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## CO<sub>2</sub> cleavage by tantalum/M (M = iridium, osmium) heterobimetallic complexes†

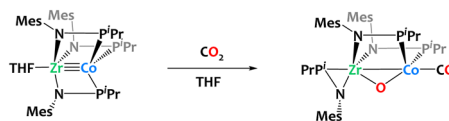
Abdelhak Lachguar,<sup>a</sup> Christopher Z. Ye,<sup>ib bc</sup> Sheridan N. Kelly,<sup>id bc</sup> Erwann Jeanneau,<sup>d</sup> Iker Del Rosal,<sup>id e</sup> Laurent Maron,<sup>id e</sup> Laurent Veyre,<sup>a</sup> Chloé Thieuleux,<sup>ib a</sup> John Arnold<sup>id \*bc</sup> and Clément Camp<sup>id \*a</sup>

A novel Ta/Os heterobimetallic complex, [Ta(CH<sub>2</sub>tBu)<sub>3</sub>(μ-H)<sub>3</sub>OsCp\*], **2**, is prepared by protonolysis of Ta(CH<sub>2</sub>tBu)(CH<sub>2</sub>tBu)<sub>3</sub> with Cp\*OsH<sub>5</sub>. Treatment of **2** and its iridium analogue [Ta(CH<sub>2</sub>tBu)<sub>3</sub>(μ-H)<sub>2</sub>IrCp\*], **1**, with CO<sub>2</sub> under mild conditions reveal the efficient cleavage of CO<sub>2</sub>, driven by the formation of a tantalum oxo species in conjunction with CO transfer to the osmium or iridium fragments, to form Cp\*Ir(CO)H<sub>2</sub> and Cp\*Os(CO)H<sub>3</sub>, respectively. This bimetallic reactivity diverges from more classical CO<sub>2</sub> insertion into metal–X (X = metal, hydride, alkyl) bonds.

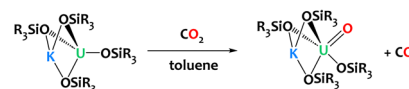
The design of synthetic bimetallic complexes associating different metals with complementary Lewis acidic/Lewis basic behaviour has raised interest for cooperative reactivity,<sup>1–10</sup> including CO<sub>2</sub> activation.<sup>11–17</sup> In many instances, these bifunctional complexes lead to CO<sub>2</sub> adducts or insertion products, in which a bent CO<sub>2</sub> fragment binds across the two metals.<sup>18–27</sup> In contrast, only a few heterobimetallic complexes have clearly exhibited the capability to cleave the C–O bond within CO<sub>2</sub>. Thomas and colleagues reported oxidative CO<sub>2</sub> cleavage across the early/late heterobimetallic complex Co(iPr<sub>2</sub>PNMes)<sub>3</sub>Zr(THF), yielding (OC)Co(iPr<sub>2</sub>PNMes)<sub>2</sub>(μ-O)Zr(iPr<sub>2</sub>PNMes) at ambient temperature (Scheme 1a).<sup>28</sup> The Mazzanti group reported the potassium-assisted reductive cleavage of CO<sub>2</sub> by a U(III) siloxide complex, resulting in CO evolution and the formation of a pentavalent

uranium oxo complex (Scheme 1b). When the potassium cation is encapsulated in 18-crown-6, bimetallic cooperativity no longer occurs, and a carbonate complex is formed instead. Our group has developed an Ir/Al-based heterobimetallic complex proficient in CO<sub>2</sub> deoxygenation, yielding Cp\*Ir(CO)H<sub>2</sub>, Cp\*IrH<sub>4</sub>, and [Al(Py)(OAr)(iBu)]<sub>2</sub>(μ-O) at room temperature (Scheme 1c).<sup>29</sup> Recently, Campos and coworkers reported the use of Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> for triggering the bimetallic cleavage of Fe-bound CO<sub>2</sub> moiety, to form an oxo carbonyl complex (Scheme 1d). The choice of the Al-based Lewis acid partner plays a pivotal role in initiating this reaction, as boron, zinc, or gold Lewis acids did not exhibit activity in this transformation.<sup>22</sup> Finding right bimetallic combinations therefore remains a major challenge for controlling reactivity.

