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Communication

A Lead-μ_2-Tetrylide Complex with Osmium(IV) Terminal Components

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ABSTRACT: A bare lead atom is a σ-donor ligand capable of linearly bonding and stabilizing two units of a classical polyhydride complex, with a high-valent metal center. As a proof of concept, we have prepared and characterized the μ_2-tetrylide complex $(P^iPr_3)_2H_4Os{=}Pb{=}OsH_4(P^iPr_3)_2$ in the reaction of $OsH_6(P^iPr_3)_2$ with $Pb\{N(SiMe_3)_2\}_2$. Although the Pb−Os bonds exhibit electrostatic interaction, the main orbital interactions result from two dative σ bonds from the lead atom to the osmium centers. The latter also provide much weaker π-backdonations.

μ_2-Tetrylide complexes challenge the current limits of molecular coordination chemistry. They are formed by a bare atom of a Group 14 element, which is located in the center between the low-valent metal ions of two identical unsaturated transition-metal compounds; $L_nM{=}E{=}ML_n$ (E = C, Si, Ge, Sn, Pb). Only a small number of compounds have been characterized.

Carbide derivatives are the only ones that have a moderately significant representation,[1] which includes complexes of rhenium,[2] iron,[3] ruthenium,[4] and rhodium.[5]

The reported complexes of silicon are rare, and their tetrylide character is sometimes controversial. In 2018, Filippou's group reported that a two-electron reduction of molybdenum compound $Tp'(CO)_2Mo{\equiv}Si{-}Mo(CO)_2(PMe_3)Tp'$ [Tp′ = κ^3-*N,N′,N″*-hydridotris(3,5-dimethylpyrazolyl)borate] with potassium graphite produces the dianion $[Tp'(CO)_2Mo{=}Si{=}Mo(CO)_2(PMe_3)Tp']^{2-}$.[6] More recently, Tilley and co-workers have observed that cobalt-promoted activation of SiH_4 bonds generates tetrahydride−dicobalt−silicide species,[7] although an AIM analysis locates two bond paths connecting silicon and two hydrides.[7b]

The first germanide species were discovered by the groups of Weiss and Hermann, between 1981 and 1985. Starting from $Mn(\eta^5\text{-}C_5R_5)(CO)_3$, they isolated $(\eta^5\text{-}C_5R_5)(CO)_2Mn{=}Ge{=}Mn(CO)_2(\eta^5\text{-}C_5R_5)$ (C_5R_5 = C_5H_4Me, C_5H_5, C_5Me_5), after an acetic acid-promoted GeH_3 dehydrogenation.[8] The family of manganese compounds has recently been augmented by the complex $(dmpe)_2HMn{=}Ge{=}MnH(dmpe)_2$, reported by the Emslie group.[9] In 2021, Arnold and co-workers crystallographically characterized the dirhenium germanide $(\eta^5\text{-}C_5H_5)(BDI)Re{=}Ge{=}Re(BDI)(\eta^5\text{-}C_5H_5)$, which was prepared by reacting $GeCl_2\cdot$dioxane with $Na[Re(\eta^5\text{-}C_5H_5)(BDI)]$ [BDI = κ^2-*N,N′*-bis(2,6-diisopropylphenyl)-3,5-dimethyl-β-diketiminate], at −78 °C.[10]

The situation with tin and lead is similar. Between 1985 and 1989, Herrmann and co-workers observed that the reactions of $Mn(\eta^5\text{-}C_5Me_5)(CO)_3$ with SnH_4 and $Mn(\eta^5\text{-}C_5H_5)(CO)_3$ with $PbCl_2$ led to $(\eta^5\text{-}C_5Me_5)(CO)_2Mn{=}Sn{=}Mn(CO)_2(\eta^5\text{-}C_5Me_5)$ and $(\eta^5\text{-}C_5H_5)(CO)_2Mn{=}Pb{=}Mn(CO)_2(\eta^5\text{-}C_5H_5)$, respectively, although only the latter was characterized by X-ray diffraction analysis.[11] In 1992 and 2015, compounds $[Bu_4N]_2[Pb\{Pt(C_6F_5)_4\}_2]$[12] and $Pb\{Pt(C_6F_5)_2(bzq)\}_2$ (bzq = 7,8-benzoquinolyl)[13] were reported. Although they show a linear Pt−Pb−Pt arrangement, both X-ray diffraction analysis and NMR spectroscopy reveal a high coordination number for the lead atom, which is provided by the *o*-fluorine substituents of C_6F_5.

