# A Rutheno-Phosphanorcaradiene as a Masked Ambiphilic Metallo-Phosphinidene

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Abstract: Reaction of the ruthenium carbene complex Cp\*(IPr)RuCl (1, IPr = 1,3-bis(Dipp)-imidazol-2-ylidene; Dipp = 2,6disopropylphenyl) with sodium phosphaethynolate (NaOCP) led to intramolecular dearomatization of one of the Dipp substituents on the Ru-bound carbene to afford a Ru-bound phosphanorcaradiene. Computations by DFT reveal a transition state characterized by a concerted process whereby CO migrates to the Ru center as the P atom adds to the  $\pi$ -system of the aryl group. The phosphanorcaradiene possesses ambiphilic properties and reacts with both nucleophilic and electrophilic substrates, resulting in re-aromatization of the ligand aryl group with net P-atom transfer to give several unusual metal-bound. P-containing main-group moieties. These new complexes include a metallo-1-phospha-3-azaallene (Ru-P=C=NR), a metallo-iminophosphanide (Ru-P=N-R), and a metallo-phosphaformazan (Ru-P(=N-N=CPh<sub>2</sub>)<sub>2</sub>). Reaction of 1 with the carbene 2,3,4,5-tetramethylimidazol-2-ylidene (IMe4) produced the corresponding phosphaalkene DippP=IMe4.

Phosphinidenes possess six valence electrons and may exist in singlet or triplet ground states.<sup>1</sup> These species are therefore regarded as analogues of carbenes, and more broadly group 14 tetrylenes ( $R_2E$ , E = C, Si, Ge, Sn, Pb). However, the monovalency of phosphinidenes (R-P) leads to higher reactivity and dramatically complicates strategies to obtain isolable examples.<sup>1–6</sup> To date, there is only one report of an isolable, persistent phosphinidene, reported by the group of Bertrand.<sup>7,8</sup> Given the highly reactive nature of phosphinidenes, they have been studied as transient intermediates generated from suitable precursors and trapped by added reagents. For example, the groups of Fritz and Protasiewicz have investigated phospha-Wittig compounds (A, Figure 1A) for the generation of phosphinidenes.<sup>9–12</sup> More recently, the Cummins group has investigated phosphinidene transfer reactions using dibenzo-7<sup>λ3</sup>-phosphanorbornadienes (**B**, Figure 1A), which expel the phosphinidene fragment with formation of anthracene.<sup>13–20</sup> The latter strategy has been used more generally for the generation of low-valent main-group entities.21,22

A strategy for stabilizing low-coordinate main-group species involves their coordination to transition metal centers, as exemplified by numerous multiply bonded terminal phosphido complexes, LnM=P.<sup>23-36</sup> Similar considerations apply to the stabilization of phosphinidene complexes  $(L_nM=\ddot{P}-R)$ , which can be generated from the cheleotropic elimination of an organic fragment from the corresponding phosphine complex: a representative example is the metal-



Figure 1. Synthetic strategies for generation of transient metallophosphinidienes.

coordinated phosphepine, (C, Figure 1A), which eliminates naphthalene to afford the phosphinidene.<sup>37–41</sup> A related type of metal-stabilized, formally electron-deficient metal-phosphorous species is represented by the hitherto unknown metallo-



Scheme 1. Synthetic logic for the preparation of transition metalstabilized low valent main-group fragments by metal (Fe, Ru, Os)mediated fragmention of anonic [A-B]-.



The Tillev group has employed 16-electron, yet inherently electron rich, piano-stool complexes Cp\*(L)MX (Cp\*

=  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>; L = phosphine, NHC; M = Ru, Os; X = halide) for the synthesis of metal complexes containing reactive group 14 intermediates. This strategy, used to obtain silylene, silene, germylene, stannylene, and metallostannylene complexes, involves substitution of halide for an anionic species poised to undergo migratory cleavage, driven by the metal center's propensity to achieve an 18-electron configuration (Scheme 1).<sup>43–49</sup> Given this background, it was of interest to explore the possibility of intramolecular cleavage of phosphaethynolate (PCO<sup>-</sup>, readily available as NaOCP) in a Cp\*(L)M-PCO complex



Scheme 2. Reaction of 1 with NaOCP to generate the metallo-phosphanorcaradiene 2.

group with inequivalent ring hydrogens (ABC spin system, by <sup>1</sup>H NMR spectroscopy). This suggests the presence of a *cis*diene structural motif and dearomatization of one of the Dipp groups. The IR spectrum contains a stretch at 1902 cm<sup>-1</sup> and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy reveals a resonance at 210 ppm, consistent with a transition metal-bound CO ligand. The molecular structure of **2**, determined by X-ray crystallography, corresponds to a metallo-phosphanorcaradiene with a Rubound CO ligand (Scheme 2). Compound **2** represents the second isolated phosphanorcaradiene, and the only one to feature a covalent transition metal-phosphorous bond.<sup>53</sup>



