

Accepted Article

Title: Dianionic Mononuclear Cyclo-P4 Complexes of Zero-Valent Molybdenum: Coordination of the Cyclo-P4 Dianion in the Absence of Intramolecular Charge Transfer

Authors: Kyle A. Mandla, Michael L. Neville, Curtis E. Moore, Arnold L. Rheingold, and Joshua S. Figueroa

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201908885 Angew. Chem. 10.1002/ange.201908885

Link to VoR: http://dx.doi.org/10.1002/anie.201908885 http://dx.doi.org/10.1002/ange.201908885

WILEY-VCH

COMMUNICATION

Dianionic Mononuclear *Cyclo*-P₄ Complexes of Zero-Valent Molybdenum: Coordination of the *Cyclo*-P₄ Dianion in the Absence of Intramolecular Charge Transfer

Kyle A. Mandla, Michael L. Neville, Curtis E. Moore, Arnold L. Rheingold and Joshua S. Figueroa*

Dedication ((optional))

Abstract: Relative to other cyclic poly-phosphorus species (i.e. cyclo-P_n), the planar cyclo-P₄ group is unique in its requirement of two additional electrons to achieve aromaticity. In the coordination chemistry of cyclo-P4 ligands, these additional electrons are supplied from one or more metal centers. However the degree of charge transfer to the cyclo-P4 ligand is highly dependent on the nature of the metal fragment to which it is bound. Reported here are unique examples of dianionic mononuclear η^4 -P₄ complexes that can be viewed as the simple coordination of the [cyclo-P4]2- dianion to a neutral metal fragment. Treatment of the neutral, molybdenum cyclo- $Mo(\eta^4-P_4)I_2(CO)(CNAr^{Dipp2})_2$ complexes and Mo(n⁴- P_4)(CO)₂(CNAr^{Dipp2})₂ with KC₈ produces the dianionic, three-legged piano stool complexes, $[Mo(\eta^4-P_4)(CO)(CNAr^{Dipp2})_2]^{2-}$ and $[Mo(\eta^4-P_4)(CO)(CNAr^{Dipp2})_2]^{2-}$ $P_4)(CO)_2(CNAr^{Dipp2})]^{2-}$, respectively. Structural, spectroscopic and computational studies on these dianions reveal a distinct similarity to the classic $\eta^6\text{-benzene}$ complex $(\eta^6\text{-}C_6H_6)\text{Mo}(\text{CO})_3$ with respect to both the valence state of the metal center and electronic population of the π -system of the planar-cyclic ligand.

Aromaticity is a central tenant of molecular orbital theory and governs the electronic stabilization of unsaturated cyclic molecules.^[1,2] While aromaticity is most well established for cyclic hydrocarbons, there has been a long standing interest in the synthesis, development and study of all-inorganic aromatic compounds, especially those featuring the heavier main group elements.[3] Of these, cyclic poly-phosphorus aromatic compounds (i.e. cyclo-Pn) have received considerable attention due to the proclivity of phosphorus, relative to other heavier maingroup elements, to form homonuclear multiple bonds.[4-6] Accordingly, there has been a vibrant coordination chemistry of cyclic poly-phosphorus compounds that mirrors the wellestablished coordination chemistry of some Hückel-type 4n+2 aromatic hydrocarbons. Examples of such coordinated polyphosphorus rings include the all-phosphorus analogue of the cyclopentadienyl ion (*i.e.* [cyclo-P₅]⁻),^[7,8] complexes of which have found wide utility as supramolecular building blocks.^[9-11] In addition, coordination compounds featuring the all-phosphorus analogue of benzene (i.e. cyclo-P₆) have been reported,^[12,13] as have complexes containing the all-phosphorus analogue of the more enigmatic cyclobutadiene dianion (i.e. cyclo-[P4]²⁻).^[14-16]

For *cyclo*-P₄ complexes in particular, the most common examples are multinuclear, where the *cyclo*-P₄ ring is bound η^4 to one metal and κ^1 to up to four other metals via the phosphorus lone pairs (Scheme 1).^[15-18] In addition, examples featuring

