removing the two extra electrons from $[P_3NiP_3]^{2-}$ results in the 16 VE eclipsed triplet D_{3h} $[P_3NiP_3]$ (**4**) which lies only 1.38 kcal/mol higher than the lowest-lying isomer of the neutral – a Ni face-capped trigonal prism (C_{2v} P_6Ni, see Figure 2S). As clearly shown in Figure 1(b), η^3-P_3^- ligands have also been well maintained in the 18 VE C_s $[P_3NiP_3]Li^-$ (**5**) and 18 VE C_{2h} $[P_3NiP_3]Li_2$(**6**) in which Li^+ countercations are incorporated to stabilize the staggered $[P_3NiP_3]^{2-}$ sandwich cores. The η^3-P_3^- deck in the classical sandwich C_s $[CpNiP_3]$ (**7**) possesses the P–P bond lengths of 2.155 Å which is slightly shorter than the corresponding r_{P-P} values in structures (**2**)–(**6**). It is also important to notice that the calculated Ni–P coordination bond lengths between 2.21 and 2.34 Å in (**2**)–(**6**) agree well with the measured Ni–P distances between 2.22 and 2.24 Å in [Cp*NiP$_3$] [30, 31], indicating that effective M–P$_3$ coordinative interactions have been formed in the complexes discussed above.

As shown in Table 1, $[E_3NiE_3]^{2-}$ sandwich complexes containing η^3-As_3^- ligands and Pd and Pt centers share similar geometrical and electronic properties with their $[P_3NiP_3]^{2-}$ counterparts. The main differences occur in the r_{M-E} distances between the metal centers (M) and the ligand atoms (E=P or As) and the r_{E-E} bond lengths between neighboring ligand atoms. It is also interesting to notice that similar D_{3d} [As$_3$NiAs$_3$] local structures exist in crystalline NiAs which possesses an interatomic distances of $r_{Ni-As} = 2.43$ Å [32]. This measured value is about 0.03 Å longer than the calculated value of $r_{Ni-As} = 2.407$ Å for D_{3d} $[As_3NiAs_3]^{2-}$) (see Table 1).

Similar to B_6C^{2-} [33] and Al_4^{2-} [34] dianions, sandwich D_{3d} $[P_3NiP_3]^{2-}$ possesses positive HOMO energies and appears to be unstable towards detachment of the outermost valence electrons. Incorporation of Li$^+$ cations to form $[P_3NiP_3]Li^-$ (**5**) and $[P_3NiP_3]Li_2$ (**6**) proves to be an effectively approach to stabilize the dianion, as shown in the following processes:

$$2P_3^-(D_{3h}) + Ni = [P_3NiP_3]^{2-}(D_{3d}) \quad \Delta E = -64.95\ \text{kcal/mol} \tag{1}$$

$$2P_3^-(D_{3h}) + Ni + Li^+ = [P_3NiP_3]Li^-(C_S) \quad \Delta E = -287.52\ \text{kcal/mol} \tag{2}$$

$$2P_3^-(D_{3h}) + Ni + 2Li^+ = [P_3NiP_3]Li_2(C_{2h}) \quad \Delta E = -426.05\ \text{kcal/mol} \tag{3}$$

The huge negative energy changes of processes (2) and (3), which turn out to be even bigger than the formation energy of −204.42 kcal/mol obtained for C_s [CpNiP$_3$] (**7**) at the same theoretical level, strongly suggest that $[P_3NiP_3]Li^-$ (**5**) and $[P_3NiP_3]Li_2$ (**6**) salts containing staggered $[P_3NiP_3]^{2-}$ sandwich cores be good candidates to be targeted in future experiments.