Figure 2. Figure 2. Proposed mechanism for the formation of **2** from the putative  $Cp^*(IPr)RuPCO$  by DFT computations at the  $\omega$ B97X-D4/def2-TZVPPD CPM(THF) level of theory.

to introduce the electron-withdrawing CO ligand and produce a metallo-phosphinidene (Scheme 1,  $A-B^- = OC-P^-$ ).<sup>50,51</sup>

Exposure of purple dark Cp\*(IPr)RuCl (1, IPr = 1, 3-bis(Dipp)imidazol-2-vlidene; Dipp \_ 2,6diisopropylphenyl) to sodium phosphaethynolate (NaOCP) in THF led to formation of a bright yellow solution within 15 minutes at room temperature.52 Workup revealed near-quantitative conversion to a product possessing an IPr ligand lacking mirror-plane symmetry, and having one Dipp

Interestingly, a phosphine analogue of 1, Cp\*(iPr<sub>3</sub>P)RuCl, reacted with NaOCP in THF to give a complex mixture of products, and the reaction proceeded similarly in the presence of various unsaturated compounds added as potential traps for a metallophosphinidene (superstoichiometric amounts of olefins, dienes, anthracene, etc.; see supporting information for details). Exposure of 1 to NaOCP in the presence of an excess of the same potential traps (vide supra) gave only 2 as the Ru-containing product. These results indicate that the trapping of an incipient metallo-phosphinidene is highly favored by intramolecular transfer of phosphorous to a πdonor within the metal complex. This is consistent with DFT computations at the ωB97X-D4/def2-TZVPPD/CPM(THF) level of theory; after metathetical exchange between the Ru-bound chloride of Cp\*(IPr)RuCl with the phosphaethynolate anion, a putative intermediate Cp\*(IPr)RuPCO is formed, which converts to 2 with COmigration and Dipp dearomatization. This process proceeds in a concerted but somewhat asynchronous manner involving CO migration to Ru prior to P-C bond formation, with no discreet intermediate (Figure 2). The barrier for this reaction is only 8.8 kcal mol-1, and the product 2 is 26.4 kcal mol<sup>-1</sup> lower in energy than the putative Cp\*(IPr)RuPCO, likely due to the thermodynamic favorability of the bonding between the electron rich Ru and the CO ligand. Attempts to observe/isolate Cp\*(L)RuPCO are currently underway.

Reaction of the nucleophile xylyl (2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) isocyanide with **2** at 70 °C over 72 h led to formation of the  $\eta^{1}$ -1-phospha-3-azaallene **3**, through re-aromatization of the Dipp moiety and formal P-atom transfer to xylyl isocyanide (Scheme 3, Figure 3). Compound **3** possesses a <sup>31</sup>P NMR resonance of –166 ppm and X-ray crystallography revealed that the P=C=NR fragment is linear and cumulene-like (P1-C1 = 1.640(7) Å *versus*  $\Sigma_{r_{cov}}$  = 1.80 Å; C1-N3 = 1.231(9) Å *versus*  $\Sigma_{r_{cov}}$  = 1.51 Å; P1-C1-N1 angle = 173.1(5) °).<sup>54</sup> The infrared spectrum contains a strong band at 1785 cm<sup>-1</sup>, comparable to a previously reported P=C=N stretch of Mes\*-P=C=N-*t*Bu (1885 cm<sup>-1</sup>; Mes\* = 2,4,6-*t*Bu<sub>3</sub>C<sub>6</sub>H<sub>3</sub>).<sup>55</sup> Several non-metal-containing 1-phospha-3-azaallene compounds have been reported, as well as Nb- and Ta-bound  $\eta^{2-}(C,N)$  1-phospha-3-azaallene complexes. In this context, compound **3** is unique in that the PCN motif is terminally bound only through the P-atom.<sup>7,8,55–59</sup>

The reaction of **2** with an excess of 2,3,4,5-tetramethylimidazol-2-ylidene (IMe<sub>4</sub>) in toluene resulted in formation of Ru-imidazol-2-yl (**4**) and the carbene-stabilized Dipp-phosphinidene (**5**) in 72% yield (Scheme 3, Figure 3). Compound **5** 



Scheme 3. Reactions of electrophiles and nucleophiles with 2.

was previously reported by Hering-Junghans, and all spectroscopic data from the isolated compound match those previously reported while X-ray crystallography verifies the reported structural assignment (Scheme 3; Figure 3).<sup>60</sup>

Thus, nucleophilic additions to **2** have been observed to proceed by two different processes. The isocyanide attacks **2** to cleave the P–C bonds of the phosphanorcaradiene motif to rearomatize the Dipp group and form **3**, while IMe<sub>4</sub> reacts to cleave a N–C bond to give **4** and **5**. The latter reaction is envisioned as proceeding by attack onto the P atom to generate an intermediate, Cp\*(IPr)(CO)Ru–P=IMe<sub>4</sub>, which undergoes P–C coupling to give **5** with trapping of the Ru product by a second equivalent of IMe<sub>4</sub> (see **Figure S1** for further mechanistic speculation). Note that a related intramolecular N–C