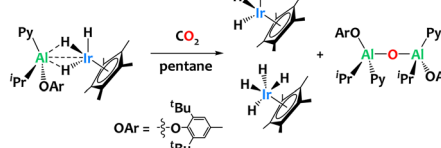
a. Thomas 2011



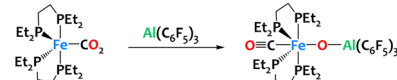
b. Mazzanti 2014



c. Camp 2021



d. Campos 2022



Scheme 1 Reports of CO<sub>2</sub> cleavage by heterobimetallic complexes relevant to the present study.<sup>22,28–30</sup>

<sup>a</sup> Laboratory of Catalysis, Polymerization, Processes and Materials (CP2M UMR 5128) CNRS, Université Claude Bernard Lyon 1, CPE-Lyon, Institut de Chimie de Lyon, 43 Bvd du 11 Novembre 1918, 69616 Villeurbanne, France. E-mail: clement.camp@univ-lyon1.fr

<sup>b</sup> Department of Chemistry, University of California, Berkeley, California 94720, USA. E-mail: arnold@berkeley.edu

<sup>c</sup> Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

<sup>d</sup> Centre de Diffraction Henri Longchambon, Université Claude Bernard Lyon 1, 5 Rue de la Doua, 69100 Villeurbanne, France

<sup>e</sup> Université de Toulouse, CNRS, INSA, UPS, UMR5215, LCPNO, 135 Avenue de Rangueil, F-31077 Toulouse, France

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The alkane elimination reaction between metal (poly)alkyls and (poly)hydride species has proven efficient for accessing heterobimetallic complexes.<sup>31–36</sup> We used this strategy to synthesize compound  $[\text{Ta}(\text{CH}_2\text{tBu})_3\text{IrH}_2\text{Cp}^*]$  **1** from the tantalum tris-neopentyl neopentylidene complex  $\text{Ta}(\text{CHtBu})(\text{CH}_2\text{tBu})_3$  and the iridium tetrahydride complex  $\text{Cp}^*\text{IrH}_4$  (Scheme 2-top).<sup>37</sup> This prompted us to extend this chemistry by investigating the reactivity of  $\text{Ta}(\text{CHtBu})(\text{CH}_2\text{tBu})_3$  towards related 6d metal polyhydrides. Treating  $\text{Ta}(\text{CHtBu})(\text{CH}_2\text{tBu})_3$  with  $\text{Cp}^*\text{OsH}_5$ <sup>38,39</sup> in a 1 : 1 stoichiometric ratio in pentane at room temperature yields the heterobimetallic complex  $[\text{Ta}(\text{CH}_2\text{tBu})_3(\mu\text{-H})_3\text{OsCp}^*]$  **2** in 98% isolated yield, accompanied by the elimination of one equivalent of neopentane (Scheme 2-middle).  $^1\text{H}$  NMR monitoring of the reaction of **2** with  $\text{Cp}^*\text{OsH}_5$  (1 equiv.) suggests the slow formation of a trinuclear  $\text{TaOs}_2$  species (see Fig. S7, ESI†), analogous to the  $\text{TaIr}_2$  species previously reported.<sup>40</sup> Surprisingly,  $\text{Cp}^*\text{ReH}_6$ <sup>41</sup> shows no reactivity towards  $\text{Ta}(\text{CHtBu})(\text{CH}_2\text{tBu})_3$  either in pentane at room temperature or in  $\text{C}_6\text{D}_6$  at 80 °C. DFT calculations indicate that the Ta/Re analogue should be thermodynamically stable: this observed lack of reactivity is thus surprising, and might be due to the lack of available coordination site at Re (see ESI† for discussion).