A recent theoretical study on the bonding situation in complexes $(\eta^5\text{-}C_5H_5)(CO)_2Mn{=}E{=}Mn(CO)_2(\eta^5\text{-}C_5H_5)$ (E = C, Si, Ge, Sn, Pb) identifies mutually orthogonal π-delocalized systems along the linear backbone. The strength of the Mn−E bond decreases down the group and is accompanied by a lower contribution of the E atom ns valence orbital to the bond. This atom acts as σ donor and π acceptor, according to the Dewar−Chatt−Duncanson bonding model.[14] On the basis of this feature of the heavier atoms of Group 14, we reasoned that the terminal L_nM components of μ_2-tetrylide complexes linked by such atoms should not necessarily carry a low-valent metal center; on the contrary, they would exhibit greater stability with terminal components of high-valence metallic centers. These metal centers have weak π-donor capacity, while they need σ-donor ligands to maintain their high valence.

Transition-metal polyhydride complexes typically involve metals in high oxidation states. Therefore, unsaturated members of this family should be excellent candidates to act as terminal L_nM components, with the heaviest Group 14 elements. Furthermore, they are mild reducing agents,[15] with reduction of the tetrylide source being the usual procedure for the preparation of the scarce μ_2-tetrylide compounds

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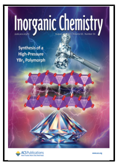

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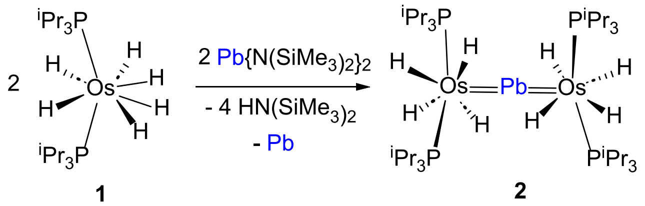
characterized to date. Complex $OsH_6(P^iPr_3)_2$ (**1**) is a prototypical polyhydride of the platinum group metals[16] and a cornerstone in the development of osmium organometallics due to its rich stoichiometric[17] and catalytic[18] reactivity and its involvement in materials science as a precursor to osmium phosphorescent emitters.[19] At temperatures above 50 °C, it loses H_2 to give the unsaturated tetrahydride $OsH_4(P^iPr_3)_2$, which has been trapped with $2e^-$ Lewis bases.[20] These precedents led us to use it to test our hypothesis and, concurrently, prepare a completely different μ_2-tetrylide complex. Tetrylene $Pb\{N(SiMe_3)_2\}_2$ was used as the lead source.[21]

Reaction of the polyhydride with the tetrylene, in toluene, at 80 °C, for 22 h produced the precipitation of metallic lead as a fine dark solid and the formation of the desired complex $(P^iPr_3)_2H_4Os{=}Pb{=}OsH_4(P^iPr_3)_2$ (**2**), according to Scheme 1. After filtration over Celite, evaporation of the resulting solution, and purification of the crude solid by crystallization from pentane, at −30 °C, complex **2** was isolated as brown crystals in ≈60% yield. The H_2 released by **1** reduces tetrylene to Pb and amine. Half of the Pb generated traps the unsaturated osmium tetrahydride, resulting from the dissociation of H_2, to form **2**. Consistent with this, we also observe that tetrylene decomposes to Pb and amine in an H_2 atmosphere.