[*] Dr. K. A. Mandla, Dr. Curtis E. Moore, Prof. Dr. Arnold L. Rheingold, Prof. Dr. J. S. Figueroa Department of Chemistry and Biochemistry University of California, San Diego 9500 Gilman Drive, MC 0358, La Jolla, CA 92093 (USA) E-mail: jsfig@ucsd.edu

Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate))



Scheme 1. Known coordination modes for the $[cyclo-P_4]^{2-}$ ligand.

the binuclear inverted sandwich motif, wherein the cyclo-P4 ring serves as a bridging ligand between two metals, have been reported in recent years (Scheme 1).^[19-23] In such species, it has been proposed that the aromaticity of the cyclo-P₄ unit is achieved by multi-center charge transfer to the central phosphacycle from two transition metal centers.^[20,21,23] Contrastingly, the mononuclear, or so-called "end-deck", cyclo-P4 complexes (Scheme 1), in which the bonding interactions between the metal center and the cyclo-P4 unit are potentially more simplified, remain uncommon. There are currently only eight structurally characterized "end-deck" cyclo-P4 complexes, all of which are either neutral or monoanionic in charge, and are limited to the metals V, Nb, Ta, Mo, Fe and Co.^[14, 24-29] However, the charge of these mononuclear complexes can create an inherent ambiguity - rather than simplification - of the bonding interactions between the metal and the cyclo-P₄ unit. This ambiguity centers on the nominal degree of metal-ligand covalency versus formal metal-toligand charge transfer. In turn, these bonding properties govern both the extent of aromaticity of the *cyclo*-P₄ unit and the valence state of the metal center. Indeed, this uncertainty is analogous to the debate on the iron cyclobutadiene complex, $Fe(\eta^4-C _{4}$ H₄)(CO)₃,^[30-32] where metal d⁸ and d⁶ electronic configurations have been proposed as limiting forms.^[33-34] Missing from the set of mononuclear cyclo-P4 complexes are examples of dianionic species, which can be viewed simply as the coordination of the $[cyclo-P_4]^{2-}$ dianion^[35] to a neutral metal fragment. Such complexes would obviate the need to invoke a charge-transfer paradigm within the bonding framework and could serve as a benchmark for other mononuclear [cyclo-P4]²⁻ complexes. Accordingly, here we report the synthesis and structures of the dianionic complexes $[(cyclo-P_4)Mo(CO)_2(CNAr^{Dipp2})]^{2-}$ $[(cyclo-P_4)Mo(CO(CNAr^{Dipp2})_2]^{2-}$ $(Ar^{Dipp2} = 2,6$ and 2,6-(2,6-(i-Pr₂)₂C₆H₃)₂C₆H₃), which are direct electronic analogues of the classic η^6 -benzene complex, $(\eta^6$ -C₆H₆)Mo(CO)₃,^[36] and allow for a direct assessment of the effects of metal coordination on the ostensible aromatic framework of the [cyclo-P₄]²⁻ dianion.

We recently reported the diiodo-monocarbonyl complex, $(\eta^{4}-P_{4})Mol_{2}(CO)(CNAr^{Dipp2})_{2}$ (1), which along with its more reduced dicarbonyl counterpart, $(\eta^{4}-P_{4})Mo(CO)_{2}(CNAr^{Dipp2})_{2}$ (2), represented the first examples of monomeric *cyclo*-P₄ complexes of molybdenum.^[28] On account of its high-valent nature, we reasoned that complex 1 could be used to access a low-valent and low-coordinate *cyclo*-P₄ complex via chemical reduction. Treatment of 1 with an excess of potassium graphite (KC₈) in THF solution resulted in a color change to dark red from orange (Scheme 2). Analysis of the reaction mixture by ¹H NMR

10.1002/anie.201908885

COMMUNICATION



Scheme 2. Synthesis of dianionic molybdenum cyclo-P4 complexes.