Identification of **2** is confirmed through a range of analytical methods including infrared (IR) and multinuclei ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^1\text{H}$ - $^1\text{H}$  COSY,  $^1\text{H}$ - $^{13}\text{C}$  HSQC and HMBC) solution NMR spectroscopy, elemental analysis, and X-ray diffraction studies. In the  $^1\text{H}$ -NMR spectrum of **2** obtained in a toluene- $d_8$  solution, the hydride resonance appears as a high-field singlet at  $\delta = -6.90$  ppm, integrating for 3H. The hydride resonance in **2** exhibits a shift of  $\Delta\delta = +4.3$  ppm from  $\text{Cp}^*\text{OsH}_5$  which is reminiscent of the observed shift from  $\text{Cp}^*\text{IrH}_4$  to **1**, of approximately  $\Delta\delta = +3.5$  ppm.<sup>37</sup> The IR spectrum of compound **2** displays a characteristic metal-hydride stretching vibration signal at  $1961\text{ cm}^{-1}$ , consistent with bridging hydrides. This value deviates significantly from that of complex  $[\text{Ta}(\text{CH}_2\text{tBu})_3\text{IrCp}^*(\text{H})_2]$ , **1**, featuring two terminal hydrides ( $\nu_{\text{Ir-H}} = 2061\text{ cm}^{-1}$ , see Fig. S6, ESI†) and that of the  $\text{Cp}^*\text{OsH}_5$  precursor, which exhibits a strong absorption at  $2083(\text{s})\text{ cm}^{-1}$  with a minor

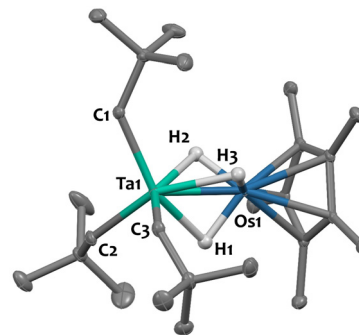
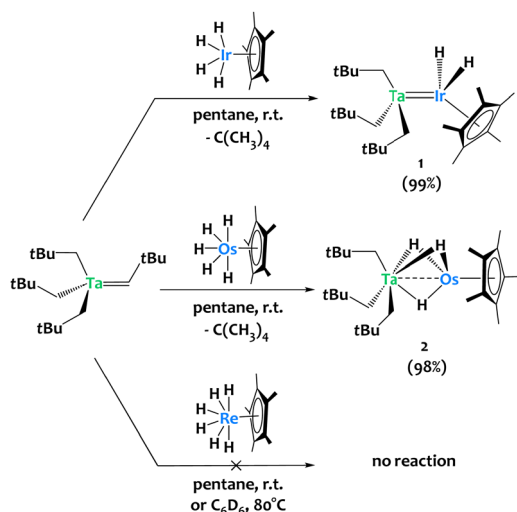


Fig. 1 Solid-state molecular structure of **2** (30% probability ellipsoids). Hydrogen atoms from the hydrocarbon ligands are omitted for clarity. Selected bond distances (Å) and angles (°): Ta1–Os1 2.4817(2), Ta1–C1 2.132(3), Ta1–C2 2.136(3), Ta1–C3 2.143(3), Os1–H1 1.45(5), Os1–H2 1.56(5), Os1–H3 1.48(8), Ta1–H1 2.07(5), Ta1–H2 2.03(5), Ta1–H3 2.07(8), Ta1–Os1– $\text{Cp}^*\text{centroid}$  178.1(1).

one at  $2214(\text{w})\text{ cm}^{-1}$ .<sup>42</sup> For comparison, the metal-hydride stretch is observed at  $1982\text{ cm}^{-1}$  in  $[\text{Hf}(\text{CH}_2\text{tBu})_3(\mu\text{-H})_3\text{IrCp}^*]$ <sup>34</sup> and at  $1952$  and  $1970\text{ cm}^{-1}$  for  $[\text{Cp}_2\text{Zr}(\text{X})(\mu\text{-H})_3\text{Os}(\text{PMe}_2\text{Ph})_3]$  ( $\text{X} = \text{Cl}$  or  $\text{H}$  respectively),<sup>43</sup> where the two metal centres are bridged by three hydride ligands.

