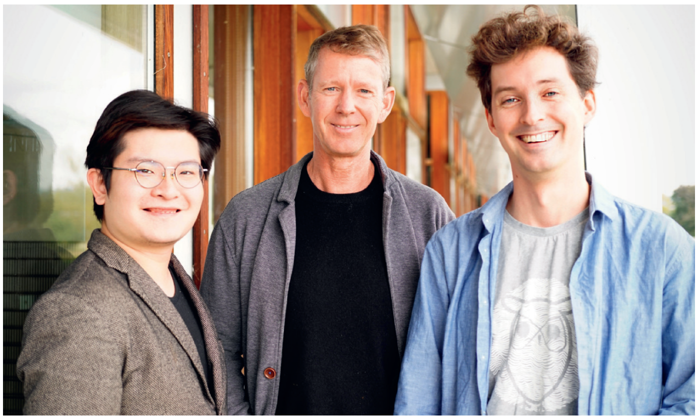
doi:10.2533/chimia.2025.855 Chimia 79 (2025) 855–858 © B. Kooij, T. H. Wong, K. Severin

# Transition Metal Complexes with *N*-Heterocyclic Vinylidene Ligands

Bastiaan Kooij, Tak Hin Wong, and Kay Severin*

*Abstract*: Transition metal complexes with *N*-heterocyclic vinylidene ligands can be obtained by combining *N*-heterocyclic diazoolefins with suitable metal precursors. The vinylidene ligands can act as potent C-donor ligands, allowing for the stabilization of electron-deficient and low-coordinate metal complexes.

**Keywords**: Diazoolefin · Organometallic chemistry · Transition metals · Vinylidene ligand



From left to right: Tak Hin Wong, Kay Severin, Bastiaan Kooij.

***Bastiaan Kooij*** is a postdoctoral researcher in the group of Prof. Kay Severin at the EPFL, Switzerland. He is interested in organometallic and main-group element chemistry, with a focus on the reactivity of novel diazo compounds. He completed his BSc and MSc at the University of Amsterdam before moving to Switzerland for his PhD and postdoctoral studies. Besides spending time in front of a glovebox, he enjoys hiking and skiing in the Alps and analog photography.

***Tak Hin Wong*** received his BSc in chemistry (International Research Enrichment track) from the Hong Kong University of Science and Technology, during which he also completed an exchange at ETH Zürich with Prof. Erick M. Carreira. He then worked as a Junior Research Associate at the Chinese University of Hong Kong with Prof. Billy Ng before beginning his PhD at the EPFL in 2022 under the supervision of Prof. Kay Severin. His current research focuses on the organometallic chemistry of diazoolefins and alkynyl triazenes.

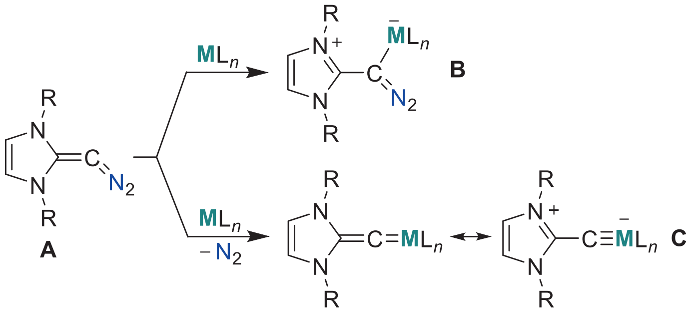
***Kay Severin*** is a professor of chemistry at the EPFL, Switzerland. His research group works on synthetic organic and inorganic chemistry, with projects ranging from small molecule activation (the chemistry of nitrous oxide) to the construction of functional nanostructures.

## 1. Introduction

Carbene complexes are accessible by reactions of metal complexes with diazoalkanes.[1] In analogy, it is possible to prepare vinylidene complexes by combining diazoolefins with suitable metal precursors. However, there is an important hurdle: the required diazo compounds tend to display very low thermal stability. Heterocumulenes of type $R^1R^2C{=}C{=}N_2$ ($R^1/R^2$ = H, alkyl, aryl) rapidly lose dinitrogen, preventing isolation.[2,3] Until recently, the existence of diazoolefins was mainly deduced from the results of trapping experiments.