spectroscopy revealed the formation of a single product featuring two distinct environments for the CNAr^{Dipp2} *iso*-propyl group methyl and methine resonances. However, only one chemical environment was present for the central aryl group, thereby indicating a product with *C*_s symmetry. In addition, ¹H-coupled, ³¹P NMR spectroscopic analysis of the reaction mixture revealed one singlet resonance centered at δ = +105 ppm. This chemical shift is within the range found for complexes **1** and **2** (δ = +90 and +60 ppm for **1**; δ = +113 ppm for **2**),^[28] which suggested that the *cyclo*-P₄ ligand remained intact upon treatment of **1** with KC₈. Notably, FTIR spectroscopy of this product in C₆D₆ solution revealed an asymmetric set of broad, low-energy v_{CN} and v_{CO} bands (1900 –

1650 cm⁻¹) consistent with both a highly reduced metal center and contact ion pairing between the complex and potassium ions.^[37] Such IR spectroscopic features have been observed previously in a number of anion transition metal complexes supported by *m*-terphenyl isocyanide ligands.^[38-40]

Attempts to obtain single crystals of this reduction product were unsuccessful under a variety of conditions. However, addition of dibenzo[18-crown-6] to the product enabled the formation of red single crystals from a toluene solution. Crystallographic structure determination revealed this species to be the dipotassium salt, [K₂(dibenzo[18-crown-6]][(η⁴- P_4)Mo(CO)(CNAr^{Dipp2})₂] ([K₂(db18-c-6)][**3**]; Figure 1). Accordingly, we formulate the initial product of reduction as a THF-solvated salt of K₂[(η^4 -P₄)Mo(CO)(CNAr^{Dipp2})₂] (K₂[**3**]), which represents a formal 4e⁻ reduction of complex 1 accompanied by the loss of two iodide ligands. In the solid state, the Mo center of [K2(db18-c-6)][3] adopts a three-legged piano stool motif that is most recognizably associated with neutral (η^6 -arene)ML₃ complexes of the Group 6 metals (L = 2e⁻ donor ligand). One potassium ion is partially encapsulated by the crown ether and makes a secondary interaction to one phosphorus atom of the cyclo-P4 ring. The other K⁺ ion is engaged in contact-ion interactions with the C=N and arene portions of the CNAr^{Dipp2} ligands as suggested from the IR spectroscopic data.^[38-40] Treatment of [K₂(db18-c-6)][3] with up to five additional equivalents of dibenzo[db18-crown-6] did not succeed in the encapsulation of the second K⁺ ion, thereby indicating that contact-ion pairing in this complex is substantial.



Figure 1. Molecular Structures of K₂(dibenzo[18-crown-6]][(η^4 -P₄)Mo(CO)(CNAr^{Dipp2})₂] ([K₂(db18-c-6)][3]; left), the dianionic portion of K₂[(η^4 -P₄)Mo(CO)₂(CNAr^{Dipp2})] (K₂[4]; middle) and the neutral paramagnetic complex (η^4 -P₄)Mol(CO)(CNAr^{Dipp2})] (6; right).^[49]

Table	1. Metrical and	Spectroscopic Parameters for n	⁴ -P ₄ Molybdenum	Complexes. av = averag	se; cent = centroid; $E = O$ or N.	
	-					