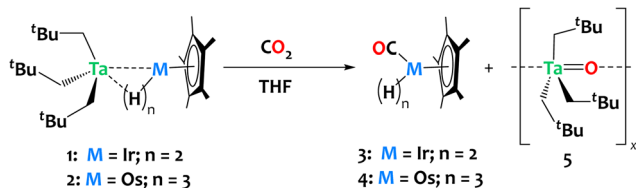
Single crystals of **2** suitable for X-ray diffraction were grown from a saturated pentane solution at  $-40\text{ °C}$ . The solid-state structure is depicted in Fig. 1. The nearly linear Ta–Os– $\text{Cp}^*\text{centroid}$  angle ( $178.1(1)^\circ$ ), indicates the presence of three bridging hydrides between the two metals, arranged in a tripod geometry around the  $\{\text{Cp}^*\text{Os}\}$  core. This angle aligns well with values reported for systems featuring similar bridging hydride motifs, such as  $[\text{CpRu}(\mu\text{-H})_4\text{OsCp}^*]$  ( $179.2(9)^\circ$ )<sup>44</sup> and  $[\text{Hf}(\text{CH}_2\text{tBu})_3(\mu\text{-H})_3\text{IrCp}^*]$  ( $179.2(3)^\circ$ ),<sup>34</sup> but starkly contrasts with that found in complex **1**, featuring two terminal Ir–H moieties ( $151.3(1)^\circ$ ). The Ta– $\text{C}_{\text{Np}}$  bond lengths (with an average value of  $2.137(5)\text{ Å}$ ) are consistent with neopentyl groups.<sup>45–47</sup> The Ta–Os distance in compound **2** is  $2.4817(2)\text{ Å}$ , which is  $0.115\text{ Å}$  shorter than the sum of the metallic radii of tantalum ( $1.343\text{ Å}$ ) and osmium ( $1.255\text{ Å}$ ).<sup>48</sup> This difference results in a formal shortness ratio (FSR) slightly below unity ( $\text{FSR} = 0.95$ ),<sup>49</sup> suggestive of some degree of metal–metal interaction, although the presence of bridging hydrides could also explain the proximity. This FSR value lies between those of complex  $[\text{Hf}(\text{CH}_2\text{tBu})_3(\mu\text{-H})_3\text{IrCp}^*]$  ( $\text{FSR} = 0.99$ ),<sup>34</sup> where the close proximity between the Hf and Ir centres likely results from bridging hydrides, and the Ta/Ir complex **1** ( $\text{FSR} = 0.90$ ),<sup>37</sup> which exhibits clear double metal–metal bonding.

To explore the potential of these heterobimetallic complexes in promoting cooperative reactivity, we investigated the reaction of **1** and **2** with  $\text{CO}_2$  (1 atm, *ca.* 6 equiv.). The reactions were carried out in tetrahydrofuran (THF) at ambient temperature, resulting in rapid discoloration of the reaction mixture within *ca.* 10 minutes in both cases. Analysis of the crude reaction mixtures by  $^1\text{H}$  NMR reveals the complete consumption of complexes **1** and **2**, with clean and quantitative formation of compounds  $\text{Cp}^*\text{Os}(\text{CO})\text{H}_3$  **3** and  $\text{Cp}^*\text{Ir}(\text{CO})\text{H}_2$  **4**, respectively derived from complexes **1** and **2**, alongside the generation of a tantalum oxo complex,  $[\text{Ta}(\text{O})(\text{CH}_2\text{tBu})_3]_x$  **5** (refer to Fig. S9 and S10 in the ESI†).



Scheme 2 Reactivity of  $\text{Ta}(\text{CHtBu})(\text{CH}_2\text{tBu})_3$  towards  $\text{Cp}^*\text{IrH}_4$ ,  $\text{Cp}^*\text{OsH}_5$  and  $\text{Cp}^*\text{ReH}_6$ .



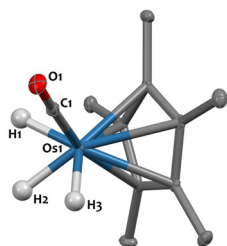


**Scheme 3** Reaction of compounds **1** and **2** with  $\text{CO}_2$ , yielding  $\text{Cp}^*\text{Ir}(\text{CO})\text{H}_2$  and  $\text{Cp}^*\text{Os}(\text{CO})\text{H}_3$ , respectively, together with the formation of  $\text{Ta}(\text{O})(\text{CH}_2\text{tBu})_3$ , **5**.