In 2021, the Hansmann group and our group reported independently the synthesis and characterization of thermally stable diazoolefins.[2,4–6] Key to success was the (formal) fusion of azole rings to the $CN_2$ group. As predicted theoretically,[7] the *N*-heterocycles provide an electronic stabilization of the heterocumulene.

In our group, we have primarily focused on the chemistry of diazoolefins of type **A** (Scheme 1).[6,8–11] These compounds can be obtained by reactions of the corresponding *N*-heterocyclic olefins with the diazo transfer reagent nitrous oxide,[6,12,13] or, as shown by Hansmann and coworkers, with organic azides.[14] The exocyclic carbon atom in **A** has a strong ylidic character, and it is possible to form adducts of type **B** with metal complexes such as AuCl, $RhCl(CO)_2$, PdCl(allyl), $AlCl_3$, or $Cr(CO)_5$.[6,11] However, it is also possible to obtain vinylidene complexes of type **C**. *N*-Heterocyclic vinylidene ligands were found to be strong C-donor ligands with diverse reactivity. The results obtained thus far are summarized below.



Scheme 1. *N*-Heterocyclic diazoolefins (**A**) can be used as ligands for metal complex (**B**) or as precursors for the synthesis of *N*-heterocyclic vinylidene complexes (**C**).

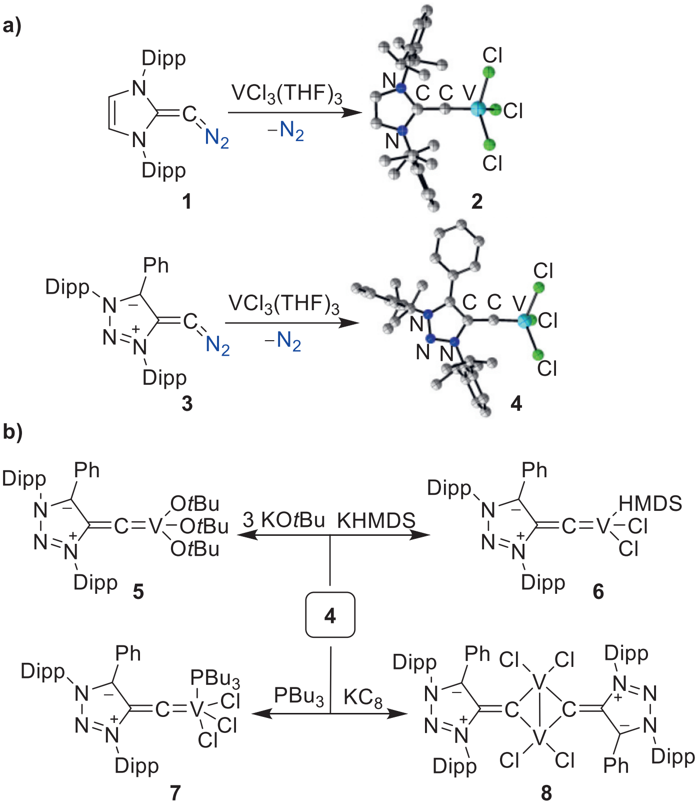
## 2. *N*-Heterocyclic Vinylidene Complexes

In their 'free' form, *N*-heterocyclic vinylidenes have a triplet ground state.[15,16] By analogy to Schrock-type carbenes, which feature alkylidene ligands in a triplet ground state,[17] we hypothesized that early transition metals could be effective in stabilizing *N*-heterocyclic vinylidenes.

---

*Correspondence: Prof. K. Severin, E-mail: kay.severin@epfl.ch
Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

The reaction of diazoolefin **1** with $VCl_3(THF)_3$ resulted in the formation of the vinylidene complex **2** (Scheme 2a).[18] In a related fashion, the vinylidene complex **4** was obtained from the mesoionic diazoolefin **3**.



Scheme 2. Synthesis of the vanadium vinylidene complexes **2** and **4** (Dipp = diisopropyl phenyl), (**a**) and reactions of complex **4** (**b**). The structures of **2** and **4** are based on crystallographic analyses.

