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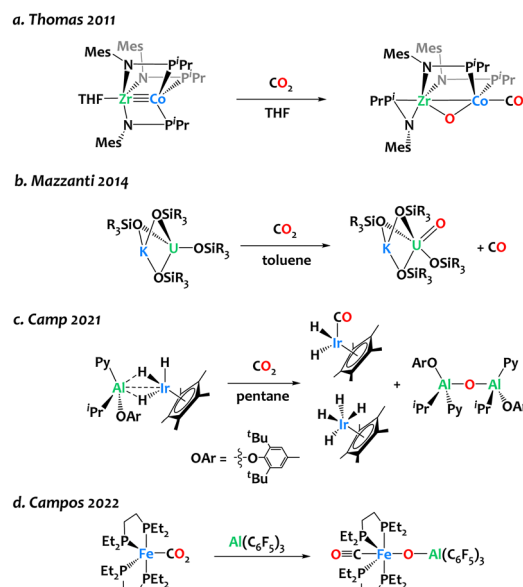
A novel Ta/Os heterobimetallic complex, [Ta(CH₂tBu)₃(μ-H)₃OsCp*], **2**, is prepared by protonolysis of Ta(CHtBu)(CH₂tBu)₃ with Cp*OsH₅. Treatment of **2** and its iridium analogue [Ta(CH₂tBu)₃(μ-H)₂IrCp*], **1**, with CO₂ under mild conditions reveal the efficient cleavage of CO₂, driven by the formation of a tantalum oxo species in conjunction with CO transfer to the osmium or iridium fragments, to form Cp*Ir(CO)H₂ and Cp*Os(CO)H₃, respectively. This bimetallic reactivity diverges from more classical CO₂ 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,^{1–10} including CO₂ activation.^{11–17} In many instances, these bifunctional complexes lead to CO₂ adducts or insertion products, in which a bent CO₂ fragment binds across the two metals.^{18–27} In contrast, only a few heterobimetallic complexes have clearly exhibited the capability to cleave the C–O bond within CO₂. Thomas and colleagues reported oxidative CO₂ cleavage across the early/late heterobimetallic complex Co(iPr₂PNMes)₃Zr(THF), yielding (OC)Co(iPr₂PNMes)₂(μ-O)Zr(iPr₂PNMes) at ambient temperature (Scheme 1a).²⁸ The Mazzanti group reported the potassium-assisted reductive cleavage of CO₂ by a U(III) siloxide complex, resulting in CO evolution and the formation of a pentavalent

CO₂ 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 CO₂ deoxygenation, yielding Cp*Ir(CO)H₂, Cp*IrH₄, and [Al(Py)(OAr)(iBu)₂(μ-O)] at room temperature (Scheme 1c).²⁹ Recently, Campos and coworkers reported the use of Al(C₆F₅)₃ for triggering the bimetallic cleavage of Fe-bound CO₂ 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.²² Finding right bimetallic combinations therefore remains a major challenge for controlling reactivity.



Scheme 1 Reports of CO₂ cleavage by heterobimetallic complexes relevant to the present study.^{22,28–30}