The insolubility of compound **5** in pentane facilitated its separation from the reaction mixtures by simple evaporation of THF followed by pentane extraction of **3** or **4**. Compound **3** was isolated in 96% yield;  $^1\text{H}$  and  $^{13}\text{C}$  NMR data are in agreement with the literature (Scheme 3).<sup>29,50</sup>

The  $^1\text{H}$ -NMR spectrum of **4**, recorded in  $\text{THF-d}_8$ , indicates that the three hydrides are not equivalent in solution, resulting in two signals at  $-10.48$  ppm and  $-12.50$  ppm integrating for 1H and 2H, respectively and coupling in the  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum (Fig. S15, ESI†). These signals are assigned to hydrides in *-trans* and *-cis* positions relative to the CO group, respectively, which is consistent with literature data.<sup>51</sup> The IR spectrum for **4** displays a broad terminal hydride stretching signal at  $2075\text{ cm}^{-1}$ , and  $\nu_{\text{CO}}$  bands at  $1932$ – $1898\text{ cm}^{-1}$ , as expected.<sup>51</sup> Diluted THF solutions of complex **4** are stable at room temperature in the dark. Yet compound **4** is reported to be unstable in the solid-state,<sup>51</sup> spontaneously eliminating  $\text{H}_2$  upon drying, which could explain the moderate 45% isolated yield. Regardless, single crystals suitable for X-ray diffraction were obtained by avoiding visible light and crystallisation from pentane at  $-40^\circ\text{C}$ . The solid-state structure of **4**, determined for the first time in this study, is shown in Fig. 2. The Os1–C1 ( $1.851(3)\text{ \AA}$ ) and O1–C1 ( $1.162(4)\text{ \AA}$ ) distances are consistent with those observed in compound  $[\text{Cp}^*\text{Os}(\text{CO})(\mu\text{-H})_2]_2$ , featuring Os–C bond lengths of  $1.833(9)\text{ \AA}$  and C–O bond lengths of  $1.18(1)\text{ \AA}$ .<sup>29</sup>

The  $^1\text{H}$ -NMR spectrum of **5** indicates that the three  $\text{CH}_2\text{tBu}$  groups are equivalent in solution, resulting in two signals at  $0.55$  ppm and  $1.12$  ppm for the  $\text{CH}_2$  and  $\text{tBu}$  moieties, respectively. Analysis of the  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **5** reveals three distinct characteristic resonances at  $104.3$ ,  $35.1$  and  $34.4$  ppm



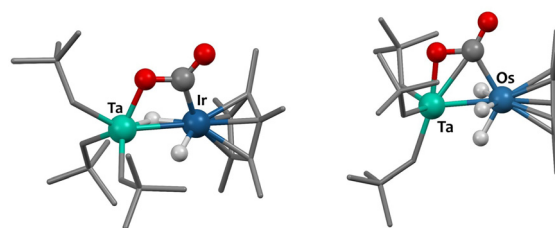
**Fig. 2** Solid-state molecular structure of **4** (30% probability ellipsoids). Hydrogen atoms from the  $\text{Cp}^*$  ligand are omitted for clarity. Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ): Os1–H1  $1.53(4)$ , Os1–H2  $1.58(4)$ , Os1–H3  $1.51(4)$ , Os1–C1  $1.851(3)$ , O1–C1  $1.162(4)$ , Os1– $\text{Cp}^*_{\text{centroid}}$   $1.916(1)$ , C1–Os1– $\text{Cp}^*_{\text{centroid}}$   $132.5(1)$ .

assigned to the  $\text{TaCH}_2$ ,  $\text{C}(\text{CH}_3)_3$  and  $\text{C}(\text{CH}_3)_3$  moieties, respectively. These assignments are confirmed by the 2D  $^1\text{H}$ – $^1\text{H}$  COSY and  $^1\text{H}$ – $^{13}\text{C}$  HSQC and HMBC data (Fig. S19–S21, ESI†). Unfortunately, we were unable to determine the XRD structure of **5**, which probably adopts oligomeric structures, given that terminal Ta-oxo species are rare in the literature.<sup>52–54</sup> To confirm the identity of **5**, we thus carried out a high resolution mass spectrometry analysis using an APCI source, which shows a clear signal for the ion  $[\text{Ta}(\text{O})(\text{CH}_2\text{tBu})_3 + \text{H}]^+$  at  $411.2086\text{ m/z}$  (see Fig. S22, ESI†).