Both complexes were analyzed by single-crystal X-ray diffraction. The analyses revealed that the vinylidene ligands are bound to the vanadium centers in a nearly linear fashion. The short C–V bonds (**2**: 1.706(2) Å; **4**: 1.704(2) Å) indicate partial triple bond character.

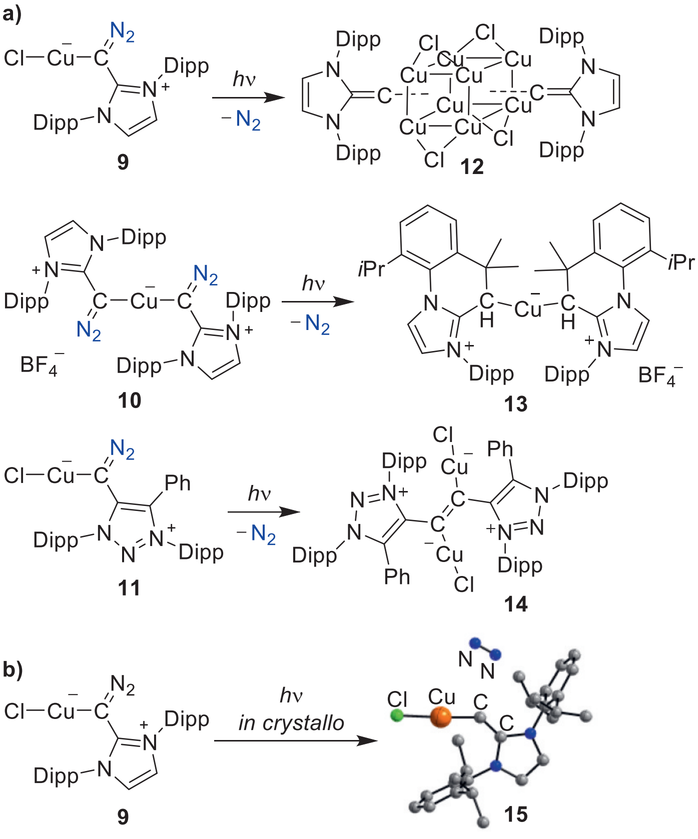
Reactivity studies were performed with complex **4**. Ligand substitution reactions with KO*t*Bu and potassium bis(trimethylsilyl) amide (KHMDS) resulted in the formation of the vinylidene complexes **5** and **6**, respectively (Scheme 2b). The metal-centered reactivity contrasts that of Fischer-type vinylidene complexes of the late transition metals, which undergo nucleophilic attack at the metal-bound carbon.[19–21] The Lewis acidity of the vanadium center in **4** is evident from its reaction with $PBu_3$, which yielded adduct **7**. Reduction of **4** with $KC_8$ in THF gave the dinuclear complex **8**, in which two V centers are bridged by two vinylidene ligands.

Studies with copper were motivated by the proposed role of reactive μ-vinylidene intermediates in azide-alkyne [2+3] cycloadditions ('click reactions').[22–24]

For our investigations, we first synthesized the adducts **9**–**11** by combining the diazoolefins **1** or **3** with $[Cu(COD)Cl]_2$ (COD = 1,5-cyclooctadiene) or $[Cu(CH_3CN)_4](BF_4)$, respectively.[25] Subsequently, we examined if the adducts could be converted photochemically into vinylidene complexes.

Irradiation of complex **9** afforded the cubic $Cu_8$ cluster **12** (Scheme 3a).[25] This complex represents the first example of an isolable copper vinylidene complex. Cluster **12** proved thermally robust, showing no decomposition upon heating.

The homoleptic complex **10** displayed a different reactivity. Irradiation resulted in loss of $N_2$ to give complex **13** with two C-bound *N*-heterocyclic olefin ligands. The transformation possibly proceeds *via* a short-lived vinylidene, followed by intramolecular C–H activation.



Scheme 3. Photochemical syntheses of the copper complexes **12**–**14**, (**a**) and *in crystallo* synthesis of the vinylidene complex **15**. (**b**) The molecular structure of **15** is based on a crystallographic analysis.