Figure 3. Solid state structures of compounds 3-to-7. For the intersecting planes of 7 the blue plane is defined by P1, N5, N6, and C2 and the pink plane is defined by P1, N3, N4, and C1.

cleavage mediated by a transient phosphinidene (generated from a carbene-stabilized phosphirene) has been reported by Stephan.<sup>17</sup>

The formations of **3**, **4**, and **5** are consistent with the reported electrophilic nature of phosphinidenes/phosphinidene equivalents.<sup>7,8,20</sup> The possibility of **2** also possessing nucleophilic character at P is suggested by the pyramidal nature of the P atom and the presumed presence of a stereochemically-active lone pair (Scheme 2). Indeed, **2** has been found to exhibit nucleophilic character. It reacted with tosyl azide at room temperature over 15 min to form **6**, which possesses a P—N double bond (P1—N1 = 1.604(3) Å *versus*  $\Sigma r_{cov}$  = 1.78 Å; Scheme 3, Figure 3), in 88% yield.<sup>54</sup> In contrast to the Staudinger reaction, in which azides oxidize trivalent phosphines to form pentavalent iminophosphiranes, the P-atom of **6** remains trivalent due to dissociation and rearomatization of the Dipp moiety. The P=NR fragment of **6** may be regarded as an iminophosphanide, and IR spectroscopy reveals the presence of a CO stretch at 1945 cm<sup>-1</sup> as well as an intense stretch at 1140 cm<sup>-1</sup>, which is in good agreement with the theoretical P=N stretch of 1100 cm<sup>-1</sup> calculated at the PBE0/def2-TZVP level of theory (see **Figure S3** and **S4** and the supporting information). Compound **6** is structurally similar to Cummins' iminophosphenium complex (NRAr)<sub>3</sub>Mo–P=N–Mes (R = R = C(CD<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>, Ar = 3,5-C,H<sub>3</sub>Me, Mes = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>); however, whereas the iminophosphenium is linear (Mo–P–N angle of 179 °), compound **6** is bent (Ru1—P1—N3 angle of 113.0(1) °).<sup>61,62</sup> Cummins has noted the isolobal analogy between the linear iminophosphenium ligand, [P=NR<sup>+</sup>], and the nitrosyl cation, [N=O<sup>+</sup>], and in this context the bent iminophosphanide [P=NR<sup>-</sup>] is analogous to the bent nitrosyl anionic ligand, [N=O<sup>-</sup>].<sup>63</sup>

Exposure of **2** to an excess of diphenyldiazaomethane at 60 °C led to formation of the Ru-(*E*,*E*)-phosphaformazan complex **7** (Scheme 3, Figure 3). Presumably, **7** is formed *via* a transient Ru-iminophosphanide (Ru–P=N-N=CPh<sub>2</sub>) which then reacts with a second equivalent of diphenyldiazomethane. The solid-state structure of **7** reveals that P–N bond distances of **7** (1.598(7) Å, Figure 3) are equivalent and shorter than the sum of covalent radii (1.78 Å).<sup>54</sup> Also, the N–N bond distances in **7**, 1.398(8) and 1.383(7) Å, are shorter than the sum of covalent radii (1.46 Å).<sup>54</sup> Interestingly, the atoms of the N-N-P-N-N motif do not reside in a single plane, but the planes that define P1-N3-N4-C1 (pink) and P1-N5-N6-C2 (blue) intersect with a dihedral angle of 25.20 ° (Figure 3). This suggests a lack of electronic delocalization in the phosphaformazan unit, even though P–N and N–N multiple bond character is implicated by the observed bond lengths (see supporting information). The IR spectrum of **7** contains a CO stretch at 1926 cm<sup>-1</sup> as well as an intense band at 1128 cm<sup>-1</sup> which is consistent with the P=N stretch observed in **6** (*vide supra*). Though the –P(=NN=RR')<sub>2</sub> fragment of **7** seems to be unprecedented, a related bis(hydrazonato) ligand  $\eta^1$ -Cp\*-P(NHN=CPh<sub>2</sub>)<sub>2</sub> has been characterized in a tungsten complex.<sup>64</sup>

In summary, a rutheno-phosphanorcaradiene, formed by reaction of 1 with NaOCP, serves as a synthetic equivalent for the metallo-phosphinidene Cp\*(IPr)(CO)Ru–P. It is apparent that intramolecular interactions play a significant role in the stabilization of 2, which forms *via* cycloaddition of the metal-bound P atom to the Dipp group of the NHC ligand. Interestingly, reactions of 2 reveal ambiphilic properties of the P-atom and formal P-atom transfer to both nucleophiles and electrophiles. The detailed mechanisms for formation of products 3–7, as well as the further potential of 2 as a metallo-phosphinidene synthon, is under investigation.