Compound/Parameter	d(P-P) _{av} (Å)	d(Mo-(η ⁴ -P ₄) _{cent}) (Å)	d(Mo-C) _{av} (Å)	v _{CE} (cm ⁻¹)	Proposed Mo
$(n^4 - P_4)Mol_0(CO)(CNAr^{Dipp2})_o$	2 157(+0.005)	2 077(3)	$C_{\rm int} = 2.119(\pm 0.001)$	voo – 2007	Valence 4
(1)	2.107(±0.000)		$C_{co} - 1.988(3)$	v _{CN} – 2142, 2104	
(η ⁴ -P ₄)Mo(CO) ₂ (CNAr ^{Dpp2}) ₂ (2)	2.163(±0.015)	2.075(1)	$\begin{array}{c} C_{iso} -2.109 (\pm 0.009) \\ C_{CO} -2.013 (\pm 0.013) \end{array}$	v _{CO} – 2001, 1941 v _{CN} – 2130, 2101	2
[K ₂ (18-c-6)][(η ⁴ -P ₄)Mo(CO)(CNAr ^{Dipp2}) ₂] ([K ₂ (18-c-6)][3])	2.160(±0.012)	2.112(2)	$\begin{array}{c} C_{iso} - 1.962 (\pm 0.019) \\ C_{CO} - 1.973 (3) \end{array}$	v _{CO} – 1654 1635 v _{CN} – 1877, 1780	0
$\begin{array}{c} {\sf K}_2[(\eta^4 {\text -} {\sf P}_4){\sf Mo}({\sf CO})_2({\sf CNAr}^{{\sf D} {\sf p}_2 {\sf P}_2})] \\ ({\sf K}_2[{\bf 4}]) \end{array}$	2.161(±0.021)	2.102(3)	$\begin{array}{c} C_{iso} - 1.972(3) \\ C_{CO} - 1.935(\pm 0.007) \end{array}$	v _{CO} –1760, 1679 v _{CN} –1981, 1915	0
[Cp ₂ Co][(η ⁴ -P ₄)Mol(CO)(CNAr ^{Dipp2}) ₂] ([Cp ₂ Co][5])	2.169(±0.010)	2.051(2)	C _{iso} -2.074(±0.009) C _{CO} -1.984(4)	v _{CO} – 1884 v _{CN} – 2050, 1997	2
(η ⁴ -P ₄)Mol(CO)(CNAr ^{Dipp2}) ₂ (6)	2.168(±0.020)	2.049(4)	$\begin{array}{c} C_{iso} - 2.116 (\pm 0.011) \\ C_{CO} - 2.004 (5) \end{array}$	v _{CO} – 1984 v _{CN} – 2137, 2121	3

WILEY-VCH

COMMUNICATION

Whereas $(\eta^4-P_4)Mol_2(CO)(CNAr^{Dipp2})_2$ (1) possesses iodide ligands that are readily lost, the dicarbonyl complex (η^4 - P_4)Mo(CO)₂(CNAr^{Dipp2})₂ (2) can also serve as a precursor to dianionic cyclo-P4 complexes upon reduction. Treatment of 2 with an excess of KC8 in THF solution followed by analysis by ^{31}P NMR spectroscopy revealed the formation of K_2[3] along with an equimolar quantity of another cyclo-P4 product, as indicated by an additional ³¹P singlet centered at δ = + 121 ppm (Scheme 2). Dissolution of this mixture in 10:1 n-pentane/THF, solubilized K₂[3], leaving a dark red precipitate that could be crystallized from a THF solution stored at -40 °C. Structure determination on single crystals produced in this manner revealed the dicarbonyl salt, $K_2[(\eta^4-P_4)Mo(CO)_2(CNAr^{Dipp2})]$ (K₂[4]), resulting from the formal loss of one CNAr^{Dipp2} ligand from complex 2. Similar to the bis-isocyanide salt [K₂(db18-c-6)][3], the molybdenum core of dicarbonyl K₂[4] adopts a threelegged piano stool motif (Figure 1). However, in the solid state, multiple contacts between the $[(\eta^4-P_4)Mo(CO)_2(CNAr^{Dipp2})]^{2-1}$ unit and the K^+ ions organize $K_2[4]$ into a linear coordination polymer (Figure S4.3). Notably, treatment of the K₂[3]/K₂[4] reaction mixture with 10.0 equivalents of CO at room temperature results in the complete formation of K₂[4] and the corresponding amount of free CNArDipp2 after 1h of stirring. However, extended reaction times and/or heating up to 80 °C does not liberate the remaining CNAr^{Dipp2} ligand from K₂[4]. Like the inability to encapsulate the second K⁺ ion in [K₂(db18c-6)][3], we attribute this lack of additional reactivity between K₂[4] and CO to the strong π -arene/cation binding^[41] capabilities of the CNAr^{Dipp2} ligand.