The computed reaction mechanism (DFT, B3PW91) is similar for **1** and **2**.  $\text{CO}_2$  undergoes first a kinetically accessible ( $13\text{ kcal mol}^{-1}$  for **1**,  $11\text{ kcal mol}^{-1}$  for **2**) nucleophilic attack by the Ir (or Os) center, which is assisted by oxygen-coordination to Ta. This results in 4-member metallacyclic intermediates shown on Fig. 3. The next step is a C–O bond breaking TS (barrier of  $9\text{ kcal mol}^{-1}$  for **1** and  $14\text{ kcal mol}^{-1}$  for **2**) to yield to products **3** (or **4**) and **5**, which formation is strongly exothermic (see ESI† for reaction profiles).

In summary, the reaction between  $\text{Cp}^*\text{OsH}_5$  and  $\text{Ta}(\text{CHtBu})(\text{CH}_2\text{tBu})_3$  affords a heterobimetallic Ta–Os complex, **2**, in high yields *via* alkane elimination. Complex **2**, along with its Ta–Ir analogue, **1**, exhibit clean  $\text{CO}_2$  cleavage reactivity, driven by the formation of a tantalum oxo species in conjunction with late metal carbonyls. Given the propensity of related transition metal alkyls and hydrides for  $\text{CO}_2$  insertion,<sup>55–59</sup> the selective, divergent bimetallic reactivity observed herein is notable. These results clearly further demonstrate how the synergistic action of early/late metal assemblies – particularly those based on tantalum – can facilitate the deoxygenation of  $\text{CO}_2$ . This understanding contributes to advancing knowledge in  $\text{CO}_2$  activation and could lead to future applications in deoxygenative chemistry.

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**Fig. 3** Computed (DFT) structures of the metallacyclic reaction intermediates.



Midi-Pyrenees (CALMIP-EOS grant 0833). LM is a senior member of the Institut Universitaire de France.

## Data availability

The data supporting this article have been included as part of the ESI.† CCDC 2351192 and 2351850 contain supplementary crystallographic data for this article; they can be obtained free of charge from The Cambridge Crystallographic Data Centre.

## Conflicts of interest

There are no conflicts to declare.