NBO analyses indicate that D_{3d} $[P_3NiP_3]^{2-}$ (**2**) possesses the net atomic charges of Ni +0.27|e| and P −0.38|e|, showing that similar to the situation in $[P_5TiP_5]^{2-}$ [14], cyclo-P_3^- ligands mainly serve as acceptors in this complex. D_{3d} $[P_3NiP_3]^{2-}$ (**2**) has the total Wiberg bond indexes (WBI) of $WBI_{Ni} = 1.98$, $WBI_P = 2.97$, $WBI_{Ni-P} = 0.33$, and $WBI_{P-P} = 1.07$, indicating that the valences of the Ni center and P ligand atoms have been well satisfied and effective Ni–P$_3$ coordination interactions and typical P–P single bonds exist in structure **2**. The net atomic charges of Ni +0.18|e| and P −0.03|e| and total bond indexes of $WBI_{Ni} = 1.90$, $WBI_P = 2.78$, $WBI_{Ni-P} = 0.32$, and $WBI_{P-P} = 1.15$ in neutral D_{3h} [P$_3$NiP$_3$] (**4**) support the conclusions obtained above.

It is interesting to notice that the calculated NICS(1) values of −22.2 ppm (**2**), −21.3 ppm (**3**), −18.4 ppm (**4**), −20.7 ppm (**5**), −21.0 ppm (**6**), and −16.6 ppm (**7**) for the sandwich structures shown in Figure 1 all appear to be even more negative than the corresponding value of −15.3 ppm obtained for cyclic-P_3^- (**1**), indicating that the local ring current effect which renders π-aromaticity to free cyclo-P_3^- has been maintained in these sandwich structures. Similar

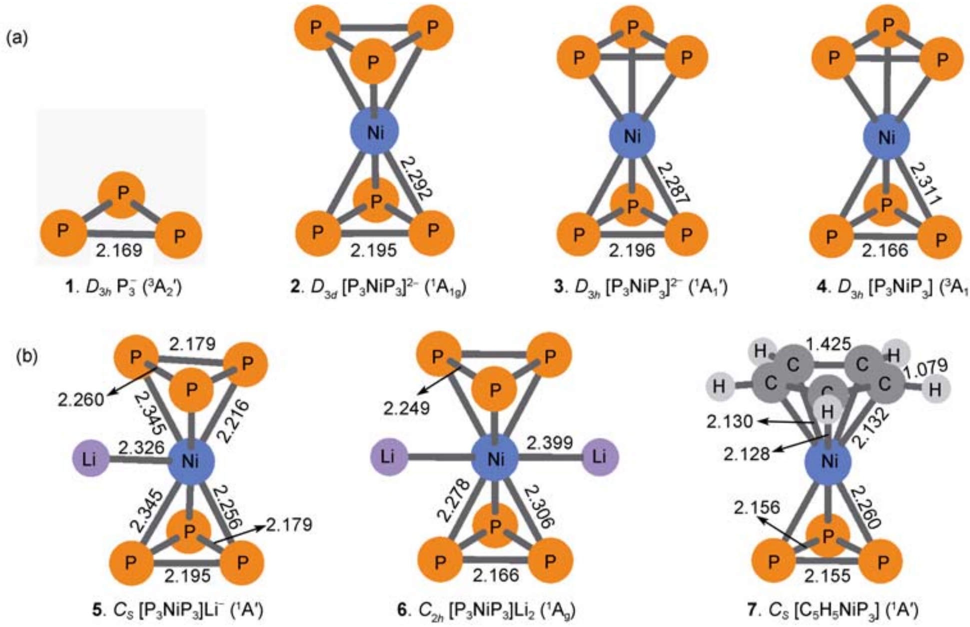

Figure 1 The optimized structures of (a) D_{3h} P_3^-, D_{3d} $[P_3NiP_3]^{2-}$, D_{3h} $[P_3NiP_3]^{2-}$, and D_{3h} [P$_3$NiP$_3$] and (b) C_s $[P_3NiP_3]Li^-$, C_{2h} $[P_3NiP_3]Li_2$, and C_s [CpNiP$_3$] at the B3LYP/6-311+G(3df) level with bond lengths indicated in Å.