The metrical parameters and IR spectroscopic features of [K2(db18-c-6)][3] and K2[4] are consistent with the coordination of a dianionic [cyclo-P4]²⁻ ligand to a low-valent molybdenum center. In addition, these data are especially informative when further compared to the neutral n^4 -P₄ complexes 1 and 2. For example, there is a remarkable consistency in average P-P bond distances across the series. For [K₂(db18-c-6)][3] and K₂[4], these average distances are identical and are essentially the same as complexes 1 and 2 (Table 1) $^{\mbox{\tiny [28]}}$ This similarity strongly suggests that the cyclo-P4 units of these complexes have a common electronic structure, irrespective of the valency of these molybdenum centers. In addition, these average P-P bond distances are slightly longer than those of the uncoordinated cyclo-tetraphosphide salt, Cs₂[cyclo-P₄]·2NH₃ (2.147(±0.002) Å),^[35,42] thereby reflecting that coordination to Mo decreases P-P π -bonding character to a measurable extent.^[43] However, there is a pronounced increase in the Mo-(n⁴-P)_{centroid} distance for [K₂(db18-c-6)][3] and K₂[4] relative to complexes 1 and 2 (Table 1) which is consistent with a decrease in metal valence state and reflects the presence of additional electron density on the metal center. Complexes [K2(db18-c-6)][3] and K2[4] also display Mo-C bond distances to both the isocyanide and CO ligands that are 0.1 Å and 0.2 Å shorter than those within 2 and 1, respectively (Table 1). These short Mo-C bond lengths coincide with vcN and vco IR signatures of [K2(18-c-6)][3] and K2[4] that are considerably lower in energy than those of 1 and 2, thereby providing additional support for increased π -backbonding interactions in the salts and, correspondingly, the presence of low-valent Mo centers.

Density functional theory (DFT) investigations provided a more detailed picture of the electronic structure of these *cyclo*-P₄ dianions and revealed a distinct electronic relationship to the classic η^6 -benzene complex, $(\eta^6-C_6H_6)Mo(CO)_3$. As shown in Figure 2, the three highest-lying molecular orbitals calculated for $[(\eta^4-P_4)Mo(CO)_2(CNAr^{Dipp2})]^{2-}$ ([4]²⁻) are a metal-based non-bonding orbital set and are consistent with the d⁶ electronic configuration of a zero-valent





Figure 3. Occupied molecular oribitals representing the interaction between molybdenum and the *cyclo*-P₄ ligand in $(\eta^4$ -P₄)Mo(CO)₂(CNAr^{Dipp2})]²⁻ ([4]²⁻; left) and benzene in $(\eta^6$ -C₆H₆)Mo(CO)₃ (right).

molybdenum center.^[44] These MOs correlate remarkably well with the e(xy, x^2-y^2) and $a_1(z^2)$ non-bonding orbital set of $C_{3\nu}$ symmetric $(n^6-C_6H_6)MO(CO)_3$ (Figure 2), with the exception that the d_{x2-y2} orbital of $[4]^{2-}$ is stabilized relative to its d_{xy} orbital. Accordingly, this breaking of the degenerate e-orbital set in [4]²⁻ is a consequence of the fact that the four-fold symmetric nature of the cyclo-P₄ ligand can accept only one δ backbonding interaction from the three-fold symmetric MoL₃ fragment.^[45] However, with respect to the primary bonding interactions between the cyclo-P4 unit and Mo, the electronic similarity of [4]²⁻ and $(\eta^6 - C_6 H_6)Mo(CO)_3$ are readily apparent (Figure 3). Both complexes possess a filled a-type molecular orbital interaction between the totally-symmetric representation of the cyclic ligand to the Mo center (Figure 3). This feature is accompanied by two filled e-symmetry interactions between the molybdenum d_{xz} and d_{yz} orbitals and the cyclic ligand, which for the cyclo-P4 unit satisfies the criteria for Hückel-type, 4n+2 aromaticity (n = 1). Correspondingly, calculation of the diatropic ring current for [4]2- 1 Å above the cyclo-P4 centroid resulted in a NICS(1) value of -7.0 ppm (NICS = nucleus-independent chemical shift).^[46-47] Notably, negative NICS(1) values have been strongly correlated with the presence of aromaticity in cyclic compounds.⁴⁷ Accordingly, this NICS(1) value for [4]2- can be compared with that calculated for $(\eta^6-C_6H_6)M_0(CO)_3$ (NICS(1) = -16.3 ppm), with