Scheme 1. Formation of 2



Complex **2** was characterized by X-ray diffraction analysis. The molecule (Figure 1) has the expected linear Os−Pb−Os backbone (exactly 180.0°) on a C_2 axis. The coordination polyhedron around each osmium can be rationalized as a pentagonal bipyramid with the phosphines in apical positions (P−Os−P = 161.54(4)° and 161.32(5)°). Hydrides are found in the base along with the lead atom. The latter is very far from the hydrides (>2.56(4) or 2.64 Å in the density functional theory (DFT)-optimized structure).[22] The absence of any Pb−H interaction was further confirmed by an AIM approach. Hydrides are of classical nature showing separations between them greater than 1.80 Å (DFT-optimized structure), in accordance with a strong σ-donor capacity of the lead atom.[23] Thus, the general structure can be described as two pentagonal bipyramids, rotated relative each other 59.93(3)°, which have a common vertex where the lead atom is located. The Os−Pb distances are almost identical, 2.5842(3) and 2.5895(3) Å. Because the point group symmetry of the molecule is D_2, the bipyramids are equivalent. Consequently, the $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 55.7 ppm, corresponding to the phosphines, which splits into a quintuplet under off-resonance conditions due to the presence of four hydrides at each metal. Although the hydride ligands are inequivalent in the bipyramids, the room temperature ^1H NMR spectrum contains only one triplet ($^2J_{H-P}$ = 14.3 Hz) at −8.07 ppm, consistent with the typical position exchange process exhibited by osmium polyhydrides in solution.[20] The exchange occurs even at low temperature; only at temperatures below 165 K, two broad signals are observed. As expected for the classical nature of the polyhydride, a 400 MHz T_1(min) value of 239 ms was obtained for this resonance, in methylcyclohexane-d_{14}, at 253 K. Complex **2** is certainly stable. Its high stability even allows the obtainment of its high-resolution mass spectrum by electron electrospray ionization, without loss of any hydride ligands ($[M]^+$; m/z 1240.5099), something highly unusual for polyhydride complexes.

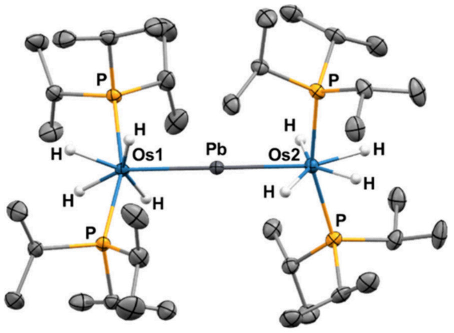


Figure 1. Molecular diagram of complex **2** (50% probability ellipsoids). Hydrogen atoms (except hydride ligands) are omitted for clarity.

The novelty of **2** and the need to understand its stability prompted us to analyze the Os−P bonds. To this end, DFT calculations at the relativistic dispersion-corrected ZORA-BP86-D3/TZ2P//RI-BP86-D3/def2-TZVP level were carried out. The optimized geometry matches the X-ray structure quite well, in particular the Pb−Os bond lengths (2.60 Å). Inspection of the occupied molecular orbitals involving the metal atoms (Figure 2) resembles that of the complex $(\eta^5\text{-}C_5H_5)(CO)_2Mn{=}Pb{=}Mn(CO)_2(\eta^5\text{-}C_5H_5)$.[14]

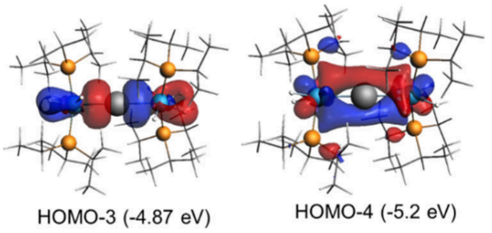


Figure 2. Selected computed molecular orbitals (isosurface value of 0.05 au) of complex **2**.

A more quantitative insight into the nature of the Pb−Os bonds was gained by applying the energy decomposition analysis (EDA) method. Explicitly, we investigated the interaction between $(P^iPr_3)_2H_4Os$ and $PbOsH_4(P^iPr_3)_2$ fragments in the two possible bonding situations, namely: (i) a dative bond, thus involving singlet fragments, and (ii) an electron-sharing bond, therefore using fragments in their triplet state. As is well-known, the calculation that gives the smallest absolute value of the orbital term ΔE_{orb} corresponds to the most reasonable description of the bond, since then the formation of such a bond produces the smallest change in the electronic structure of the fragments.[24] From the data in Table 1, it becomes evident that dative bonding represents the best description of the bonding in **2**.