## Associated Content (supporting information)

The Supporting information is available free of charge at [X] and contains synthetic details, crystallographic data, full characterization data (*e.g.* NMR, IR, EA data, etc.), as well as computational details.

Accession Codes 2312066 (2), 2312067 (3), 2312062 (4), 2312063 (5), 2312064 (6) and 2312065 (7) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <u>www.ccdc.ac.uk/data\_request/cif</u> or by emailing <u>data\_request@ccdc.cam.ac.uk</u>, or by contacting The Cambridge Crystallographic Data Centre,12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

#### **Author Information**

The authors declare no competing financial interests.

#### Acknowledgements

This work was funded by the National Science Foundation under grant no. CHE-1954808. The German Research Council (DFG) is acknowledged for the support within the project Sche 384/32-2. T.G.S. thanks the Arnold and Mabel Beckman Foundation for the Arnold O. Beckman Postdoctoral Fellowship. This research used the resources of the Advanced Light Source (ALS), which is a DOE Office of Science User Facility under contract no. DE-AC02- 05CH11231. We acknowledge the UC Berkeley CheXray X-ray crystallographic facility and the advice of Dr. Simon J. Teat (ALS). NMR spectra were collected at the College of Chemistry NMR facility, at the University of California, Berkeley; we thank Dr. Hasan Celik for assistance with NMR spectroscopy. The J. Arnold laboratory at University of California Berkeley is thanked for use of their IR instrumentation.

