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

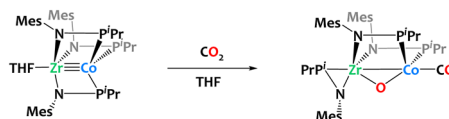
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A novel Ta/Os heterobimetallic complex, [Ta(CH<sub>2</sub>tBu)<sub>3</sub>(μ-H)<sub>3</sub>OsCp\*], **2**, is prepared by protonolysis of Ta(CH<sub>2</sub>tBu)(CH<sub>2</sub>tBu)<sub>3</sub> with Cp\*OsH<sub>5</sub>. Treatment of **2** and its iridium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

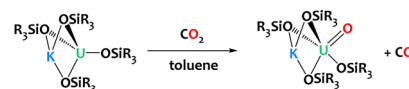
The design of synthetic bimetallic complexes associating different metals with complementary Lewis acidic/Lewis basic behaviour has raised interest for cooperative reactivity,<sup>1–10</sup> including CO<sub>2</sub> activation.<sup>11–17</sup> In many instances, these bifunctional complexes lead to CO<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.

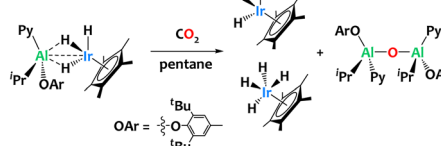
a. Thomas 2011



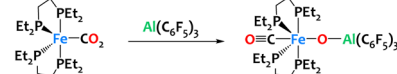
b. Mazzanti 2014



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>

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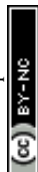
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The alkane elimination reaction between metal (poly)alkyls and (poly)hydride species has proven efficient for accessing heterobimetallic complexes.<sup>31–36</sup> We used this strategy to synthesize compound  $[\text{Ta}(\text{CH}_2\text{tBu})_3\text{IrH}_2\text{Cp}^*]$  **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  $\text{TaOs}_2$  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 (<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  $\text{Cp}^*\text{IrH}_4$  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

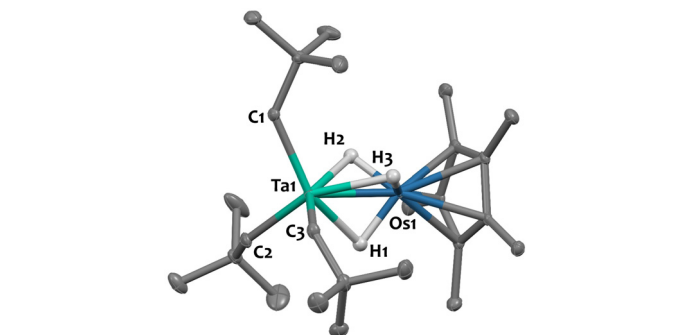
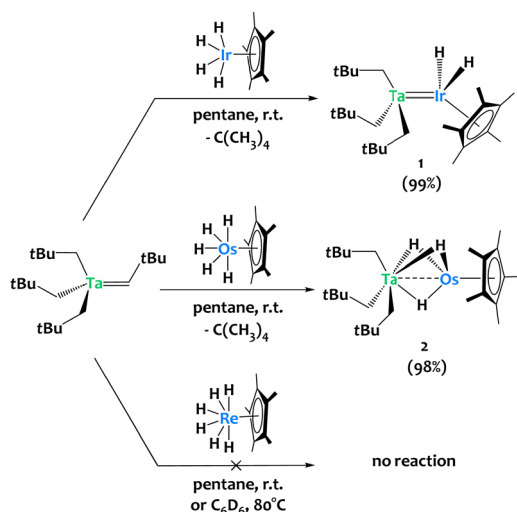


Fig. 1 Solid-state molecular structure of **2** (30% probability ellipsoids). Hydrogen atoms from the hydrocarbon ligands are omitted for clarity. Selected bond distances (Å) and angles (°): Ta1–Os1 2.4817(2), Ta1–C1 2.132(3), Ta1–C2 2.136(3), Ta1–C3 2.143(3), Os1–H1 1.45(5), Os1–H2 1.56(5), Os1–H3 1.48(8),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

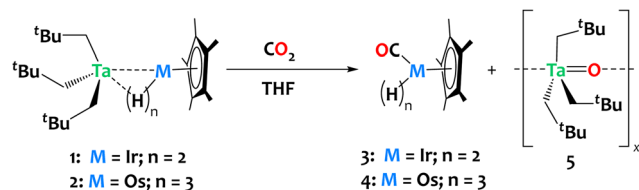
Single crystals of **2** suitable for X-ray diffraction were grown from a saturated pentane solution at  $-40\text{ °C}$ . The solid-state structure is depicted in Fig. 1. The nearly linear Ta–Os– $\text{Cp}^*\text{centroid}$  angle ( $178.1(1)^\circ$ ), indicates the presence of three bridging hydrides 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 <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 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  $\text{Cp}^*\text{ReH}_6$ .



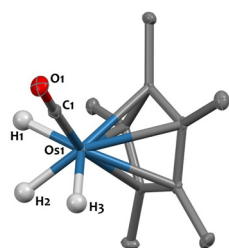


**Scheme 3** Reaction of compounds **1** and **2** with  $\text{CO}_2$ , yielding  $\text{Cp}^*\text{Ir}(\text{CO})\text{H}_2$  and  $\text{Cp}^*\text{Os}(\text{CO})\text{H}_3$ , respectively, together with the formation of  $\text{Ta}(\text{O})(\text{CH}_2\text{tBu})_3$ , **5**.

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



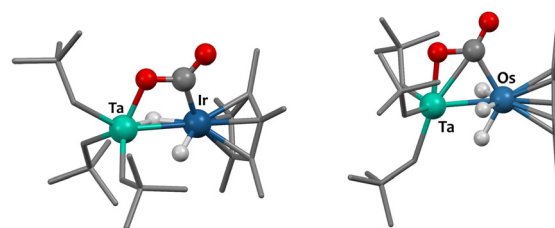
**Fig. 2** Solid-state molecular structure of **4** (30% probability ellipsoids). Hydrogen atoms from the  $\text{Cp}^*$  ligand are omitted for clarity. Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ): Os1–H1  $1.53(4)$ , Os1–H2  $1.58(4)$ , Os1–H3  $1.51(4)$ , Os1–C1  $1.851(3)$ ,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

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