Table 1. EDA (Energy Values in kcal/mol) of Complex **2**

	dative bond (singlet + singlet)	electron-sharing (triplet + triplet)
ΔE_{int}	−82.1	−151.6
ΔE_{Pauli}	185.8	268.8
ΔE_{elstat}	−149.5	−200.2
ΔE_{orb}	−87.9	−189.7
$\Delta E_{\text{orb}}(\rho_1)$	−55.6	−54.0
$\Delta E_{\text{orb}}(\rho_2)$	−11.7	−4.7
ΔE_{disp}	−30.5	−30.5

The natural orbital for chemical valence (NOCV) extension of the EDA method was next applied to identify and quantify the main orbital interactions contributing to the total ΔE_{orb} term. From the data of Table 1, two main orbital interactions characterize the Pb−Os bond: a σ donation from a lone pair of the lead atom, mainly located at the p_x atomic orbital, to a vacant d atomic orbital of the osmium center [LP(Pb) → $d_{x^2-y^2}$(Os)], denoted as ρ_1, and a π-backdonation from a doubly occupied d atomic orbital of the osmium center to the vacant p_z atomic orbital of the lead atom [d_{xz}(Os) → p_z(Pb)], denoted as ρ_2 (Figure 3). According to the computed stabilizing energies, $\Delta E(\rho)$, the σ-donation clearly dominates over the π-backdonation, which is comparatively much weaker. Therefore, from the point of view of orbital interaction, the bonding situation involving the Os−Pb−Os backbone of **2** can be summarized as follows: a bare lead atom establishes two strong dative σ bonds with two osmium centers, using its two available lone pairs. At the same time, the osmium centers provide weaker π-backdonations to the vacant p_z atomic orbital of the lead atom. This situation resembles that described for the complexes $(\eta^5\text{-}C_5H_5)(CO)_2Mn{=}E{=}Mn(CO)_2(\eta^5\text{-}C_5H_5)$ (E = heavy element of Group 14) but sharply contrasts with that found in plumbylones, where the lead atom maintains its lone pairs to act as an electron acceptor.[25] On the other hand, it should be noted that the orbital interaction is not the main contributor to the bonding. According to the data in Table 1, the Pb−Os bond exhibits a strong electrostatic interaction (≈56% of the total attractions), which is not surprising according to the significantly different computed NBO charges of the involved atoms: +1.19e for Pb and −1.16e for Os.

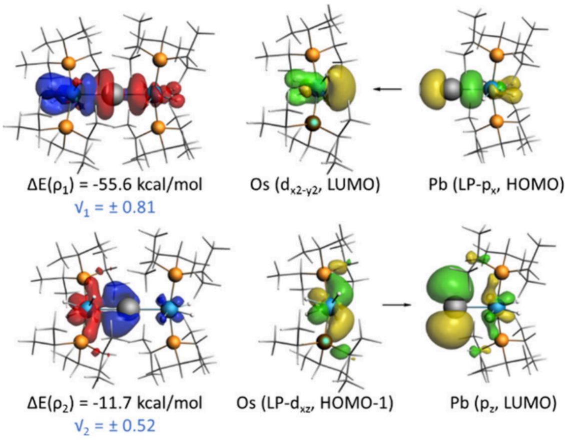


Figure 3. Contour plots of the main NOCV deformation densities ρ (isosurface value of 0.001 au), associated energies ΔE(ρ) and interacting orbitals compound **2**. The electronic charge flows from red to blue. The eigenvalues |ν| indicate the relative size of the charge flow.

The classical or nonclassical nature of the transition-metal polyhydride complex is determined by the basicity of the metal center, which is governed by the electron-donating capacity of its ligands. Electron-donating groups favor classical polyhydrides, while those with good acceptor properties benefit nonclassical interactions.[17,26] The preparation of **2** containing a classical osmium(IV) tetrahydride as terminal components allows us to conclude that a bare lead atom is a strong σ-donor ligand in coordination chemistry, strong enough to be able to join and stabilize two units of a classical polyhydride complex in a linear manner. This finding also demonstrates that μ_2-tetrylide complexes can contain two identical unsaturated terminal components of a high-valent metal center, in contrast to what has been observed so far.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.4c02520.

