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CO₂ cleavage by tantalum/M (M = iridium, osmium) heterobimetallic complexes[†]

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A novel Ta/Os heterobimetallic complex, $[Ta(CH_2tBu)_3(\mu-H)_3OsCp^*]$, 2, is prepared by protonolysis of Ta(CHtBu)(CH_2tBu)_3 with Cp*OsH₅. Treatment of 2 and its iridium analogue $[Ta(CH_2tBu)_3(\mu-H)_2IrCp^*]$, 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 potassiumassisted reductive cleavage of CO₂ by a U(m) 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 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 Febound 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.



 $\label{eq:scheme1} \begin{array}{l} \mbox{Reports of CO}_2 \mbox{ cleavage by heterobimetallic complexes relevant to the present study.} \mbox{$^{22.28-30}$} \end{array}$

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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 [Ta(CH2tBu)3IrH2Cp*] 1 from the tantalum tris-neopentyl neopentylidene complex Ta(CHtBu)(CH2tBu)3 and the iridium tetrahydride complex Cp*IrH₄ (Scheme 2-top).³⁷ This prompted us to extend this chemistry by investigating the reactivity of Ta(CHtBu) (CH₂tBu)₃ towards related 6d metal polyhydrides. Treating Ta (CHtBu)(CH₂tBu)₃ with Cp*OsH₅^{38,39} in a 1:1 stoichiometric ratio in pentane at room temperature yields the heterobimetallic complex $[Ta(CH_2tBu)_3(\mu-H)_3OsCp^*]$ 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 TaIr₂ species previously reported.⁴⁰ Surprisingly, Cp*ReH₆⁴¹ shows no reactivity towards Ta(CHtBu)(CH₂tBu)₃ either in pentane at room temperature or in C₆D₆ 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-d₈ 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*OsH₅ which is reminiscent of the observed shift from Cp*IrCH₄ 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 [Ta(CH₂*t*Bu)₃IrCp*(H)₂], 1, featuring two terminal hydrides ($\nu_{Ir-H} = 2061$ cm⁻¹, see Fig. S6, ESI†) and that of the Cp*OsH₅ precursor, which exhibits a strong absorption at 2083 (s) cm⁻¹ with a minor



Scheme 2 Reactivity of $Ta(CHtBu)(CH_2tBu)_3$ 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–Cp $*_{centroid}$ 178.1(1).

one at 2214 (w) cm⁻¹.⁴² For comparison, the metal-hydride stretch is observed at 1982 cm⁻¹ in $[Hf(CH_2tBu)_3(\mu-H)_3IrCp^*]^{34}$ and at 1952 and 1970 cm⁻¹ for $[Cp_2Zr(X)(\mu-H)_3Os(PMe_2Ph)_3]$ (X = 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-Cp*_{centroid} angle $(178.1(1)^{\circ})$, indicates the presence of three bridging hydrides between the two metals, arranged in a tripod geometry around the {Cp*Os} core. This angle aligns well with values reported for systems featuring similar bridging hydride motifs, such as $[CpRu(\mu-H)_4OsCp^*]$ (179.2(9)°)⁴⁴ and $[Hf(CH_2tBu)_3]$ $(\mu-H)_3$ IrCp*] (179.2(3)°),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) Å) are consistent with neopentyl groups.45-47 The Ta-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).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 [Hf(CH₂tBu)₃(µ-H)₃IrCp*] (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 metalmetal bonding.

To explore the potential of these heterobimetallic complexes in promoting cooperative reactivity, we investigated the reaction of **1** and **2** with CO₂ (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 Cp*Os(CO)H₃ **3** and Cp*Ir(CO)H₂ **4**, respectively derived from complexes **1** and **2**, alongside the generation of a tantalum oxo complex, $[Ta(O)(CH_2tBu)_3]_x$ **5** (refer to Fig. S9 and S10 in the ESI[†]).



Scheme 3 Reaction of compounds **1** and **2** with CO_2 , 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 $[Cp^*Os(CO)(\mu-H)]_2$, 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 CH_2tBu groups are equivalent in solution, resulting in two signals at 0.55 ppm and 1.12 ppm for the CH_2 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



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 $[Ta(O)(CH_2tBu)_3 + H]^+$ at 411.2086 *m/z* (see Fig. S22, ESI[†]).

The computed reaction mechanism (DFT, B3PW91) is similar for 1 and 2. CO_2 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*OsH₅ and Ta(CH*t*Bu) (CH₂*t*Bu)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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