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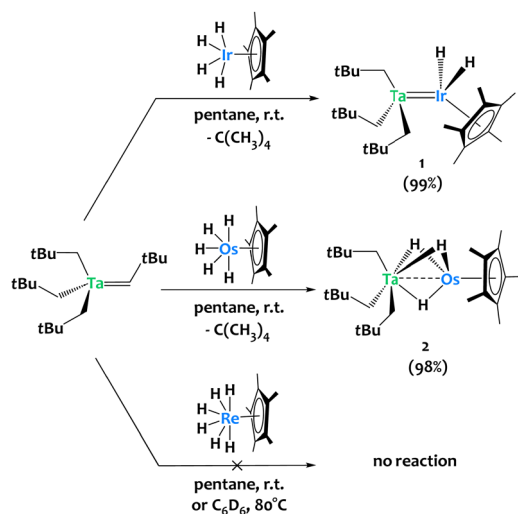
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The alkane elimination reaction between metal (poly)alkyls and (poly)hydride species has proven efficient for accessing heterobimetallic complexes.^{31–36} We used this strategy to synthesize compound $[\text{Ta}(\text{CH}_2\text{tBu})_3\text{IrH}_2\text{Cp}^*]$ **1** from the tantalum tris-neopentyl neopentylidene complex $\text{Ta}(\text{CHtBu})(\text{CH}_2\text{tBu})_3$ and the iridium tetrahydride complex Cp^*IrH_4 (Scheme 2-top).³⁷ 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 Cp^*OsH_5 ^{38,39} 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). ¹H NMR monitoring of the reaction of **2** with Cp^*OsH_5 (1 equiv.) suggests the slow formation of a trinuclear TaOs₂ species (see Fig. S7, ESI†), analogous to the TaIr_2 species previously reported.⁴⁰ Surprisingly, Cp^*ReH_6 ⁴¹ shows no reactivity towards $\text{Ta}(\text{CHtBu})(\text{CH}_2\text{tBu})_3$ either in pentane at room temperature or in C_6D_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 (¹H, ¹³C, ¹H–¹H COSY, ¹H–¹³C HSQC and HMBC) solution NMR spectroscopy, elemental analysis, and X-ray diffraction studies. In the ¹H-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 Cp^*OsH_5 which is reminiscent of the observed shift from Cp^*IrCH_4 to **1**, of approximately $\Delta\delta = +3.5$ ppm.³⁷ The IR spectrum of compound **2** displays a characteristic metal-hydride stretching vibration signal at 1961 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 Cp^*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 Cp^*IrH_4 , Cp^*OsH_5 and Cp^*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 $2214\text{ (w)}\text{ cm}^{-1}$.⁴² For comparison, the metal-hydride stretch is observed at 1982 cm^{-1} in $[\text{Hf}(\text{CH}_2\text{tBu})_3(\mu\text{-H})_3\text{IrCp}^*]$ ³⁴ and at 1952 and 1970 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 H respectively),⁴³ 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 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 $[\text{CpRu}(\mu\text{-H})_4\text{OsCp}^*]$ ($179.2(9)^\circ$)⁴⁴ and $[\text{Hf}(\text{CH}_2\text{tBu})_3(\mu\text{-H})_3\text{IrCp}^*]$ ($179.2(3)^\circ$),³⁴ but starkly contrasts with that found in complex **1**, featuring two terminal Ir–H moieties ($151.3(1)^\circ$). The Ta– C_{Np} bond lengths (with an average value of $2.137(5)\text{ Å}$) are consistent with neopentyl groups.^{45–47} The Ta–Os distance in compound **2** is $2.4817(2)\text{ Å}$, which is 0.115 Å shorter than the sum of the metallic radii of tantalum (1.343 Å) and osmium (1.255 Å).⁴⁸ This difference results in a formal shortness ratio (FSR) slightly below unity (FSR = 0.95),⁴⁹ 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),³⁴ where the close proximity between the Hf and Ir centres likely results from bridging hydrides, and the Ta/Ir complex **1** (FSR = 0.90),³⁷ 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 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 ¹H 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 CO₂, yielding Cp*Ir(CO)H₂ and Cp*Os(CO)H₃, respectively, together with the formation of Ta(O)(CH₂tBu)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; ¹H and ¹³C NMR data are in agreement with the literature (Scheme 3).^{29,50}

The ¹H-NMR spectrum of **4**, recorded in THF-d₈, 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 ¹H-¹H 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.⁵¹ The IR spectrum for **4** displays a broad terminal hydride stretching signal at 2075 cm⁻¹, and ν_{CO} bands at 1932–1898 cm⁻¹, as expected.⁵¹ 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,⁵¹ spontaneously eliminating H₂ 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)]₂, featuring Os–C bond lengths of 1.833(9) Å and C–O bond lengths of 1.18(1) Å.²⁹

The ¹H-NMR spectrum of **5** indicates that the three CH₂tBu groups are equivalent in solution, resulting in two signals at 0.55 ppm and 1.12 ppm for the CH₂ and tBu moieties, respectively. Analysis of the ¹³C{¹H}-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*_{centroid} 1.916(1), C1–Os1–Cp*_{centroid} 132.5(1).

assigned to the TaCH₂, C(CH₃)₃ and C(CH₃)₃ moieties, respectively. These assignments are confirmed by the 2D ¹H-¹H COSY and ¹H-¹³C 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.^{52–54} 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)(CH₂tBu)₃ + H]⁺ at 411.2086 *m/z* (see Fig. S22, ESI†).

The computed reaction mechanism (DFT, B3PW91) is similar for **1** and **2**. CO₂ undergoes first a kinetically accessible (13 kcal mol⁻¹ for **1**, 11 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 kcal mol⁻¹ for **1** and 14 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 Cp*OsH₃ and Ta(CH₂tBu)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 CO₂ 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 CO₂ insertion,^{55–59} 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 CO₂. This understanding contributes to advancing knowledge in CO₂ activation and could lead to future applications in deoxygenative chemistry.

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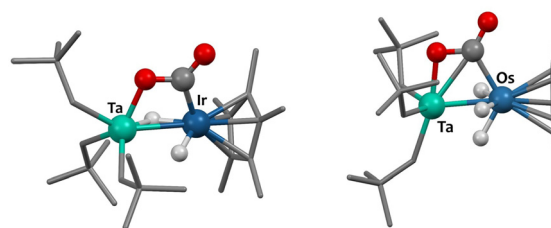


Fig. 3 Computed (DFT) structures of the metallacyclic reaction intermediates.



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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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