General information, structural analysis of complex **2**, computational data, and NMR and IR spectra (PDF)

Cartesian coordinates of computed complex (XYZ)

Accession Codes

CCDC 2360977 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or 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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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Reinholdt, A.; Bendix, J. Transition Metal Carbide Complexes. *Chem. Rev.* **2022**, *122*, 830−902.

(2) Young, R. D.; Hill, A. F.; Cavigliasso, G. E.; Stranger, R. [(μ-C){Re(CO)$_2$(η-C$_5$H$_5$)}$_2$]: A Surprisingly Simple Bimetallic Carbido Complex. *Angew. Chem., Int. Ed.* **2013**, *52*, 3699−3702.

(3) (a) Mansuy, D.; Lecomte, J.-P.; Chottard, J.-C.; Bartoli, J.-F. Formation of a Complex with a Carbide Bridge between Two Iron Atoms from the Reaction of (Tetraphenylporphyrin)iron(II) with Carbon Tetraiodide. *Inorg. Chem.* **1981**, *20*, 3119−3121. (b) Rossi, G.; Goedken, V. L.; Ercolani, C. μ-Carbido-bridged Iron Phthalocyanine Dimers: Synthesis and Characterization. *J. Chem. Soc., Chem. Commun.* **1988**, 46−47. (c) Colomban, C.; Kudrik, E. V.; Tyurin, D. V.; Albrieux, F.; Nefedov, S. E.; Afanasiev, P.; Sorokin, A. B. Synthesis and characterization of μ-nitrido, μ-carbido and μ-oxo dimers of iron octapropylporphyrazine. *Dalton Trans.* **2015**, *44*, 2240−2251.

(4) Solari, E.; Antonijevic, S.; Gauthier, S.; Scopelliti, R.; Severin, K. Formation of a Ruthenium μ-Carbide Complex with Acetylene as the Carbon Source. *Eur. J. Inorg. Chem.* **2007**, *2007*, 367−371.

(5) Barnett, H. J.; Burt, L. K.; Hill, A. F. Simple generation of a dirhodium μ-carbido complex via thiocarbonyl reduction. *Dalton Trans.* **2018**, *47*, 9570−9574.

(6) Ghana, P.; Arz, M. I.; Chakraborty, U.; Schnakenburg, G.; Filippou, A. C. Linearly Two-Coordinated Silicon: Transition Metal Complexes with the Functional Groups M≡Si—M and M=Si=M. *J. Am. Chem. Soc.* **2018**, *140*, 7187−7198.

(7) (a) Handford, R. C.; Smith, P. W.; Tilley, T. D. Activations of all Bonds to Silicon (Si-H, Si-C) in a Silane with Extrusion of [CoSiCo] Silicide Cores. *J. Am. Chem. Soc.* **2019**, *141*, 8769−8772. (b) Handford, R. C.; Nguyen, T. T.; Teat, S. J.; Britt, R. D.; Tilley, T. D. Direct Transformation of SiH$_4$ to a Molecular L(H)$_2$Co=Si=Co(H)$_2$L Silicide Complex. *J. Am. Chem. Soc.* **2023**, *145*, 3031−3039. (c) Handford, R. C.; Tilley, D. A [CoSiH$_2$] Silylene Synthon Provides Modular Access to Homo- and Heterobimetallic [Co=Si=M] (M = Co, Fe) Silicide Complexes. *J. Am. Chem. Soc.* **2023**, *145*, 24690−24697.

