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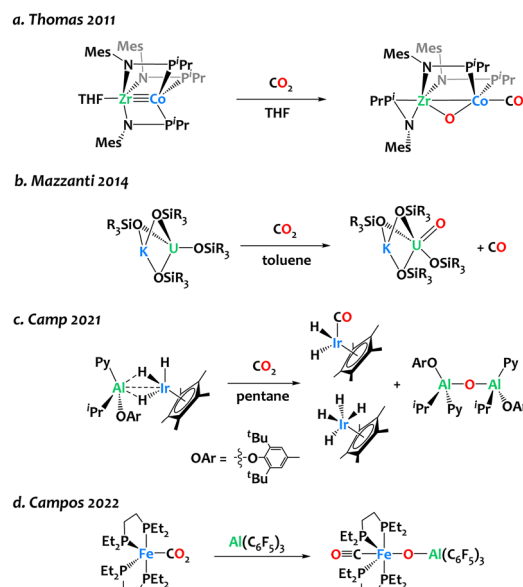
A novel Ta/Os heterobimetallic complex, [Ta(CH<sub>2</sub>tBu)<sub>3</sub>(μ-H)<sub>3</sub>OsCp\*], **2**, is prepared by protonolysis of Ta(CHtBu)(CH<sub>2</sub>tBu)<sub>3</sub> with Cp\*OsH<sub>5</sub>. Treatment of **2** and its iridium analogue [Ta(CH<sub>2</sub>tBu)<sub>3</sub>(μ-H)<sub>2</sub>IrCp\*], **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

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

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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.



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

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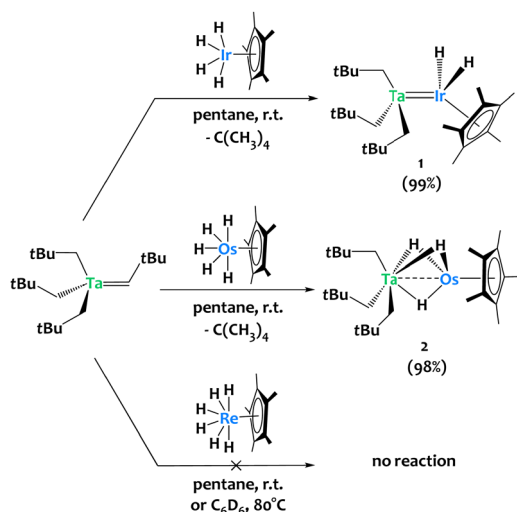
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The alkane elimination reaction between metal (poly)alkyls and (poly)hydride species has proven efficient for accessing heterobimetallic complexes.<sup>31–36</sup> We used this strategy to synthesize compound  $[\text{Ta}(\text{CH}_2\text{tBu})_3\text{IrH}_2\text{Cp}^*]$  **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). <sup>1</sup>H NMR monitoring of the reaction of **2** with  $\text{Cp}^*\text{OsH}_5$  (1 equiv.) suggests the slow formation of a trinuclear TaOs<sub>2</sub> 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 (<sup>1</sup>H, <sup>13</sup>C, <sup>1</sup>H–<sup>1</sup>H COSY, <sup>1</sup>H–<sup>13</sup>C HSQC and HMBC) solution NMR spectroscopy, elemental analysis, and X-ray diffraction studies. In the <sup>1</sup>H-NMR spectrum of **2** obtained in a toluene-*d*<sub>8</sub> 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  $\text{Cp}^*\text{IrCH}_4$  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



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  $\text{Cp}^*\text{ReH}_6$ .

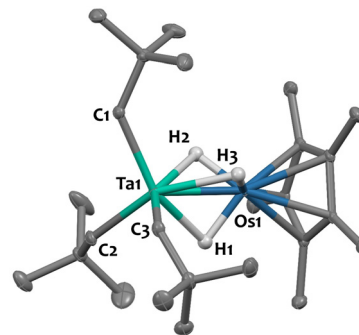


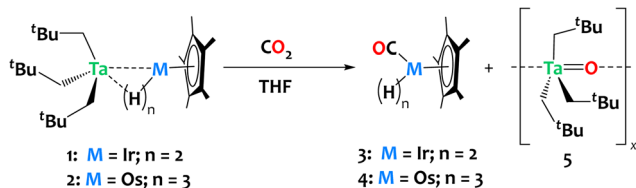
Fig. 1 Solid-state molecular structure of **2** (30% probability ellipsoids). Hydrogen atoms from the hydrocarbon ligands are omitted for clarity. Selected bond distances (Å) and angles (°): Ta1–Os1 2.4817(2), Ta1–C1 2.132(3), Ta1–C2 2.136(3), Ta1–C3 2.143(3), Os1–H1 1.45(5), Os1–H2 1.56(5), Os1–H3 1.48(8), 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 (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  $[\text{Hf}(\text{CH}_2\text{tBu})_3(\mu\text{-H})_3\text{IrCp}^*]$  (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** (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 <sup>1</sup>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†).