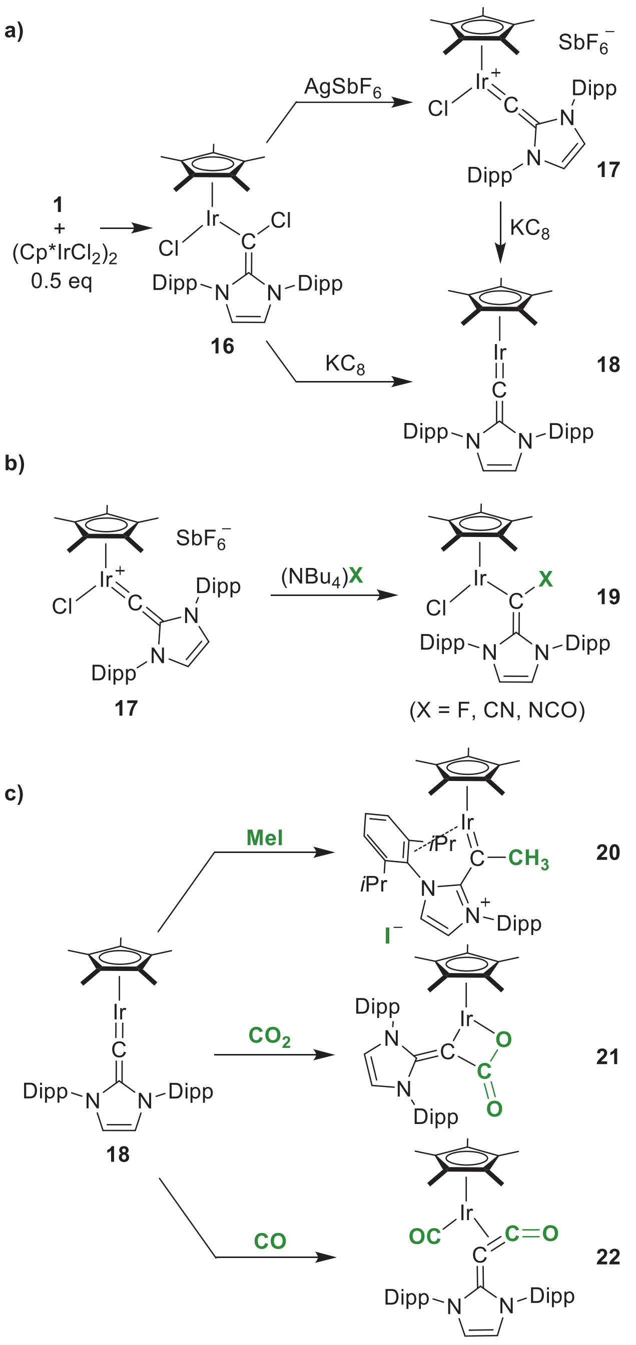
Irradiation of complex **11** gave the dinuclear complex **14**. Crystallographic analysis showed a central Cu–C=C–Cu double bond, indicating that the targeted vinylidene had dimerized by C-C coupling. The organic ligand of complex **14** can be described as a cumulene of the type (NHC)=C=C=(NHC) (NHC= *N*-heterocyclic carbene). Previous attempts to isolate such cumulenes had not been successful.[26,27] Complex **14** shows that (NHC)=C=C=(NHC) cumulenes can be stabilized by coordination to Lewis acidic metal complexes such as CuCl.

The complexes **12**–**14** likely arise from transient vinylidenes that undergo cluster formation, C–H activation, or C–C coupling. We were able to obtain experimental evidence for such an intermediate by *in crystallo* photolysis[28,29] of complex **9**. Irradiation of a single-crystal at 100 K promoted *in crystallo* conversion of **9** to **15** and $N_2$ (Scheme 3b). DFT calculations suggest a triplet ground state for **15**, with the spin density mostly concentrated on the metallated carbon atom and on the Cu center.

Motivated by the results with vanadium and copper, we investigated whether *N*-heterocyclic vinylidene complexes could also be formed with other transition metals.