COMMUNICATION



Scheme 3. Synthesis of the neutral paramagnetic cyclo-P₄ complex 6.

the more positive value for $[4]^{2-}$ arising from the contributions of the exo-cyclic phosphorus lone pairs, which are known to oppose calculated diatropic ring currents.[48]

Whereas the experimental and computational data for [3]²⁻ and [4]²⁻ support the view of an aromatic [cyclo-P₄]² dianion bound to a zero-valent metal fragment, it is important to emphasize that the structural parameters of the cyclo-P4 units within complexes 1 and 2 also indicate the presence of an aromatic [cyclo-P4]²⁻ dianionic unit. This observation suggests that, for this particular system, formal charge transfer from the Mo center to the cyclo-P4 ligand in the neutral complexes 1 and 2 is significant and Hückel-type aromaticity is established. Accordingly, dianions [3]²⁻ and [4]²⁻, which represent an end-point in metal-based valence states, are best contextualized for their capacity to benchmark electron deficiency at the metal center, especially when the structural and/or spectroscopic properties of the cyclo-P4 ligand indicate aromatic character. Further illustrating this conclusion are the metrical and spectroscopic parameters of the neutral, paramagnetic cyclo-P4 complex, (η4-P4)MoI(CO)(CNArDipp2)2 (6), which was prepared according to the route shown in Scheme 3 through the intermediacy of the salt [Cp₂Co][(η⁴-P₄)MoI(CO)(CNAr^{Dipp2})₂] ([Cp₂Co][5]). Monoiodide 6 exhibits average P-P bond distances that are similar to the other mononuclear molybdenum cyclo-P₄ complexes, thereby signifying the presence of a $[cyclo-P_4]^{2-}$ unit (Table 1; Figure 1). However, the Mo- $(\eta^4$ -P)_{centroid} distance in **6** is shorter than those for [K₂(db18-c-6)][3] and K₂[4], while its v(CN) and v(CO) stretches are intermediate between those of complexes 1 and 2. These data indicate that complex 6 possesses an Mo center in a higher-valent state than [K2(db18-c-6)][3], K2[4] and 2, but not diiodide 1.

Accordingly, we believe this series represents a unique case where metal-based valence modulation has been identified for cyclo-P4 complexes featuring the same metal center and a similar ancillary environment. Given that cyclo-P4 complexes are desirable initial products in the activation of white phosphorus (P4) by transition-metal centers, the ability to understand and benchmark metal-based redox changes within these complexes may aid in the development of new phosphorus-atom functionalization processes. We are currently investigating this potential with the aim of developing transformations for [K₂(db18-c-6)][3] and K₂[4] that cooperatively involve redox equivalents from both the Mo center and the cyclo-P₄ ligand.

Acknowledgements

We are grateful to the U.S. National Science Foundation for support of this work (CHE-1802646) and to the Alexander von Humboldt Foundation for a Fellowship to J.S.F.

Keywords: Phosphorus • Aromaticity • cyclo-P4 • Molybdenum • Isocyanide

Conflict of Interest

The authors declare no conflict of interest.