### References

- (1) Mathey, F. *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; G. Thieme Verlag: Stuttgart, Germany, 1990.
- (2) Grützmacher, H.-F.; Šilhan, W.; Schmidt, U. Über Phosphinidene, 5. Notiz Zum Nachweis von Phenyl- Und Methylphosphiniden Beim Thermischen Zerfall von Cyclophosphinen Durch Pyrolyse-Massenspektrometrie. *Chem. Ber.* **1969**, *102* (9), 3230–3232. https://doi.org/https://doi.org/10.1002/cber.19691020943.
- (3) Schmidt, U. Formation, Detection, and Reactions of Phosphinidenes (Phosphanediyls). *Angew. Chem. Int. Ed. English* **1975**, *14* (8), 523–528. https://doi.org/https://doi.org/10.1002/anie.197505231.
- (4) Bock, H.; Bankmann, M. Evidence for Surface Phosphinidene Intermediates [RP → Mg] in the Heterogeneous Dechlorination of Alkyldichlorophosphanes RPCl<sub>2</sub> by Mg Metal. *J. Chem. Soc. Chem. Commun.* **1989**, No. 16, 1130–1132. https://doi.org/10.1039/C39890001130.
- (5) Cowley, A. H.; Gabbai, F.; Schluter, R.; Atwood, D. New Approaches to the Generation of Phosphinidenes. *J. Am. Chem. Soc.* **1992**, *114* (8), 3142–3144. https://doi.org/10.1021/ja00034a073.
- (6) Li, X.; Lei, D.; Chiang, M. Y.; Gaspar, P. P. General Approaches to Phosphinidenes via Retroadditions. *J. Am. Chem. Soc.* **1992**, *114* (22), 8526–8531. https://doi.org/10.1021/ja00048a026.
- (7) Hansmann, M. M.; Jazzar, R.; Bertrand, G. Singlet (Phosphino)Phosphinidenes Are Electrophilic. *J. Am. Chem. Soc.* **2016**, *138* (27), 8356–8359. https://doi.org/10.1021/jacs.6b04232.
- Liu, L.; Ruiz, D. A.; Munz, D.; Bertrand, G. A Singlet Phosphinidene Stable at Room Temperature. *Chem* 2016, 1 (1), 147–153. https://doi.org/10.1016/j.chempr.2016.04.001.
- (9) Fritz, G.; Vaahs, T.; Fleischer, H.; Matern, E. tBu<sub>2</sub>P-P=PBrtBu<sub>2</sub>. LiBr and the Formation of tBu<sub>2</sub>P-P. *Angew. Chem. Int. Ed. English* **1989**, *28* (3), 315–316. https://doi.org/https://doi.org/10.1002/anie.198903151.
- (10) Shah, S.; Protasiewicz, J. D. 'Phospha-Variations' on the Themes of Staudinger and Wittig: Phosphorus Analogs of Wittig Reagents. *Coord. Chem. Rev.* 2000, 210 (1), 181–201. https://doi.org/https://doi.org/10.1016/S0010-8545(00)00311-8.
- (11) Protasiewicz, J. D.; Hering-Junghans, C. Phosphanylidenephosphoranes. In *Encyclopedia of Inorganic and Bioinorganic Chemistry*; John Wiley & Sons, Ltd, 2022; pp 1–27. https://doi.org/https://doi.org/10.1002/9781119951438.eibc2795.
- (12) Shah, S.; Yap, G. P. A.; Protasiewicz, J. D. Crystal Structure of the Phosphanylidene-Σ4-Phosphorane DmpP=PMe<sub>3</sub> (Dmp=2,6-Mes<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) and Reactions with Electrophiles. *J. Organomet. Chem.* **2000**, *608* (1), 12–20. https://doi.org/https://doi.org/10.1016/S0022-328X(00)00284-9.
- (13) Eckhardt, A. K.; Riu, M.-L. Y.; Müller, P.; Cummins, C. C. Staudinger Reactivity and Click Chemistry of Anthracene (A)-Based Azidophosphine N<sub>3</sub>PA. *Inorg. Chem.* **2022**, *61* (3), 1270–1274. https://doi.org/10.1021/acs.inorgchem.1c03753.
- (14) Riu, M.-L. Y.; Transue, W. J.; Rall, J. M.; Cummins, C. C. An Azophosphine Synthetic Equivalent of Mesitylphosphaazide and Its 1,3-Dipolar Cycloaddition Reactions. *J. Am. Chem. Soc.* 2021, 143 (20), 7635–7640. https://doi.org/10.1021/jacs.1c03333.
- (15) Geeson, M. B.; Transue, W. J.; Cummins, C. C. Organoiron- and Fluoride-Catalyzed Phosphinidene Transfer to Styrenic Olefins in a Stereoselective Synthesis of Unprotected Phosphiranes. J. Am. Chem. Soc. 2019, 141 (34), 13336–13340. https://doi.org/10.1021/jacs.9b07069.
- (16) Transue, W. J.; Nava, M.; Terban, M. W.; Yang, J.; Greenberg, M. W.; Wu, G.; Foreman, E. S.; Mustoe, C. L.; Kennepohl, P.; Owen, J. S.; Billinge, S. J. L.; Kulik, H. J.; Cummins, C. C. Anthracene as a Launchpad for a Phosphinidene Sulfide and for Generation of a Phosphorus–Sulfur Material Having the Composition P<sub>2</sub>S, a Vulcanized Red Phosphorus That Is Yellow. *J. Am. Chem. Soc.* **2019**, *141* (1), 431–440. https://doi.org/10.1021/jacs.8b10775.
- (17) Liu, L. L.; Zhou, J.; Cao, L. L.; Andrews, R.; Falconer, R. L.; Russell, C. A.; Stephan, D. W. A Transient Vinylphosphinidene via a Phosphirene–Phosphinidene Rearrangement. *J. Am. Chem. Soc.* **2018**, *140* (1), 147– 150. https://doi.org/10.1021/jacs.7b11791.
- (18) Eckhardt, A. K.; Riu, M.-L. Y.; Ye, M.; Müller, P.; Bistoni, G.; Cummins, C. C. Taming Phosphorus Mononitride. *Nat. Chem.* **2022**, *14* (8), 928–934. https://doi.org/10.1038/s41557-022-00958-5.
- (19) Transue, W. J.; Velian, A.; Nava, M.; García-Iriepa, C.; Temprado, M.; Cummins, C. C. Mechanism and Scope of Phosphinidene Transfer from Dibenzo-7-Phosphanorbornadiene Compounds. *J. Am. Chem. Soc.* 2017, *139* (31), 10822–10831. https://doi.org/10.1021/jacs.7b05464.
- (20) Velian, A.; Cummins, C. C. Facile Synthesis of Dibenzo-7λ3-Phosphanorbornadiene Derivatives Using Magnesium Anthracene. J. Am. Chem. Soc. 2012, 134 (34), 13978–13981. https://doi.org/10.1021/ja306902j.
- (21) Bakewell, C.; Garçon, M.; Kong, R. Y.; O'Hare, L.; White, A. J. P.; Crimmin, M. R. Reactions of an Aluminum(I) Reagent with 1,2-, 1,3-, and 1,5-Dienes: Dearomatization, Reversibility, and a Pericyclic Mechanism. *Inorg. Chem.* 2020, 59 (7), 4608–4616. https://doi.org/10.1021/acs.inorgchem.9b03701.
- (22) Lutters, D.; Severin, C.; Schmidtmann, M.; Müller, T. Activation of 7-Silanorbornadienes by N-Heterocyclic

Carbenes: A Selective Way to N-Heterocyclic-Carbene-Stabilized Silylenes. J. Am. Chem. Soc. 2016, 138 (18), 6061–6067. https://doi.org/10.1021/jacs.6b02824.