(8) (a) Gäde, W.; Weiss, E. Dicarbonyl-η^5-methylcyclopentadienyl-Manganiobis[dicarbonyl- η^5-methylcyclopentadienylmanganio(Mn-Mn)]Germanium, [(η^5-CH$_3$C$_5$H$_4$)Mn(CO)$_2$],Ge und Bis-[Dicarbonyl-η^5-methylcyclopentadienyl-manganio]-Germanium, [η^5-CH$_3$C$_5$H$_4$Mn(CO)$_2$]$_2$Ge. Neuartuge Verbindungen Mit Einer BZW. Zwei Mn-Ge-Doppelbindungen. *J. Organomet. Chem.* **1981**, *213*, 451−460. (b) Melzer, D.; Weiss, E. Ge-Mn-Mehrfachbindungen in [(η^5-C$_5$H$_5$)Mn(CO)]$_2$Ge und [(η^5-C$_5$H$_5$)Mn(CO)$_2$]$_3$Ge. [(η^5-C$_5$H$_5$)$_2$V]$_2$GeH$_2$, Eine Metallverbindung Mit Einer GeH$_2$-Brücke. *J. Organomet. Chem.* **1984**, *263*, 67−73. (c) Korp, J. D.; Bernal, I.; Hörlein, R.; Serrano, R.; Herrmann, W. A. Synthesis, X-Ray Crystal and Molecular Structure of μ-Germanium-bis[dicarbonyl(η^5-pentamethylcyclopentadienyl)-manganese], μ-Ge-[(η^5-C$_5$Me$_5$)Mn(CO)$_2$]$_2$. *Chem. Ber.* **1985**, *118*, 340−347.

(9) Price, J. S.; Vargas-Baca, I.; Emslie, D. J. H.; Britten, J. F. Reactions of [(dmpe)$_2$MnH(C$_2$H$_4$)] with hydrogermanes to form germylene, germyl, hydrogermane, and germanide complexes. *Dalton Trans.* **2023**, *52*, 14880−14895.

(10) Ouellette, E. T.; Carpentier, A.; Brackbill, I. J.; Lohrey, T. D.; Douair, I.; Maron, L.; Bergman, R. G.; Arnold, J. σ or π? Bonding interactions in a series of rhenium metallotetrylenes. *Dalton Trans.* **2021**, *50*, 2083−2092.

(11) (a) Herrmann, W.; Kneuper, H.-J.; Herdtweck, E. Multiple Bonds between "Naked" Lead and Transition Metals-The First Example. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1062−1063. (b) Herrmann, W. Multiple Bonds between Transition Metals and Elements: Links between Inorganic Solid State Organometallic Chemistry. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 56−76. (c) Herrmann, W. A.; Kneuper, H.-J.; Herdtweck, E. Brückenständige Zinn-Atome in Organomangan-Komplexen: Aufbau, Strukturchemie und Reaktivität von Mangan-Zinn-Mehrfachbindungen. *Chem. Ber.* **1989**, *122*, 437−444.

(12) Usón, R.; Forniés, R.; Falvello, L. R.; Usón, M. A.; Usón, I. Synthesis and Molecular Structure of (NBu$_4$)$_2${Pb[Pt(C$_6$F$_5$)$_4$]$_2$}, the First Lead(II) Compound Linearly Bonded to Two Metal Atoms. *Inorg. Chem.* **1992**, *31*, 3697−3698.

(13) Forniés, J.; Giménez, N.; Ibáñez, S.; Lalinde, E.; Martín, A.; Moreno, M. T. An Extended Chain and Trinuclear Complexes Based on Pt(II)-M (M = Tl(I), Pb(II)) Bonds: Contrasting Photophysical Behavior. *Inorg. Chem.* **2015**, *54*, 4351−4363.

(14) Parvathy, P.; Parameswaran, P. Inorganometallic allenes [(Mn(η^5-C$_5$H$_5$)(CO)$_2$)$_2$-(μ-E)] (E = Si-Pb): bis-allylic anionic delocalization similar to organometallic allene but differential σ-donation and π-backdonation. *Phys. Chem. Chem. Phys.* **2023**, *25*, 26526−26537.

(15) (a) Westerberg, D. E.; Sutherland, B. R.; Huffman, J. C.; Caulton, K. G. Synthetic and Mechanistic Features of Dinuclear Reductive Elimination between Re$_2$H$_8$(PMe$_2$Ph)$_4$ and Several Tin(II) Reagents. *J. Am. Chem. Soc.* **1988**, *110*, 1642−1643. (b) Saint-Denis, T. G.; Zhang, B.; Settineri, N. S.; Handford, R. C.; Hall, M. B.; Tilley, T. D. Dimetalloylene (M-E-M) Complexes of Heavier Main Group Elements Ge, Sn, Pb, Bi via Cleavage of E-X Bonds (X=N(SiMe$_3$)$_2$, O^{t}Bu) with an Iridium Hydride. *Chem. Eur. J.* **2023**, *29*, e202301863.

