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Reactivity of Tantalum/Iridium and Hafnium/Iridium Alkyl Hydrides with Alkyl Lithium Reagents: Nucleophilic Addition, Alpha-H Abstraction or Hydride Deprotonation?

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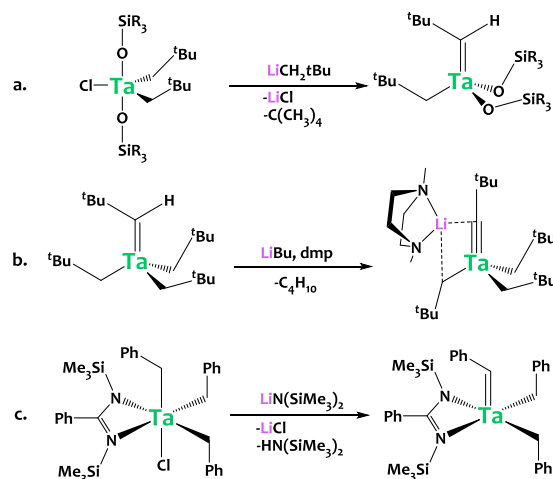
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ABSTRACT: Cp*IrH₄ reacts with Hf(Np)₄ (Np = CH₂C(CH₃)₃) to yield the heterobimetallic complex [Hf(Np)₃(μ-H)₃IrCp*], **2**. Treatment of **2** with neopentyl lithium (NpLi) results in the nucleophilic addition of a neopentyl moiety onto the Hf center, restoring Hf(Np)₄ and displacing the Cp*IrH₃⁻ iridate fragment. By contrast, treatment of the tantalum/iridium analogue, [Ta(Np)₃IrH₂(Cp*)], **1**, with NpLi triggers the α-hydrogen abstraction at a Ta-neopentyl moiety and leads to the formation of the alkylidene *-ate* complex [Li][{Ta(CH^tBu)(Np)₂}{IrH₂Cp*}], **4**. The benzylidene analogue, [K][{Ta(CHPh)(Np)₂}{IrH₂Cp*}], **5**, is obtained upon reacting **1** with benzyl potassium. An unusual vinyl oxo species, [Li(THF)₃Ta(O)(Np)₂{μ-C₂H₃}IrH(Cp*)], **6**, is formed when the reaction of **1** with NpLi is carried out in THF, due to THF fragmentation.

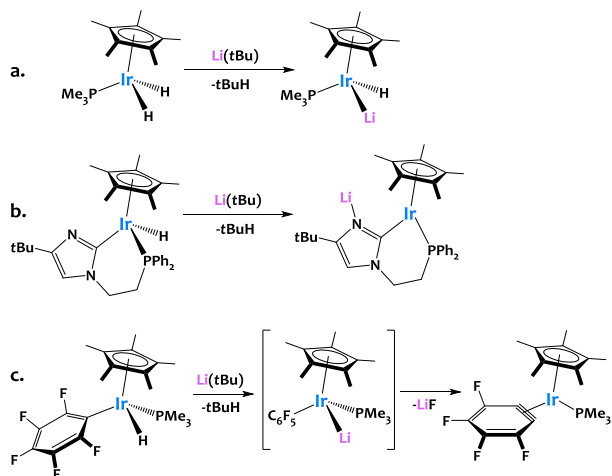
INTRODUCTION

Treatment of metal alkyl or hydride complexes with strong bases, such as alkyl lithium or alkyl potassium reagents, is a powerful methodology to generate key intermediates in organometallic chemistry. A typical example is the base-assisted preparation of early metal alkylidenes/alkylidyne *via* α-H abstraction,¹⁻³ which are strategic active species in reactions such as alkyne,⁴ alkene⁵ and alkane⁶ metathesis or carbonyl olefination.⁷ Representative examples of such α-H abstractions induced by external bases,⁸⁻¹⁰ involving tantalum complexes relevant to this work, are given in Scheme 1.

Another attractive example is the use of lithium alkyls as basic organometallic agents for the deprotonation of iridium hydride species. This was first reported by Bergman, leading to strongly basic iridate species (Scheme 2-a) active in C-H bond activation and dehydrohalogenation reactions.¹¹⁻¹⁴ Rheingold also used this approach to generate nucleophilic iridate complexes (Scheme 2-b & 2-c),¹⁵ which can lead to rare η²-benzyne species through dehalogenation.^{16,17}

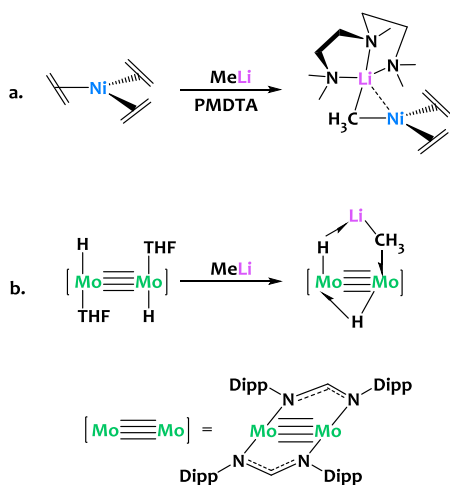


Scheme 1. Archetypal alpha-H abstraction reactions of tantalum complexes promoted by external bases.⁸⁻¹⁰