When a solution of the diazoolefin **1** in toluene was added to a solution of $(Cp^*IrCl_2)_2$ at 60 °C, complex **16** was formed as the main product (Scheme 4a).[30] As revealed by XRD analysis, complex **16** features an *N*-heterocyclic vinyl ligand. To date, only a limited number of transition metal complexes with *N*-heterocyclic vinyl ligands (also known as 'anionic *N*-heterocyclic olefins') have been reported.[31–33] The formation of complex **16** is thought to proceed *via* a diazoolefin adduct of type **A** (Scheme 1), followed by loss of dinitrogen and chloride migration from Ir to Ca.

The C–Cl bond formation could be reversed by the addition of $AgSbF_6$, resulting in the formation of complex **17** with a terminal



Scheme 4. Synthesis (**a**) and reactivity (**b** and **c**) of the iridium vinylidene complexes **17** and **18**.

*N*-heterocyclic vinylidene ligand (Scheme 4a). Reduction of complex **17** with $KC_8$ gave the vinylidene complex **18** in high yield. The same product could also be accessed by reduction of **16** using $KC_8$ again. Single-crystal XRD analysis revealed that complex **16** adopts a distinctive 'pogo stick' geometry.

The vinylidene complexes **17** and **18** have both very short Ir–C bonds and elongated IrC–C bonds. Accordingly, they can also be described as complexes with imidazolium carbyne ligands.

Having obtained two distinct vinylidene complexes, we next investigated their reactivity. Since complex **17** was obtained by chloride abstraction, we assumed that we could convert it back into complexes with *N*-heterocyclic vinyl ligands by addition of halides or pseudo-halides. Indeed, upon the addition of $(NBu_4)X$ salts (X = F, CN, NCO) to a solution of complex **17** , the neutral adducts **19** were formed (Scheme 4b).[30]

The addition reactions show that the metal-bound carbon of the vinylidene ligand in complex **17** is electrophilic. This finding is consistent with computational results, which indicate that complex **17** possesses a low-lying LUMO with a significant contribution at $C_\alpha$.

Reactivity studies with the 'pogo stick' complex **18** showed that $C_\alpha$ is nucleophilic, rather than electrophilic. A reaction with methyl iodide resulted in a C-C coupling reaction to give the ionic complex **20**. Additional evidence for the nucleophilic nature of complex **18** was provided by its ability to react with $CO_2$ and CO (Scheme 4c). Overall, the reactivity of the 'pogo stick' complex **18** closely matches that reported for the imido complex Cp*Ir(N*t*Bu), which was described by Bergman and coworkers.[34,35] The similarity indicates that *N*-heterocyclic vinylidenes can serve as both structural and functional analogues of imido ligands.

## 3. Conclusions

*N*-Heterocyclic diazoolefins were found to be well-suited precursors for the synthesis of metal complexes with *N*-heterocyclic vinylidene ligands. Thus far, there was only very limited knowledge about complexes with *N*-heterocyclic vinylidene ligands.[36] Our work has shown that these ligands can act as potent C-donor ligands, allowing for the stabilization of electron-deficient and low-coordinate metal complexes.

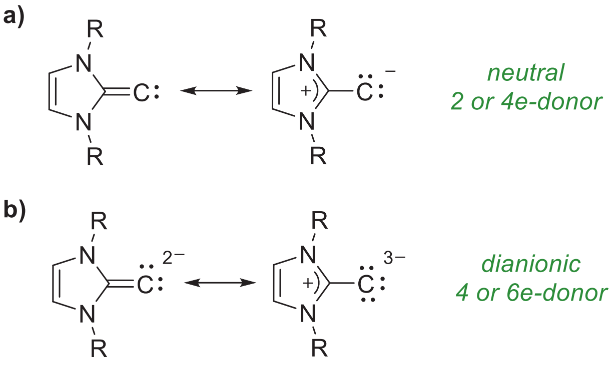


Fig. 1. *N*-Heterocyclic vinylidene ligands can be described as formally neutral or dianionic ligands.