- (23) Kramkowski, P.; Baum, G.; Radius, U.; Kaupp, M.; Scheer, M. Novel Complexes with a Short Tungsten– Phosphorus Triple Bond. *Chem. Eur. J.* **1999**, *5* (10), 2890–2898.
- https://doi.org/https://doi.org/10.1002/(SICI)1521-3765(19991001)5:10<2890::AID-CHEM2890>3.0.CO;2-#.
  Balázs, G.; Sierka, M.; Scheer, M. Antimony–Tungsten Triple Bond: A Stable Complex with a Terminal Antimony Ligand. *Angew. Chem. Int. Ed.* 2005, *44* (31), 4920–4924. https://doi.org/https://doi.org/10.1002/anie.200500781.
- (25) Curley, J. J.; Piro, N. A.; Cummins, C. C. A Terminal Molybdenum Arsenide Complex Synthesized from Yellow Arsenic. *Inorg. Chem.* 2009, 48 (20), 9599–9601. https://doi.org/10.1021/ic9016068.
- (26) Johnson, B. P.; Balázs, G.; Scheer, M. Low-Coordinate E<sub>1</sub> Ligand Complexes of Group 15 Elements—A Developing Area. Coord. Chem. Rev. 2006, 250 (9), 1178–1195. https://doi.org/https://doi.org/10.1016/j.ccr.2005.11.023.
- (27) Scheer, M.; Müller, J.; Baum, G.; Scheer, M.; Müller, J.; Baum, G.; Häser, M. Reaction Behaviour of a Complex Containing a Tungsten Phosphorus Triple Bond with σ-Acceptor Compounds of Group 13. *Chem. Commun.* 1998, No. 9, 1051–1052. https://doi.org/10.1039/A801136B.
- (28) Balázs, G.; Gregoriades, L. J.; Scheer, M. Triple Bonds between Transition Metals and the Heavier Elements of Groups 14 and 15. *Organometallics* **2007**, *26* (13), 3058–3075. https://doi.org/10.1021/om0701080.
- (29) Scheer, M.; Müller, J.; Häser, M. Complexes Containing Phosphorus and Arsenic as Terminal Ligands. *Angew. Chemie Int. Ed. English* **1996**, *35* (21), 2492–2496. https://doi.org/https://doi.org/10.1002/anie.199624921.
- (30) Buss, J. A.; Oyala, P. H.; Agapie, T. Terminal Molybdenum Phosphides with d Electrons: Radical Character Promotes Coupling Chemistry. *Angew. Chemie Int. Ed.* **2017**, *56* (46), 14502–14506. https://doi.org/https://doi.org/10.1002/anie.201707921.
- (31) Joost, M.; Transue, W. J.; Cummins, C. C. Terminal Tungsten Pnictide Complex Formation through Pnictaethynolate Decarbonylation. *Chem. Commun.* **2017**, 53 (77), 10731–10733. https://doi.org/10.1039/C7CC06841G.
- (32) Abbenseth, J.; Diefenbach, M.; Hinz, A.; Alig, L.; Würtele, C.; Goicoechea, J. M.; Holthausen, M. C.; Schneider, S. Oxidative Coupling of Terminal Rhenium Pnictide Complexes. *Angew. Chemie Int. Ed.* 2019, *58* (32), 10966–10970. https://doi.org/https://doi.org/10.1002/anie.201905130.
- (33) Mösch-Zanetti, N. C.; Schrock, R. R.; Davis, W. M.; Wanninger, K.; Seidel, S. W.; O'Donoghue, M. B. Triamidoamine Complexes of Molybdenum and Tungsten That Contain Metal-E (E = N, P, and As) Single, Double, or Triple Bonds. J. Am. Chem. Soc. 1997, 119 (45), 11037–11048. https://doi.org/10.1021/ja971727z.
- (34) Zanetti, N. C.; Schrock, R. R.; Davis, W. M. Monomeric Molybdenum and Tungsten Complexes That Contain a Metal–Phosphorus Triple Bond. Angew. Chem. Int. Ed. English 1995, 34 (18), 2044–2046. https://doi.org/https://doi.org/10.1002/anie.199520441.