- P. v. R. Schleyer, H. Jiao, Pure Appl, Chem. 1996, 68, 209-[1] 218.
- M. K. Cyrañski, Z. Czarnocki, G. [2] T. M. Krygowski, Häfelinger, A. R. Katritzky, Tetrahedron 2000, 56, 1783-1796
- [3] Y. Matsuo, M. Maruyama, Chem. Commun. 2012, 48, 9334-9342.
- [4] M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, T. Higuchi, J. Am. Chem. Soc. 1981, 103, 4587-4589.
- A. H. Cowley, A. Decken, N. Norman, C. Krüger, F. Lutz, H. [5] Jacobsen, T. Ziegler, J. Am. Chem. Soc. 1997, 119, 3389-3390
- P. P. Power, Chem. Rev. 1999, 99, 3463-3503. [6]
- O. J. Scherer, T. Brück, Angew. Chem. Int. Ed. 1987, 26, 59. [7]
- [8] E. Urne žius, W. W. Brennessel, C. J. Cramer, J. E. Ellis, P. v. R. Schleyer, *Science* **2002**, *295*, 832-834. J. Bai, A. V. Virovets, M. Scheer, *Angew. Chem. Int. Ed.*
- [9] 2002, 41, 1737-1740.
- [10] J. Bai, A. V. Virovets, M. Scheer, Science 2003, 300, 781-783.
- [11] H. Brake, E. Peresypkina, C. Heindl, A. V. Virovets, W. Kremer, M. Scheer, Chem. Sci. 2019, 10, 2940-2944.
- [12] O. J. Scherer, H. Sitzmann, G. Wolmershäuser, Angew. Chem. Int. Ed. 1985, 24, 351-353.
- [13] M. Fleischmann, D. Dielmann, L. J. Gregoriades, E. V. Peresypkina, A. V. Virovets, S. Huber, A. Y. Timoshkin, G. Balázs, M. Scheer, Angew. Chem. Int. Ed. 2015, 54, 13110-13115.
- [14] O. J. Scherer, J. Vondung, G. Wolmershäuser, Angew. Chem. Int. Ed. 1989, 28, 1355-1357.
- M. E. Barr, S. K. Smith, B. Spencer, L. F. Dahl, [15] Organometallics 1991, 10, 3983-3991.
- [16] M. Scheer, E. Herrmann, J. Sieler, M. Oehme, Angew. Chem. Int. Ed. 1991, 30, 969-971.
- [17] M. Scheer, U. Becker, J. C. Huffman, M. H. Chisholm, J. Organomet. Chem. 1993, 461, C1-C3.
- M. Modl, S. Heinl, G.; Balázs, F. Delgado Calvo, M. [18] Caporali, G. Manca, M. Keilwerth, K. Meyer, M. Peruzzini, M. Scheer, Chem. Eur. J. 2019, 25, 6300-6305.
- A. S. P. Frey, F. G. N.; Cloke, P. B. Hitchcock, J. C. Green, [19] New J. Chem. 2011, 35, 2022-2026.
- S. Yao, N. Lindenmaier, Y. Xiong, S. Inoue, T. Szilvási, M. [20] Adelhardt, J. Sutter, K. Meyer, M. Driess, Angew. Chem. Int. Ed. 2015, 54, 1250-1254.
- S. Pelties, T. Maier, D. Herrmann, B. de Bruin, C. [21] Rebreyend, S. Gärtner, I. G. Shenderovich, R. Wolf, Chem. Eur. J. 2017, 23, 6094-6102.
- F. Spitzer, C. Graßl, G. Balázs, E. Mädl, M. Keilwerth, E. M. [22] Zolnhofer, K. Meyer, Chem. Eur. J. 2017, 23, 2716-2721.
- [23] Stephens, F. H., Ph.D. thesis, Massachusetts Institute of Technology 2004.
- [24] O. J. Scherer, R. Winter, G. Wolmershäuser, G Z. Anorg. Chem. 1993. 619. 827-835.
- [25] M. Herberhold, G.Frohmader, W, Milius, J. Organomet. Chem. 1996, 522, 185-196.
- F. Dielmann, A.Timoshkin, M. Piesch, M. Scheer, Angew. [26] Chem. Int. Ed. 2017, 56, 1671-1675.
- [27] A. Cavaillé, N. Saffon-Merceron, N. Nebra, M. Fustier-Boutignon, N. Mézailles, Angew. Chem. Int. Ed. 2018, 57, 1874-1878
- K. A. Mandla, C. E. Moore, A. L Rheingold, J. S. Figueroa, [28] Angew. Chem. Int. Ed. 2018, 58, 1779-1783.
- [29] U. Chakraborty, J. Leitl, B. Mühldorf, M. Bodensteiner, S. Pelties, R. Wolf., Dalton Trans. 2018, 47, 3693-3697.