When described as a formally neutral ligand, *N*-heterocyclic vinylidenes can donate two or four electrons (Fig. 1a). Such a description seems appropriate for the iridium complex **17**, for example. The vanadium complexes **2** and **4**, on the other hand, are best described as V(V) complexes with dianionic vinylidene ligands. Similarly, the 'pogo stick' complex **18** can be regarded as an Ir(III) complex with a dianionic vinylidene. In its dianionic form, the vinylidene ligand is able to donate up to six electrons to the metal center (Fig. 1b). An analogous situation is found for imido ligands of type $RN^{2-}$, which can act as 2σ, 4π-donor ligands.[37] The use of *N*-heterocyclic vinylidenes as surrogates for imido ligands offers an intriguing avenue for future investigations, given the prevalence of imido ligands in a wide range of transition metal catalysts.

### *Acknowledgements*

The work was supported by the Swiss National Science Foundation (# 200020_181974).

Received: October 6, 2025

---

[1] B. D. Bergstrom, L. A. Nickerson, J. T. Shaw, L. W. Souza, *Angew. Chem. Int. Ed.* **2021**, *60*, 6864, https://doi.org/10.1002/anie.202007001.
[2] M. M. Hansmann, *Angew. Chem. Int. Ed.* **2023**, *62*, e202304574, https://doi.org/10.1002/anie.202304574.
[3] R. Knorr, *Chem. Rev.* **2004**, *104*, 3795, https://doi.org/10.1021/cr030616h.
[4] P. W. Antoni, C. Golz, J. J. Holstein, D. A. Pantazis, M. M. Hansmann, *Nat. Chem.* **2021**, *13*, 587, https://doi.org/10.1038/s41557-021-00675-5.

[5] P. W. Antoni, J. Reitz, M. M. Hansmann, *J. Am. Chem. Soc*. **2021**, *143*, 12878, https://doi.org/10.1021/jacs.1c06906.

[6] P. Varava, Z. Dong, R. Scopelliti, F. Fadaei-Tirani, K. Severin, *Nat. Chem*. **2021**, *13*, 1055, https://doi.org/10.1038/s41557-021-00790-3.

[7] S. Klein, R. Tonner, G. Frenking, *Chem. – Eur. J.* **2010**, *16*, 10160, https://doi.org/10.1002/chem.201000174.

[8] P. Varava, T. H. Wong, Z. Dong, A. Yu. Gitlina, A. Sienkiewicz, W. Feuerstein, R. Scopelliti, F. Fadaei-Tirani, K. Severin, *Angew. Chem. Int. Ed*. **2023**, *62*, e202303375, https://doi.org/10.1002/anie.202303375.

[9] B. Kooij, Z. Dong, F. Fadaei-Tirani, R. Scopelliti, K. Severin, *Angew. Chem. Int. Ed*. **2023**, *62*, e202308625, https://doi.org/10.1002/anie.202308625.

[10] W. Feuerstein, P. Varava, F. Fadaei-Tirani, R. Scopelliti, K. Severin, *Chem. Commun*. **2021**, *57*, 11509, https://doi.org/10.1039/d1cc05161j.

[11] B. Kooij, D. Chen, F. Fadaei-Tirani, K. Severin, *Angew. Chem. Int. Ed*. **2024**, *63*, e202407945, https://doi.org/10.1002/anie.202407945.

[12] A. Genoux, K. Severin, *Chem. Sci*. **2024**, *15*, 13605, https://doi.org/10.1039/d4sc04530k.

[13] K. Severin, *Chem. Soc. Rev*. **2015**, *44*, 6375, https://doi.org/10.1039/c5cs00339c.

[14] J. Reitz, P. W. Antoni, J. J. Holstein, M. M. Hansmann, *Angew. Chem. Int. Ed*. **2023**, *62*, e202301486, https://doi.org/10.1002/anie.202301486.

[15] M.-D. Su, C.-C. Chuang, *Theor. Chem. Acc*. **2013**, *132*, 1, https://doi.org/10.1007/s00214-013-1360-x.

[16] Y. Kutin, J. Reitz, P. W. Antoni, A. Savitsky, D. A. Pantazis, M. Kasanmascheff, M. M. Hansmann, *J. Am. Chem. Soc*. **2021**, *143*, 21410, https://doi.org/10.1021/jacs.1c11062.

[17] C. D. Montgomery, *J. Chem. Educ*. **2015**, *92*, 1653, https://doi.org/10.1021/acs.jchemed.5b00036.