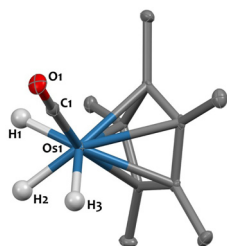


**Scheme 3** Reaction of compounds **1** and **2** with CO<sub>2</sub>, yielding Cp\*Ir(CO)H<sub>2</sub> and Cp\*Os(CO)H<sub>3</sub>, respectively, together with the formation of Ta(O)(CH<sub>2</sub>tBu)<sub>3</sub>, **5**.

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; <sup>1</sup>H and <sup>13</sup>C NMR data are in agreement with the literature (Scheme 3).<sup>29,50</sup>

The <sup>1</sup>H-NMR spectrum of **4**, recorded in THF-d<sub>8</sub>, 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 <sup>1</sup>H-<sup>1</sup>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 cm<sup>-1</sup>, and ν<sub>CO</sub> bands at 1932-1898 cm<sup>-1</sup>, 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 H<sub>2</sub> 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 °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) Å) and O1-C1 (1.162(4) Å) distances are consistent with those observed in compound [Cp\*Os(CO)(μ-H)]<sub>2</sub>, featuring Os-C bond lengths of 1.833(9) Å and C-O bond lengths of 1.18(1) Å.<sup>29</sup>

The <sup>1</sup>H-NMR spectrum of **5** indicates that the three CH<sub>2</sub>tBu groups are equivalent in solution, resulting in two signals at 0.55 ppm and 1.12 ppm for the CH<sub>2</sub> and tBu moieties, respectively. Analysis of the <sup>13</sup>C{<sup>1</sup>H}-NMR spectrum of **5** reveals three distinct characteristic resonances at 104.3, 35.1 and 34.4 ppm



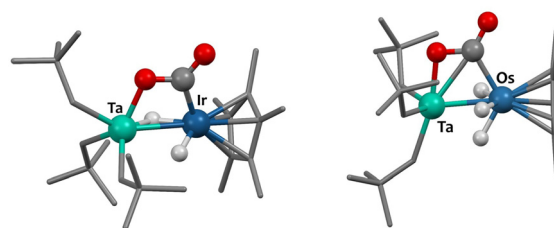
**Fig. 2** Solid-state molecular structure of **4** (30% probability ellipsoids). Hydrogen atoms from the Cp\* ligand are omitted for clarity. Selected bond distances (Å) and angles (°): Os1-H1 1.53(4), Os1-H2 1.58(4), Os1-H3 1.51(4), Os1-C1 1.851(3), O1-C1 1.162(4), Os1-Cp\*<sub>centroid</sub> 1.916(1), C1-Os1-Cp\*<sub>centroid</sub> 132.5(1).

assigned to the TaCH<sub>2</sub>, C(CH<sub>3</sub>)<sub>3</sub> and C(CH<sub>3</sub>)<sub>3</sub> moieties, respectively. These assignments are confirmed by the 2D <sup>1</sup>H-<sup>1</sup>H COSY and <sup>1</sup>H-<sup>13</sup>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 [Ta(O)(CH<sub>2</sub>tBu)<sub>3</sub> + H]<sup>+</sup> at 411.2086 *m/z* (see Fig. S22, ESI†).

The computed reaction mechanism (DFT, B3PW91) is similar for **1** and **2**. CO<sub>2</sub> undergoes first a kinetically accessible (13 kcal mol<sup>-1</sup> for **1**, 11 kcal mol<sup>-1</sup> 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 kcal mol<sup>-1</sup> for **1** and 14 kcal mol<sup>-1</sup> 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 Cp\*OsH<sub>3</sub> and Ta(CH<sub>2</sub>tBu)<sub>3</sub> affords a heterobimetallic Ta-Os complex, **2**, in high yields *via* alkane elimination. Complex **2**, along with its Ta-Ir analogue, **1**, exhibit clean CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub>. This understanding contributes to advancing knowledge in CO<sub>2</sub> 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.

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