WILEY-VCH

COMMUNICATION

- [30] H. Longuet-Higgins, L. E. Orgel, J. Chem. Soc. 1956, 1969.
- [31] R. P. Dodge, V. Schomaker, *Nature* **1960**, *186*, 798-799.
- [32] W. Oberhansli, L. F. Dahl, Inorg. Chem. 1965, 4, 150-157.
- [33] D. Clack, K. Warren, Inorg. Chim. Acta 1978, 27, 105-108.
- [34] B. E. Bursten, R. F. Fenske, Inorg. Chem. 1979, 18, 1760-1765.
- [35] F. Kraus, J. C. Aschenbrenner, N. Korber, Angew. Chem. Int. Ed. 2003, 42, 4030-4033.
- [36] E. O. Fischer, K. Ofele, H. Essler, W. Frohlich, J. P. Mortensen, W. Semmlinger, Z. Naturforsch. B 1958, 13b, 458-459.
- [37] A. Macchioni, Chem. Rev. 2005, 105, 2039-2074.
- [38] G. W. Margulieux, N. Weidemann, D. C. Lacy, C. E. Moore,
 A. L. Rheingold, J. D. Figueroa, *J. Am. Chem. Soc* 2010, 132, 5033-5035.
- [39] C. C. Mokhtarzadeh, G. W. Margulieux, A. E. Carpenter, N. Weidemann, C. E. Moore, A. L. Rheingold, J. S. Figueroa, *Inorg. Chem.* 2015, 54, 5579-5587.
- [40] A. E. Carpenter, C. Chan, A. L. Rheingold, J. S. Figueroa, Organometallics 2016, 35, 2319-2326.
- [41] D. A. Dougherty, Acc. Chem. Res. 2013, 46, 885-893.

- [42] F. Kraus, N. Korber, Chem. Eur. J. 2005, 11, 5945-5959.
- [43] P. v. R. Schleyer, B. Kiran, D. V. Simion, T. S. Sorensen, J. Am. Chem. Soc 1999, 122, 510-513.
- [44] E. L. Muetterties, J. R. Bleeke, E. J. Wucherer, T. A. Albright, *Chem. Rev.* **1982**, *82*, 499-525.
- [45] V. M. Rayón, G. Frenking, Organometallics 2003, 22, 3304-3308.
- [46] Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. v. R. Schleyer, *Chem. Rev.* 2005, 105, 3842-3888.
- [47] P. v. R. Schleyer, M. Manoharan, Z.-X. Wang, B. Kiran, H. Jiao, R. Puchta, N. J. R.van Eikema Hommes, *Organic Letters* 2001, 3, 2465-2468.
- [48] J. O. C. Jimenez-Halla, E. Matito, J. Robles, M. Sola, *J. Organomet. Chem.* 2006, 691, 4359–4366.
 [49] CCDC 1936286, 1936287, 1936288 and 1936289 ([K₂(db18-
- [49] CCDC 1936286, 1936287, 1936288 and 1936289 ([K₂(db18-c-6)][3], K₂[4], [Cp₂Co][5], 6) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

WILEY-VCH

COMMUNICATION

Entry for the Table of Contents (Please choose one layout)

COMMUNICATION

More Charge, More Clarity: cyclobutadiene Like the dianion, the cyclic, polyphosphorus cyclo-P₄ dianion creates an electronic structure ambiguity when found in neutral transition metal complexes. Here, dianionic cyclo-P4 complexes are reported which can be viewed as the simple binding of [cyclo- P_4]²⁻ to a metal.



K. A. Mandla, M. L. Neville, C. E. Moore, A. L. Rheingold and J. S. Figueroa

Page No. – Page No.

Dianionic Mononuclear Cyclo-P₄ Complexes of Zero-Valent Molybdenum: Coordination of the Cyclo-P₄ Dianion in the Absence of Intramolecular Charge Transfer