- (35) Senthil, S.; Kwon, S.; Fehn, D.; Im, H.; Gau, M. R.; Carroll, P. J.; Baik, M.-H.; Meyer, K.; Mindiola, D. J. Metal-Ligand Cooperativity to Assemble a Neutral and Terminal Niobium Phosphorus Triple Bond (Nb≡P). Angew. Chem. Int. Ed. 2022, 61 (52), e202212488. https://doi.org/https://doi.org/10.1002/anie.202212488.
- (36) Cherry, J.-P. F.; Stephens, F. H.; Johnson, M. J. A.; Diaconescu, P. L.; Cummins, C. C. Terminal Phosphide and Dinitrogen Molybdenum Compounds Obtained from Pnictide-Bridged Precursors. *Inorg. Chem.* 2001, 40 (27), 6860–6862. https://doi.org/10.1021/ic015592g.
- (37) Borst, M. L. G.; Bulo, R. E.; Winkel, C. W.; Gibney, D. J.; Ehlers, A. W.; Schakel, M.; Lutz, M.; Spek, A. L.; Lammertsma, K. Phosphepines: Convenient Access to Phosphinidene Complexes. *J. Am. Chem. Soc.* 2005, 127 (16), 5800–5801. https://doi.org/10.1021/ja050817y.
- (38) Aktaş, H.; Slootweg, J. C.; Lammertsma, K. Nucleophilic Phosphinidene Complexes: Access and Applicability. *Angew. Chem. Int. Ed.* **2010**, *49* (12), 2102–2113. https://doi.org/https://doi.org/10.1002/anie.200905689.
- (39) Huttner, G.; Evertz, K. Phosphinidene Complexes and Their Higher Homologs. *Acc. Chem. Res.* **1986**, *19* (12), 406–413. https://doi.org/10.1021/ar00132a005.
- (40) Mathey, F. The Development of a Carbene-like Chemistry with Terminal Phosphinidene Complexes. *Angew. Chem. Int. Ed. English* **1987**, *26* (4), 275–286. https://doi.org/https://doi.org/10.1002/anie.198702753.
- (41) Hitchcock, P. B.; Lappert, M. F.; Leung, W.-P. The First Stable Transition Metal (Molybdenum or Tungsten) Complexes Having a Metal–Phosphorus(III) Double Bond: The Phosphorus Analogues of Metal Aryl- and Alkyl-Imides; X-Ray Structure of [Mo(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(=PAr)](Ar = C<sub>6</sub>H<sub>2</sub>But<sub>3</sub>-2,4,6). *J. Chem. Soc. Chem. Commun.* **1987**, No. 17, 1282–1283. https://doi.org/10.1039/C39870001282.
- (42) Sun, J.; Verplancke, H.; Schweizer, J. I.; Diefenbach, M.; Würtele, C.; Otte, M.; Tkach, I.; Herwig, C.; Limberg, C.; Demeshko, S.; Holthausen, M. C.; Schneider, S. Stabilizing P≡P: P<sub>2</sub><sup>2–</sup>, P<sub>2</sub><sup>–</sup>, and P<sub>2</sub><sup>0</sup> as Bridging Ligands. *Chem* **2021**, *7* (7), 1952–1962. https://doi.org/https://doi.org/10.1016/j.chempr.2021.06.006.
- (43) Fasulo, M. E.; Glaser, P. B.; Tilley, T. D. Cp\*(P'Pr<sub>3</sub>)RuOTf: A Reagent for Access to Ruthenium Silylene Complexes. Organometallics 2011, 30 (20), 5524–5531. https://doi.org/10.1021/om200795x.
- (44) Glaser, P. B.; Tilley, T. D. Synthesis and Chemistry of the 16-Electron Osmium Complex  $[OsBr(\eta^5-C_5Me_5)(P'Pr_3)]$ . *Eur. J. Inorg. Chem.* **2001**, 2001 (11), 2747–2750. https://doi.org/https://doi.org/10.1002/1099-