Table 1 Calculated bond lengths ($r_{\mathrm{M-E}}$/Å and $r_{\mathrm{E-E}}$/Å), net atomic charges (q_{M}/|e| and q_{E}/|e|), total Wiberg bond indexes ($\mathrm{WBI_M}$, $\mathrm{WBI_E}$, $\mathrm{WBI_{M-E}}$, $\mathrm{WBI_{E-E}}$), the lowest vibrational frequencies ($V_{\min}$/cm^{-1}), NICS(1) values (in ppm) , and CCSD(T) relative energies (ΔE/kcal/mol) obtained for D_{3d} $[\mathrm{E_3ME_3}]^{2-}$ and D_{3h} $[\mathrm{E_3ME_3}]^{2-}$ sandwiches (E = As, P; M = Ni, Pd, Pt) at B3LYP/6-311+G(3df) structures

	$r_{\mathrm{M-E}}$	$R_{\mathrm{E-E}}$	q_{M}	q_{E}	$\mathrm{WBI_M}$	$\mathrm{WBI_E}$	$\mathrm{WBI_{M-E}}$	$\mathrm{WBI_{E-E}}$	$V_{\min}$	NICS(1)	ΔE
D_{3d} $[\mathrm{P_3NiP_3}]^{2-}$ ($^1\mathrm{A_{1g}}$)	2.292	2.195	+0.27	−0.38	1.98	2.97	0.33	1.07	+43	−22.2	0.00
D_{3h} $[\mathrm{P_3NiP_3}]^{2-}$ ($^1\mathrm{A}_1'$)	2.287	2.196	+0.23	−0.37	1.95	2.97	0.33	1.07	−49	−21.3	+1.98
D_{3d} $[\mathrm{As_3NiAs_3}]^{2-}$ ($^1\mathrm{A_{1g}}$)	2.407	2.443	+0.21	−0.37	1.94	2.93	0.32	1.05	+19	−24.8	0.00
D_{3h} $[\mathrm{As_3NiAs_3}]^{2-}$ ($^1\mathrm{A}_1'$)	2.398	2.448	+0.18	−0.36	1.90	2.94	0.32	1.05	−24	−23.9	+0.85
D_{3d} $[\mathrm{P_3PdP_3}]^{2-}$ ($^1\mathrm{A_{1g}}$)	2.454	2.195	+0.19	−0.37	1.90	2.97	0.32	1.07	+51	−20.9	0.00
D_{3h} $[\mathrm{P_3PdP_3}]^{2-}$ ($^1\mathrm{A}_1'$)	2.455	2.194	+0.16	−0.36	1.90	2.97	0.32	1.07	−55	−19.9	+3.99
D_{3d} $[\mathrm{As_3PdAs_3}]^{2-}$ ($^1\mathrm{A_{1g}}$)	2.562	2.444	+0.18	−0.36	1.84	2.93	0.31	1.06	+29	−23.1	0.00
D_{3h} $[\mathrm{As_3PdAs_3}]^{2-}$ ($^1\mathrm{A}_1'$)	2.560	2.444	+0.15	−0.36	1.84	2.94	0.31	1.05	−30	−22.0	+3.60
D_{3d} $[\mathrm{P_3PtP_3}]^{2-}$ ($^1\mathrm{A_{1g}}$)	2.456	2.204	+0.13	−0.36	2.19	2.97	0.36	1.05	+57	−19.4	0.00
D_{3h} $[\mathrm{P_3PtP_3}]^{2-}$ ($^1\mathrm{A}_1'$)	2.455	2.201	+0.10	−0.35	2.22	2.98	0.37	1.05	−62	−18.1	+4.81
D_{3d} $[\mathrm{As_3PtAs_3}]^{2-}$ ($^1\mathrm{A_{1g}}$)	2.567	2.452	+0.10	−0.35	2.16	2.93	0.36	1.04	+35	−22.2	0.00
D_{3h} $[\mathrm{As_3PtAs_3}]^{2-}$ ($^1\mathrm{A}_1'$)	2.565	2.452	+0.07	−0.35	2.18	2.94	0.36	1.03	−36	−20.9	+2.16

