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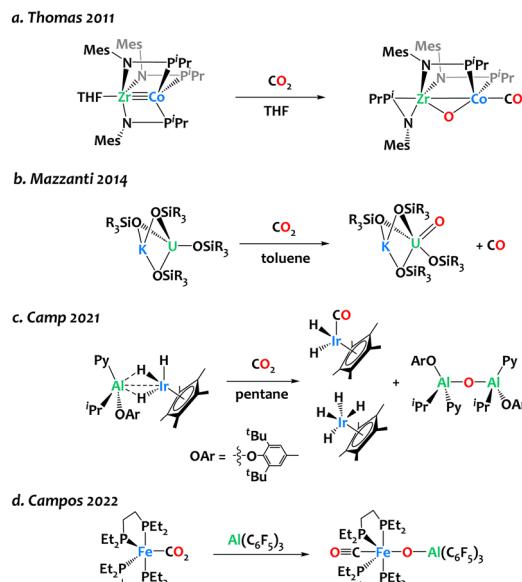
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A novel Ta/Os heterobimetallic complex,  $[\text{Ta}(\text{CH}_2\text{tBu})_3(\mu\text{-H})_3\text{OsCp}^*]$ , 2, is prepared by protonolysis of  $\text{Ta}(\text{CH}_2\text{tBu})(\text{CH}_2\text{tBu})_3$  with  $\text{Cp}^*\text{OsH}_5$ . Treatment of 2 and its iridium analogue  $[\text{Ta}(\text{CH}_2\text{tBu})_3(\mu\text{-H})_2\text{IrCp}^*]$ , 1, with  $\text{CO}_2$  under mild conditions reveal the efficient cleavage of  $\text{CO}_2$ , driven by the formation of a tantalum oxo species in conjunction with CO transfer to the osmium or iridium fragments, to form  $\text{Cp}^*\text{Ir}(\text{CO})\text{H}_2$  and  $\text{Cp}^*\text{Os}(\text{CO})\text{H}_3$ , respectively. This bimetallic reactivity diverges from more classical  $\text{CO}_2$  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  $\text{CO}_2$  activation.<sup>11–17</sup> In many instances, these bifunctional complexes lead to  $\text{CO}_2$  adducts or insertion products, in which a bent  $\text{CO}_2$  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  $\text{CO}_2$ . Thomas and colleagues reported oxidative  $\text{CO}_2$  cleavage across the early/late heterobimetallic complex  $\text{Co}(\text{iPr}_2\text{PNMes})_3\text{Zr}(\text{THF})$ , yielding  $(\text{OC})\text{Co}(\text{iPr}_2\text{PNMes})_2(\mu\text{-O})\text{Zr}(\text{iPr}_2\text{PNMes})$  at ambient temperature (Scheme 1a).<sup>28</sup> The Mazzanti group reported the potassium-assisted reductive cleavage of  $\text{CO}_2$  by a  $\text{U}(\text{III})$  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  $\text{CO}_2$  deoxygenation, yielding  $\text{Cp}^*\text{Ir}(\text{CO})\text{H}_2$ ,  $\text{Cp}^*\text{IrH}_4$ , and  $[\text{Al}(\text{Py})(\text{OAr})(\text{iBu})]_2(\mu\text{-O})$  at room temperature (Scheme 1c).<sup>29</sup> Recently, Campos and coworkers reported the use of  $\text{Al}(\text{C}_6\text{F}_5)_3$  for triggering the bimetallic cleavage of Fe-bound  $\text{CO}_2$  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  $\text{CO}_2$  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 Bd 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 Diffractométrie 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  $\text{Ta}(\text{CH}_2\text{tBu})(\text{CH}_2\text{tBu})_3$  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  $\text{Ta}(\text{CH}_2\text{tBu})(\text{CH}_2\text{tBu})_3$  towards related 6d metal polyhydrides. Treating  $\text{Ta}(\text{CH}_2\text{tBu})(\text{CH}_2\text{tBu})_3$  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<sup>†</sup>), 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  $\text{Ta}(\text{CH}_2\text{tBu})(\text{CH}_2\text{tBu})_3$  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<sup>†</sup> 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  $\text{Cp}^*\text{IrCH}_4$  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 cm<sup>–1</sup>, 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 ( $\nu_{\text{Ir-H}} = 2061$  cm<sup>–1</sup>, see Fig. S6, ESI<sup>†</sup>) and that of the  $\text{Cp}^*\text{OsH}_5$  precursor, which exhibits a strong absorption at 2083 (s) cm<sup>–1</sup> with a minor