(16) Aracama, M.; Esteruelas, M. A.; Lahoz, F. J.; López, J. A.; Meyer, U.; Oro, L. A.; Werner, H. Synthesis, Reactivity, Molecular Structure, and Catalytic Activity of the Novel Dichlorodihydridoosmium(IV) Complexes OsH$_2$Cl$_2$(PR$_3$)$_2$ (PR$_3$ = P-*i*-Pr3, PMe-*t*-Bu$_2$). *Inorg. Chem.* **1991**, *30*, 288−293.

(17) Esteruelas, M. A.; López, A. M.; Oliván, M. Polyhydrides of Platinum Group Metals: Nonclassical Interactions and σ-Bond Activation Reactions. *Chem. Rev.* **2016**, *116*, 8770−8847.

(18) Babón, J. C.; Esteruelas, M. A.; López, A. M. Homogeneous catalysis with polyhydride complexes. *Chem. Soc. Rev.* **2022**, *51*, 9717−9758.

(19) Buil, M. L.; Esteruelas, M. A.; López, M. A. Recent Advances in Synthesis of Molecular Heteroleptic Osmium and Iridium Phosphorescent Emitters. *Eur. J. Inorg. Chem.* **2021**, *2021*, 4731−4761.

(20) (a) Esteruelas, M. A.; Lledós, A.; Martín, M.; Maseras, F.; Osés, R.; Ruiz, N.; Tomás, J. Synthesis and Characterization of Mixed-Phosphine Osmium Polyhydrides: Hydrogen Delocalization in [OsH$_5$P$_3$]$^+$ Systems. *Organometallics* **2001**, *20*, 5297−5309. (b) Eguillor, B.; Esteruelas, M. A.; García-Raboso, J.; Oliván, M.; Oñate, E. Stoichiometric and Catalytic Deuteration of Pyridine and Methylpyridines by H/D Exchange with Benzene-d_6 Promoted by an Unsaturated Osmium Tetrahydride Species. *Organometallics* **2009**, *28*, 3700−3709. (c) Babón, J. C.; Esteruelas, M. A.; Fernández, I.; López, A. M.; Oñate, E. Evidence for a Bis(Elongated σ)-Dihydrideborate Coordinated to Osmium. *Inorg. Chem.* **2018**, *57*, 4482−4491. (d) Babón, J. C.; Esteruelas, M. A.; Fernández, I.; López, A. M.; Oñate, E. Reduction of Benzonitriles via Osmium-Azavinylidene Intermediates Bearing Nucleophilic and Electrophilic Centers. *Inorg. Chem.* **2019**, *58*, 8673−8684.

(21) Cabeza, J. A.; Reynes, J. F.; García, F.; García-Álvarez, P.; García-Soriano, R. Fast and scalable solvent-free access to Lappert's heavier tetrylenes E{N(SiMe$_3$)$_2$}$_2$ (E = Ge, Sn, Pb) and ECl{N(SiMe$_3$)$_2$} (E = Ge, Sn). *Chem. Sci.* **2023**, *14*, 12477−12483.

(22) This separation is significantly longer than the Pb−H bond lengths reported for Pb(μ-H)M complexes, which are in the range of 1.92−2.37 Å. See, for example: (a) Schneider, J.; Sindlinger, C. P.;