## References

- 1 P. Buchwalter, J. Rosé and P. Braunstein, *Chem. Rev.*, 2015, **115**, 28–126.
- 2 E. K. Van Den Beuken and B. L. Feringa, *Tetrahedron*, 1998, **54**, 12985–13011.
- 3 J. A. Mata, F. E. Hahn and E. Peris, *Chem. Sci.*, 2014, **5**, 1723–1732.
- 4 A. Lachguar, A. V. Pichugov, T. Neumann, Z. Dubrawski and C. Camp, *Dalt. Trans.*, 2023, **53**, 1393–1409.
- 5 J. Campos, *Nat. Rev. Chem.*, 2020, **4**, 696–702.
- 6 N. P. Mankad, *Chem. Commun.*, 2018, **54**, 1291–1302.
- 7 B. G. Cooper, J. W. Napoline and C. M. Thomas, *Catal. Rev.*, 2012, **54**, 1–40.
- 8 B. Chatterjee, W. C. Chang, S. Jena and C. Werlé, *ACS Catal.*, 2020, **10**, 14024–14055.
- 9 T. S. Hollingsworth, R. L. Hollingsworth, R. L. Lord and S. Groyzman, *Dalt. Trans.*, 2018, **47**, 10017–10024.
- 10 C. Z. Ye, I. Del Rosal, S. N. Kelly, I. J. Brackbill, L. Maron, C. Camp and J. Arnold, *Chem. Sci.*, 2024, **15**, 9784–9792.
- 11 C. Zhang, P. Gotico, R. Guillot, D. Dragoe, W. Leibl, Z. Halime and A. Aukauloo, *Angew. Chem., Int. Ed.*, 2023, **62**, e202214665.
- 12 D. Ghosh, S. Sinhababu, B. D. Santarsiero and N. P. Mankad, *J. Am. Chem. Soc.*, 2020, **142**, 12635–12642.
- 13 M. Pérez-Jiménez, H. Corona, F. de la Cruz-Martínez and J. Campos, *Chem. – A Eur. J.*, 2023, **29**, e202301428.
- 14 Z. B. G. Fickenscher, P. Lönnecke, A. K. Müller, O. Hollóczki, B. Kirchner and E. Hey-Hawkins, *Molecules*, 2023, **28**, 2574.
- 15 J. Ye, R. C. Cammarota, J. Xie, M. V. Vollmer, D. G. Truhlar, C. J. Cramer, C. C. Lu and L. Gagliardi, *ACS Catal.*, 2018, **8**, 4955–4968.
- 16 J. R. Prat, C. A. Gaggioli, R. C. Cammarota, E. Bill, L. Gagliardi and C. C. Lu, *Inorg. Chem.*, 2020, **59**, 14251–14262.
- 17 A. Lachguar, I. Del Rosal, L. Maron, E. Jeanneau, L. Veyre, C. Thieuleux and C. Camp, *J. Am. Chem. Soc.*, 2024, DOI: [10.1021/jacs.4c02172](https://doi.org/10.1021/jacs.4c02172).
- 18 S. Sinhababu, M. R. Radzhabov, J. Telser and N. P. Mankad, *J. Am. Chem. Soc.*, 2022, **144**, 3210–3221.
- 19 J. Hicks, A. Mansikkamäki, P. Vasko, J. M. Goicoechea and S. Aldridge, *Nat. Chem.*, 2019, **11**, 237–241.
- 20 M. Devillard, R. Declercq, E. Nicolas, A. W. Ehlers, J. Backs, N. Saffon-Merceron, G. Bouhadir, J. C. Slootweg, W. Uhl and D. Bourissou, *J. Am. Chem. Soc.*, 2016, **138**, 4917–4926.
- 21 G. Fachinetti, C. Floriani and P. F. Zanazzi, *J. Am. Chem. Soc.*, 1978, **100**, 7405–7407.
- 22 H. Corona, M. Pérez-Jiménez, F. de la Cruz-Martínez, I. Fernández and J. Campos, *Angew. Chem., Int. Ed.*, 2022, **61**, e202207581.
- 23 C. Yoo and Y. Lee, *Chem. Sci.*, 2016, **8**, 600–605.
- 24 E. G. Lundquist, J. C. Huffman and K. G. Caulton, *J. Am. Chem. Soc.*, 1986, **108**, 8309–8310.
- 25 T. A. Hanna, A. M. Baranger and R. G. Bergman, *J. Am. Chem. Soc.*, 1995, **117**, 11363–11364.
- 26 J. R. Pinkes, B. D. Steffey, J. C. Vites and A. R. Cutler, *Organometallics*, 1994, **13**, 21–23.
- 27 N. J. Hartmann, G. Wu and T. W. Hayton, *Chem. Sci.*, 2018, **9**, 6580–6588.
- 28 J. P. Krogman, B. M. Foxman and C. M. Thomas, *J. Am. Chem. Soc.*, 2011, **133**, 14582–14585.
- 29 L. Escomel, I. Del Rosal, L. Maron, E. Jeanneau, L. Veyre, C. Thieuleux and C. Camp, *J. Am. Chem. Soc.*, 2021, **143**, 4844–4856.