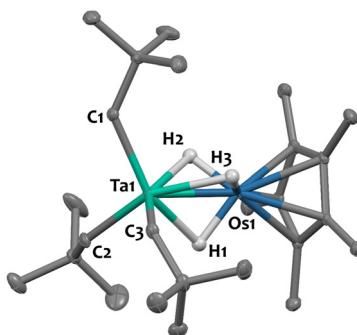
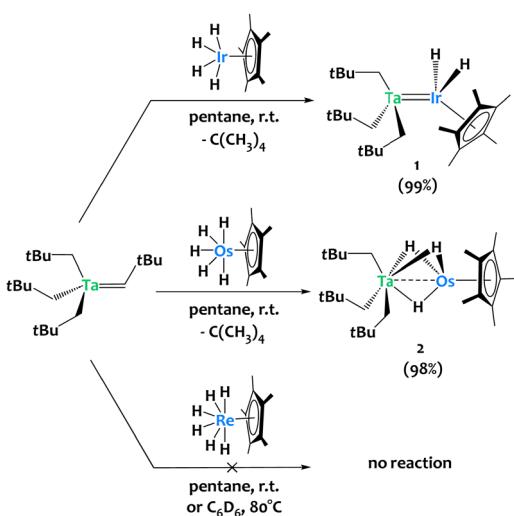


Fig. 1 Solid-state molecular structure of **2** (30% probability ellipsoids). Hydrogen atoms from the hydrocarbon ligands are omitted for clarity. Selected bond distances (Å) and angles (°):  $\text{Ta1}-\text{Os1}$  2.4817(2),  $\text{Ta1}-\text{C1}$  2.132(3),  $\text{Ta1}-\text{C2}$  2.136(3),  $\text{Ta1}-\text{C3}$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

one at 2214 (w) cm<sup>–1</sup>.<sup>42</sup> For comparison, the metal-hydride stretch is observed at 1982 cm<sup>–1</sup> in  $[\text{Hf}(\text{CH}_2\text{tBu})_3(\mu\text{-H})_3\text{IrCp}^*]$ <sup>34</sup> and at 1952 and 1970 cm<sup>–1</sup> 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.

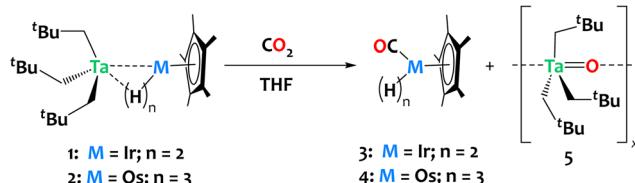
Single crystals of **2** suitable for X-ray diffraction were grown from a saturated pentane solution at –40 °C. The solid-state structure is depicted in Fig. 1. The nearly linear  $\text{Ta}-\text{Os}-\text{Cp}^*\text{centroid}$  angle (178.1(1)°), indicates the presence of three bridging hydrides between 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)°)<sup>44</sup> and  $[\text{Hf}(\text{CH}_2\text{tBu})_3(\mu\text{-H})_3\text{IrCp}^*]$  (179.2(3)°),<sup>34</sup> but starkly contrasts with that found in complex **1**, featuring two terminal Ir-H moieties (151.3(1)°). The  $\text{Ta}-\text{C}_{\text{NP}}$  bond lengths (with an average value of 2.137(5) Å) are consistent with neopentyl groups.<sup>45–47</sup> The  $\text{Ta}-\text{Os}$  distance in compound **2** is 2.4817(2) Å, which is 0.115 Å shorter than the sum of the metallic radii of tantalum (1.343 Å) and osmium (1.255 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 **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 discolouration 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<sup>†</sup>).



Scheme 2 Reactivity of  $\text{Ta}(\text{CH}_2\text{tBu})(\text{CH}_2\text{tBu})_3$  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  $1\text{H}$  and  $2\text{H}$ , respectively and coupling in the  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum (Fig. S15, ESI $^\ddagger$ ). 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  $-40\text{ }^\circ\text{C}$ . 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  $[\text{Cp}^*\text{Os}(\text{CO})(\mu\text{-H})_2]$ , 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

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 $^\ddagger$ ). 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 $^\ddagger$ ).

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 $^\ddagger$  for reaction profiles).

In summary, the reaction between  $\text{Cp}^*\text{OsH}_5$  and  $\text{Ta}(\text{CH}_2\text{tBu})_3$  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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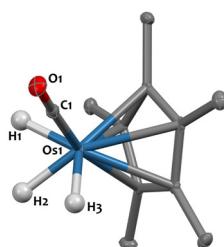


Fig. 2 Solid-state molecular structure of **4** (30% probability ellipsoids). Hydrogen atoms from the  $\text{Cp}^*$  ligand are omitted for clarity. Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ): Os1–H1  $1.53(4)$ , Os1–H2  $1.58(4)$ , Os1–H3  $1.51(4)$ , Os1–C1  $1.851(3)$ , O1–C1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

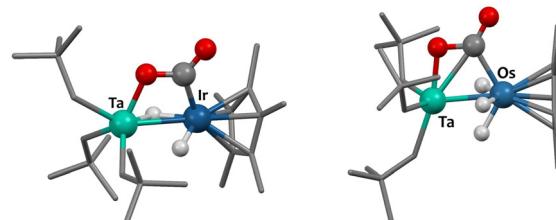


Fig. 3 Computed (DFT) structures of the metallacyclic reaction intermediates.



Midi-Pyrénées (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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