NICS(1) values have been obtained for other sandwich complexes tabulated in Table 1 (including the eclipsed D_{3h} $[\mathrm{E_3ME_3}]^{2-}$ transition-state structures). This phenomenon originates from the unique occupied MOs of the systems involving mainly the π and σ orbitals of cyclo-$\mathrm{P_3^-}$ and Ni 3d orbitals (for details, see Figure 3S). As shown in Figure 2, the totally delocalized π HOMO-3($\mathrm{a_2''}$) of cyclo-$\mathrm{P_3^-}$ which generates the π-aromaticity of the free cyclo-$\mathrm{P_3^-}$ (**1**) has been basically preserved in the HOMO-5 ($\mathrm{a_{2u}}$) and HOMO-9($\mathrm{a_{1g}}$) of D_{3d} $[\mathrm{P_3NiP_3}]^{2-}$ (**2**) with slight distortions (note that HOMO-9($\mathrm{a_{1g}}$) also contains considerable contribution from Ni $3\mathrm{d}_z^2$). Similar MOs exist for other sandwich complexes in Figure 1 and Table 1. It is these MOs that render aromaticity to the sandwich complexes studied.

To facilitate future PES characterization of these sandwich structures, we also calculated the first vertical detachment energies (VDEs) of the C_s $[\mathrm{E_3ME_3}]\mathrm{Li}^-$ monoanions studied in this work as the energy differences between the anions and their neutrals at the C_s anionic structures. For $[\mathrm{P_3MP_3}]\mathrm{Li}^-$ monoanions at B3LYP level, VDE = 2.82 eV, 2.77 eV, and 2.79 eV for M = Ni, Pd, and Pt, respectively. The corresponding values of $[\mathrm{As_3MAs_3}]\mathrm{Li}^-$ series are VDE = 2.83, 2.74, and 2.81 eV. These VDE values between 2.7 and 2.9 eV lie well within the energy range of the conventional excitation energy of 355 nm (3.496 eV) [19, 34].

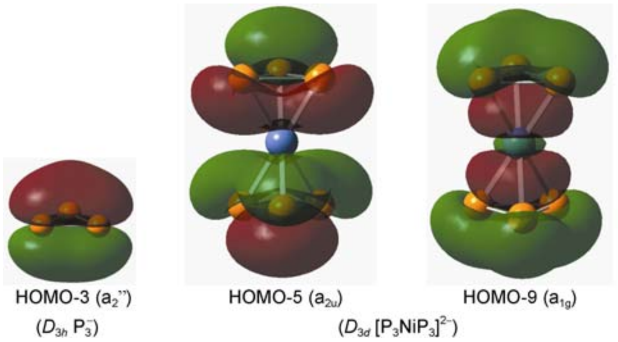

Figure 2 Pictures of the molecular orbitals contributing to the aromaticities of D_{3h} $\mathrm{P_3^-}$ and D_{3d} $[\mathrm{P_3NiP_3}]^{2-}$.

4 Summary

We have presented strong theoretical evidences at various levels for the possibilities of carbon-free D_{3d} $[\mathrm{E_3ME_3}]^{2-}$ transition metal sandwich complexes containing aromatic η^3-$\mathrm{P_3^-}$ and η^3-$\mathrm{As_3^-}$ ligands in this work. These heptaatomic phosphametallocenes and arsenametallocenes prove to be the global minima of the systems and are possible to be targeted in future experiments. Similar to other experimentally known cyclo-E_n-containing complexes [1–14], carbon-free $[\mathrm{E_3ME_3}]^{2-}$ sandwiches may be produced and characterized in reaction processes with white phosphorus $\mathrm{P_4}$ or yellow $\mathrm{As_4}$ as starting materials.

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