Eichele, K.; Schubert, H.; Wesemann, L. Low-Valent Lead Hydride and Its Extreme Low-Field ^{1} H NMR Chemical Shift. *J. Am. Chem. Soc.* **2017**, *139*, 6542−6545. (b) Queen, J. D.; Fettinger, J. C.; Power, P. P. Two quasi-stable lead(II) hydrides at ambient temperature. *Chem. Commun.* **2019**, *55*, 10285−10287. (c) Widemann, M.; Eichele, K.; Schubert, H.; Sindlinger, C. P.; Klenner, S.; Pöttgen, R.; Wesemann, L. Synthesis and Hydrogenation of Heavy Homologues of Rhodium Carbynes: $[(Me_3P)_2(Ph_3P)Rh/E\text{-}Ar^*]$ (E = Sn, Pb). *Angew. Che. Int. Ed.* **2021**, *60*, 5882−5889. (d) Widemann, M.; Aicher, F. S. W.; Bonath, M.; Eichele, K.; Maichle-Mössmer, C.; Schubert, H.; Sirsch, P.; Anwander, R.; Wesemann, L. Molecular Ln(III)-H-E(II) Linkages (Ln═Y, Lu; E═Ge, Sn, Pb). *Chem. Eur. J.* **2022**, *28*, e202201032.

(23) In contrast, the π-acceptor CO group provides a nonclassical nature to the $OsH_4(P^iPr_3)_2$ moiety. See: Gusev, D. G.; Kuhlman, R. L.; Renkema, K. B.; Eisenstein, O.; Caulton, K. C. Structure and H_2-Loss Energies of $OsHX(H_2)(CO)L_2$ Complexes (L = $P(t\text{-}Bu)_2Me$, $P(i\text{-}Pr)_3$; X = Cl, I, H): Attempted Correlation of $^{1}J(H\text{-}D)$, T_{1min}, and $\Delta G^{\neq}$. *Inorg. Chem.* **1996**, *35*, 6775−6783.

(24) (a) Jerabek, P.; Schwerdtfeger, P.; Frenking, G. Dative and Electron-Sharing Bonding in Transition Metal Compounds. *J. Comput. Chem.* **2019**, *40*, 247−264. (b) Fernández, I.; Holzmann, N.; Frenking, G. The Valence Orbitals of the Alkaline-Earth Atoms. *Chem. Eur. J.* **2020**, *26*, 14194−14210. (c) Sorbelli, D.; Belpassi, L.; Belanzoni, P. Cooperative small molecule activation by apolar and weakly polar bonds through the lens of a suitable computational protocol. *Chem. Commun.* **2024**, *60*, 1222−1238.

(25) (a) Frenking, G.; Tonner, R.; Klein, S.; Takagi, N.; Shimizu, T.; Krapp, A.; Pandey, K. K.; Parameswaran, P. New bonding modes of carbon and heavier group 14 atoms Si-Pb. *Chem. Soc. Rev.* **2014**, *43*, 5106−5139. (b) Xu, J.; Pan, S.; Yao, S.; Frenking, G.; Driess, M. The Heaviest Bottleable Metallylone: Synthesis of a monoatomic Zero-Valent Lead Complex ("Plumbylone"). *Angew. Chem., Int. Ed.* **2022**, *61*, e202209442.

(26) (a) Jessop, P. G.; Morris, R. H. Reactions of transition metal dihydrogen complexes. *Coord. Chem. Rev.* **1992**, *121*, 155−284. (b) Kubas, G. J. Metal-dihydrogen and σ-bond coordination: the consummate extension of the Dewar-Chatt-Duncanson model for metal-olefin π bonding. *J. Organomet. Chem.* **2001**, *635*, 37−68. (c) Jia, G.; Lin, Z.; Lau, C. P. Reactions of Dihydrogen-(norbornadiene) Complexes. *Eur. J. Inorg. Chem.* **2003**, *2003*, 2551−2562. (d) Kubas, G. J. Fundamentals of H_2 Binding and Reactivity on Transition Metals Underlying Hydrogenase Function and H_2 Production and Storage. *Chem. Rev.* **2007**, *107*, 4152−4205. (e) Morris, R. H. Dihydrogen, dihydride and in between: NMR and structural properties of iron group complexes. *Coord. Chem. Rev.* **2008**, *252*, 2381−2394. (f) Kubas, G. J. Activation of dihydrogen and coordination of molecular H_2 on transition metals. *J. Organomet. Chem.* **2014**, *751*, 33−49. (g) Crabtree, R. H. Dihydrogen Complexation. *Chem. Rev.* **2016**, *116*, 8750−8769.