[18] B. Kooij, Z. Dong, P. Varava, F. Fadaei-Tirani, R. Scopelliti, L. Piveteau, A. Bornet, K. Severin, *Chem. Commun*. **2022**, *58*, 4204, https://doi.org/10.1039/d2cc00768a.

[19] S. W. Roh, K. Choi, C. Lee, *Chem. Rev*. **2019**, *119*, 4293, https://doi.org/10.1021/acs.chemrev.8b00568.

[20] B. M. Trost, A. McClory, *Chem. – Asian J*. **2008**, *3*, 164, https://doi.org/10.1002/asia.200700247.

[21] C. Bruneau, P. H. Dixneuf, *Angew. Chem., Int. Ed*. **2006**, *45*, 2176, https://doi.org/10.1002/anie.200501391.

[22] B. T. Worrell, J. A. Malik, V. V. Fokin, *Science* **2013**, *340*, 457, https://doi.org/10.1126/science.1229506.

[23] J. E. Hein, V. V. Fokin, *Chem. Soc. Rev*. **2010**, *39*, 1302, https://doi.org/10.1039/B904091A.

[24] B. F. Straub, *Chem. Commun*. **2007**, *37*, 3868, https://doi.org/10.1039/B706926J.

[25] B. Kooij, P. Varava, F. Fadaei-Tirani, R. Scopelliti, D. A. Pantazis, G. P. Van Trieste, III, D. C. Powers, K. Severin, *Angew. Chem. Int. Ed.* **2023**, *62*, e202214899, https://doi.org/10.1002/anie.202214899.

[26] D. C. Georgiou, I. Mahmood, M. A. Haghighatbin, C. F. Hogan, J. L. Dutton, *Pure Appl. Chem*. **2017**, *89*, 791, https://doi.org/10.1515/pac-2016-1126.

[27] D. C. Georgiou, B. D. Stringer, C. F. Hogan, P. J. Barnard, D. J. D. Wilson, N. Holzmann, G. Frenking, J. L. Dutton, *Chem. – Eur. J.* **2015**, *21*, 3377, https://doi.org/10.1002/chem.201405416.

[28] K. A. Reid, D. C. Powers, *Chem. Commun*. **2021**, *57*, 4993, https://doi.org/10.1039/D1CC01684A.

[29] A. Das, G. P. Van Trieste, D. C. Powers, *Comments Inorg. Chem*. **2020**, *40*, 116, https://doi.org/10.1080/02603594.2020.1747054.

[30] T. H. Wong, P. Varava, F. Fadaei-Tirani, R. Scopelliti, K. Severin, *J. Am. Chem. Soc*. **2025**, *147*, 19911, https://doi.org/10.1021/jacs.5c04371.

[31] I. C. Watson, Y. Zhou, M. J. Ferguson, E. Rivard, *Z. Anorg. Allg. Chem*. **2022**, *648*, e202200082, https://doi.org/10.1002/zaac.202200082.

[32] I. C. Watson, M. J. Ferguson, E. Rivard, *Inorg. Chem*. **2021**, *60*, 18347, https://doi.org/10.1021/acs.inorgchem.1c02961.

[33] M. Fischer, M. M. D. Roy, S. Hüller, M. Schmidtmann, R. Beckhaus, *Dalton Trans*. **2022**, *51*, 10690, https://doi.org/10.1039/D2DT00014H.

[34] D. S. Glueck, F. J. Hollander, R. G. Bergman, *J. Am. Chem. Soc*. **1989**, *111*, 2719, https://doi.org/10.1021/ja00189a059.

[35] D. S. Glueck, J. Wu, F. J. Hollander, R. G. Bergman, *J. Am. Chem. Soc*. **1991**, *113*, 2041, https://doi.org/10.1021/ja00006a026.

[36] B. J. Frogley, A. F. Hill, *Chem. Commun*. **2019**, *55*, 15077, https://doi.org/10.1039/C9CC07760J.

[37] D. E. Wigley, *Prog. Inorg. Chem*. **1994**, *42*, 239, https://doi.org/10.1002/9780470166437.ch4.

## *License and Terms*

The definitive version of this article is the electronic one that can be found at https://doi.org/10.2533/chimia.2025.855