0682(200111)2001:11<2747::AID-EJIC2747>3.0.CO;2-B.

- (45) Glaser, P. B.; Tilley, T. D. Synthesis and Reactivity of Silyl and Silylene Ligands in the Coordination Sphere of the 14-Electron Fragment Cp\*(<sup>i</sup>Pr<sub>3</sub>P)Os+. Organometallics **2004**, 23 (24), 5799–5812. https://doi.org/10.1021/om0400620.
- (46) Campion, B. K.; Heyn, R. H.; Tilley, T. D. Preparation and Reactivity of 16-Electron 'Half-Sandwich' Ruthenium Complexes; X-Ray Crystal Structure of (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Ru(PPr<sup>i</sup><sub>3</sub>)Cl. *J. Chem. Soc. Chem. Commun.* **1988**, No. 4, 278– 280. https://doi.org/10.1039/C39880000278.
- (47) Campion, B. K.; Heyn, R. H.; Tilley, T. D. Ruthenium(IV) Silyl Hydride Complexes via Reaction of Silanes with 16-Electron [Ru(n<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)(PPr<sup>i</sup><sub>3</sub>)X](X = CI, CH<sub>2</sub>SiHPh<sub>2</sub>, SiMePh<sub>2</sub>) Complexes. Hydride Migrations to an H<sub>2</sub>-Silene Ligand. J. Chem. Soc. Chem. Commun. **1992**, No. 17, 1201–1203. https://doi.org/10.1039/C39920001201.
- (48) Campion, B. K.; Heyn, R. H.; Tilley, T. D. Preparation, Isolation, and Characterization of Transition-Metal η<sup>2</sup>-Silene Complexes. X-ray Crystal Structure of (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)[P(*i*-Pr)<sub>3</sub>]Ru(H)(η<sup>2</sup>-CH<sub>2</sub>SiPh<sub>2</sub>). J. Am. Chem. Soc. **1988**, 110 (22), 7558–7560. https://doi.org/10.1021/ja00230a058.
- (49) Hayes, P. G.; Waterman, R.; Glaser, P. B.; Tilley, T. D. Synthesis, Structure, and Reactivity of Neutral Hydrogen-Substituted Ruthenium Silylene and Germylene Complexes. *Organometallics* 2009, 28 (17), 5082–5089. https://doi.org/10.1021/om900348m.
- (50) Basappa, S.; Bhawar, R.; Nagaraju, D. H.; Bose, S. K. Recent Advances in the Chemistry of the Phosphaethynolate and Arsaethynolate Anions. *Dalton Trans.* **2022**, *51* (10), 3778–3806. https://doi.org/10.1039/D1DT03994F.
- (51) Goicoechea, J. M.; Grützmacher, H. The Chemistry of the 2-Phosphaethynolate Anion. *Angew. Chem. Int. Ed.* **2018**, *57* (52), 16968–16994. https://doi.org/https://doi.org/10.1002/anie.201803888.
- (52) Huang, J.; Stevens, E. D.; Nolan, S. P.; Petersen, J. L. Olefin Metathesis-Active Ruthenium Complexes Bearing a Nucleophilic Carbene Ligand. *J. Am. Chem. Soc.* **1999**, *121* (12), 2674–2678. https://doi.org/10.1021/ja9831352.
- (53) Liu, L. L.; Zhou, J.; Andrews, R.; Stephan, D. W. A Room-Temperature-Stable Phosphanorcaradiene. J. Am. Chem. Soc. 2018, 140 (24), 7466–7470. https://doi.org/10.1021/jacs.8b04930.
- (54) Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S. Covalent Radii Revisited. *Dalton Trans.* 2008, No. 21, 2832–2838. https://doi.org/10.1039/b801115j.
- (55) Yoshifuji, M.; Niitsu, T.; Toyota, K.; Inamoto, N.; Hirotsu, K.; Odagaki, Y.; Higuchi, T.; Nagase, S. X-ray Structure of a Sterically Protected 1-Aza-3-Phospha-Allene. *Polyhedron* **1988**, 7 (21), 2213–2216. https://doi.org/https://doi.org/10.1016/S0277-5387(00)81807-0.
- (56) Wilson, D. W. N.; Franco, M. P.; Myers, W. K.; McGrady, J. E.; Goicoechea, J. M. Base Induced Isomerisation of a Phosphaethynolato-Borane: Mechanistic Insights into Boryl Migration and Decarbonylation to Afford a Triplet Phosphinidene. *Chem. Sci.* 2020, *11* (3), 862–869. https://doi.org/10.1039/C9SC05969E.
- (57) Grundmann, A.; Sárosi, M. B.; Lönnecke, P.; Hey-Hawkins, E. Organotantalum Phosphaketene and Phosphaazaallene Complexes. *Eur. J. Inorg. Chem.* 2014, 2014 (19), 2997–3001. https://doi.org/https://doi.org/10.1002/ejic.201402400.
- (58) Alexander, J. B.; Glueck, D. S.; Yap, G. P. A.; Rheingold, A. L. Synthesis, Structure, and Reactivity of the First Phosphaazaallene-Metal Complex. *Organometallics* **1995**, *14* (7), 3603–3606. https://doi.org/10.1021/om00007a076.
- (59) Fischer, M.; Hering-Junghans, C. On 1,3-Phosphaazaallenes and Their Diverse Reactivity. *Chem. Sci.* 2021, 12 (30), 10279–10289. https://doi.org/10.1039/D1SC02947A.
- (60) Siewert, J.-E.; Schumann, A.; Hering-Junghans, C. Phosphine-Catalysed Reductive Coupling of Dihalophosphanes. *Dalt. Trans.* 2021, *50* (42), 15111–15117. https://doi.org/10.1039/D1DT03095G.
- (61) Laplaza, C. E.; Davis, W. M.; Cummins, C. C. A Molybdenum–Phosphorus Triple Bond: Synthesis, Structure, and Reactivity of the Terminal Phosphido (P<sup>3-</sup>) Complex [Mo(P)(NRAr)<sub>3</sub>]. *Angew. Chem. Int. Ed. English* **1995**, 34 (18), 2042–2044. https://doi.org/https://doi.org/10.1002/anie.199520421.
- Martinez, J. L.; Lutz, S. A.; Beagan, D. M.; Gao, X.; Pink, M.; Chen, C.-H.; Carta, V.; Moënne-Loccoz, P.; Smith, J. M. Stabilization of the Dinitrogen Analogue, Phosphorus Nitride. ACS Cent. Sci. 2020, 6 (9), 1572–1577. https://doi.org/10.1021/acscentsci.0c00944.
- (63) Hoffmann, R. Building Bridges Between Inorganic and Organic Chemistry (Nobel Lecture). *Angew. Chem. Int. Ed. English* **1982**, *21* (10), 711–724. https://doi.org/10.1002/anie.198207113.
- (64) Seidl, M.; Stubenhofer, M.; Timoshkin, A. Y.; Scheer, M. Reaction of Pentelidene Complexes with Diazoalkanes: Stabilization of Parent 2,3-Dipnictabutadienes. *Angew. Chemie Int. Ed.* 2016, 55 (45), 14037–14040. https://doi.org/https://doi.org/10.1002/anie.201607793.