- 30 O. Cooper, C. Camp, J. Pécaut, C. E. Kefalidis, L. Maron, S. Gambarelli and M. Mazzanti, *J. Am. Chem. Soc.*, 2014, **136**, 6716–6723.
- 31 M. V. Butovskii, C. Döring, V. Bezugly, F. R. Wagner, Y. Grin and R. Kempe, *Nat. Chem.*, 2010, **2**, 741–744.
- 32 C. J. Isaac, F. M. Miloserdov, A. F. Pécharman, J. P. Lowe, C. L. McMullin and M. K. Whittlesey, *Organometallics*, 2022, **41**, 2716–2730.
- 33 L. Escomel, E. Jeanneau, C. Thieuleux and C. Camp, *Inorganics*, 2024, **12**, 72.
- 34 S. Lassalle, J. Petit, R. L. Falconer, V. Hérault, E. Jeanneau, C. Thieuleux and C. Camp, *Organometallics*, 2022, **41**, 1675–1687.
- 35 C. Z. Ye, I. Del Rosal, M. A. Boreen, E. T. Ouellette, D. R. Russo, L. Maron, J. Arnold and C. Camp, *Chem. Sci.*, 2022, **14**, 861–868.
- 36 L. Escomel, N. Soulé, E. Robin, I. Del Rosal, L. Maron, E. Jeanneau, C. Thieuleux and C. Camp, *Inorg. Chem.*, 2022, **61**, 5715–5730.
- 37 S. Lassalle, R. Jabbour, P. Schiltz, P. Berruyer, T. K. Todorova, L. Veyre, D. Gajan, A. Lesage, C. Thieuleux and C. Camp, *J. Am. Chem. Soc.*, 2019, **141**, 19321–19335.
- 38 C. L. Gross and G. S. Girolami, *Organometallics*, 2007, **26**, 160–166.
- 39 C. L. Gross, S. R. Wilson and G. S. Girolami, *J. Am. Chem. Soc.*, 1994, **116**, 10294–10295.
- 40 S. Lassalle, R. Jabbour, I. Del Rosal, L. Maron, E. Fonda, L. Veyre, D. Gajan, A. Lesage, C. Thieuleux and C. Camp, *J. Catal.*, 2020, **392**, 287–301.
- 41 W. A. Herrmann, H. G. Theiler, P. Kiprof, J. Tremmel and R. Blom, *J. Organomet. Chem.*, 1990, **395**, 69–84.
- 42 C. L. Gross and G. S. Girolami, *Organometallics*, 2007, **26**, 160–166.
- 43 J. W. Bruno, J. C. Huffman, M. A. Green and K. G. Caulton, *J. Am. Chem. Soc.*, 1984, **106**, 8310–8312.
- 44 T. Shima and H. Suzuki, *Organometallics*, 2005, **24**, 3939–3945.
- 45 L. J. Guggenberger and R. R. Schrock, *J. Am. Chem. Soc.*, 1975, **97**, 2935.
- 46 R. Srivastava, E. A. Quadrelli and C. Camp, *Dalt. Trans.*, 2020, **49**, 3120–3128.
- 47 R. Srivastava, R. Moneuse, J. Petit, P.-A. A. Pavard, V. Dardun, M. Rivat, P. Schiltz, M. Solari, E. Jeanneau, L. Veyre, C. Thieuleux, E. A. Quadrelli and C. Camp, *Chem. – Eur. J.*, 2018, **24**, 4361–4370.
- 48 L. Pauling, *J. Am. Chem. Soc.*, 1947, **69**, 542–553.
- 49 F. A. Cotton, *Acc. Chem. Res.*, 1978, **11**, 225–232.
- 50 D. M. Heinekey, D. A. Fine, T. G. P. Harper and S. T. Michel, *Can. J. Chem.*, 1995, **73**, 1116–1125.
- 51 J. K. Hoyano and W. A. G. Graham, *J. Am. Chem. Soc.*, 1982, **104**, 3722–3723.
- 52 J. I. Fostvedt, M. A. Boreen, R. G. Bergman and J. Arnold, *Inorg. Chem.*, 2021, **60**, 9912–9931.
- 53 S. M. Mullins, R. G. Bergman and J. Arnold, *Organometallics*, 1999, **18**, 4465–4467.
- 54 P. Horrillo-Martínez, B. O. Patrick, L. L. Schafer and M. D. Fryzuk, *Dalt. Trans.*, 2012, **41**, 1609–1616.
- 55 M. K. Whittlesey, R. N. Perutz and M. H. Moore, *Organometallics*, 1996, **15**, 5166–5169.
- 56 O. R. Allen, S. J. Dalgarno, L. D. Field, P. Jensen, A. J. Turnbull and A. C. Willis, *Organometallics*, 2008, **27**, 2092–2098.
- 57 J. Sánchez-Nieves and P. Royo, *J. Organomet. Chem.*, 2001, **621**, 299–303.
- 58 M. A. Rankin and C. C. Cummins, *J. Am. Chem. Soc.*, 2010, **132**, 10021–10023.
- 59 J. M. Mörsdorf and J. Ballmann, *Inorg. Chem.*, 2021, **60**, 18291–18295.