Scheme 2. Deprotonation of iridium hydrides by organolithium reagents.^{11–17}

Besides their basic character, alkali metal alkyl reagents are good nucleophiles which can coordinate to transition metals through unusual multicenter bonds (Scheme 3).^{18–20} In the 1980s it was, for instance, reported that alkyl lithium reagents could generate highly reactive Ni(0) olefin complexes containing coordinated Li-C bonds (Scheme 3-a).¹⁹ Very recently, Carmona reported the addition of organolithium reagents onto the quadruple bond of a dimolybdenum hydride core, resulting in five-center six-electron bonding within the H-Mo-Mo-C-Li metallacycles (Scheme 3-b).²⁰ This strategy can be used to generate electron-rich heterometallic systems which are particularly promising for synergistic reactivity, yet underexplored.^{21–23}



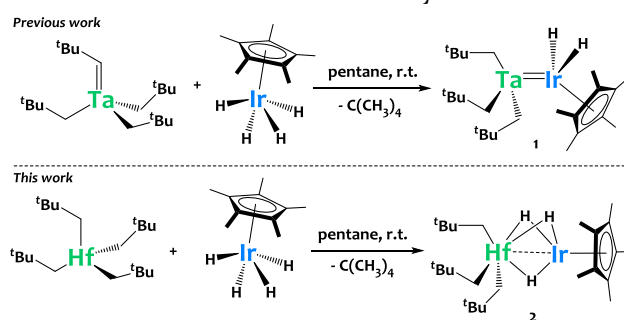
Scheme 3. Coordination of methyllithium to organometallic species.^{19,20}

We recently reported the preparation of the tantalum/iridium complex $[\text{Ta}(\text{CH}_2^t\text{Bu})_3\text{IrH}_2(\text{Cp}^*)]$, **1**,²⁴ by deprotonation of Cp^*IrH_4 with the Ta perhydrocarbyl complex $\text{Ta}(\text{CH}^t\text{Bu})(\text{CH}_2^t\text{Bu})_3$ (Scheme 4). Compound **1**, together with silica-supported analogues, demonstrated interest for the cooperative activation of C-H bonds.^{24–26} Herein we report the synthesis of a hafnium/iridium ana-

logue, which displays bridging hydride ligands in contrast to the tantalum/iridium complex which features a direct metal-metal bond. These early/late bimetallic complexes contain the features discussed above for reactivity with alkyl lithium reagents: M-alkyl moieties (M = Hf, Ta), Ir hydrides and in the case of **1**, a multiple metal-metal bond. Thus, we report their reactivity with organolithium reagents and delineate reactivity trends between these unusual early/late heterobimetallic complexes.

RESULTS AND DISCUSSION

Treatment of Cp^*IrH_4 with $\text{Hf}(\text{Np})_4$ (Np = $\text{CH}_2\text{C}(\text{CH}_3)_3$) in pentane at room temperature affords the heterobimetallic complex $[\text{Hf}(\text{CH}_2^t\text{Bu})_3(\mu\text{-H})_3\text{IrCp}^*]$, **2**, in 93% isolated yield (Scheme 4). ¹H NMR reaction monitoring shows that one equivalent of neopentane is released in the process. This alkane elimination process is typically observed when a nucleophilic metal alkyl derivative is reacted with a Brønsted acidic metal hydride.^{12,24,27–29}



Scheme 4. Syntheses of M/Ir (M = Hf, Ta) heterobimetallic complexes by alkane elimination.

The ¹H and ¹³C NMR spectra of **2** are in agreement with the proposed structure, with a hydride resonance found at -11.1 ppm and integrating for 3H. The minimum spin-lattice relaxation time (T_{min}) measured for this hydride signal is 1.46 s (500 MHz spectrometer) at a temperature of -50°C: this large value is in agreement with a classical hydride description.^{30–34} The infrared spectrum for **2** exhibits a characteristic metal-hydride stretch at 1982 cm^{-1} . This value is significantly shifted in comparison with that of the Ta-Ir analogue ($\nu_{\text{Ir-H}} = 2056 \text{ cm}^{-1}$),²⁴ **1** (Scheme 4), which corroborates the different binding modes of the hydrides in the two compounds (bridging versus terminal). For comparison, compounds $[\text{Cp}^*\text{Ir}(\mu\text{-H})_3\{\text{Ln}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2)_2\}]$ Ln = Y, Dy, Lu, in which the two metal centers are bridged by three hydride ligands, exhibit metal-hydride stretches at 1990, 1988 and 1994 cm^{-1} respectively.³⁵ The solid-state structure of **2**, determined by single-crystal X-ray diffraction, is shown in Figure 1. The approximately linear Hf-Ir-Cp*_{centroid} angle (179.2(3)°) suggests the presence of 3 bridging hydrides across the two metals, arranged to favour a three-legged piano stool coordination geometry around the $\{\text{Cp}^*\text{Ir}\}$ core. This value is in excellent agreement with values reported for systems featuring a $\text{Cp}^*\text{Ir}(\mu\text{-H})_3$ bridging motif such as $[\text{Cp}^*\text{Ir}(\mu\text{-H})_3\{\text{Ta}(\text{CH}_2^t\text{Bu})_2\}\{\text{IrH}_2\text{Cp}^*\}]$ (178.9°)²⁵; $[\text{Cp}^*\text{Ir}(\mu\text{-H})_3\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})]$ (178.8°)³⁶; $[(\text{Cp}^*\text{Ir})_2(\mu\text{-H})_3][\text{ClO}_4]$ (179.3°)³⁷ and $[\text{Cp}^*\text{Ir}(\mu\text{-H})_3\text{Hf}(\text{CH}_2\text{TMS})_2\text{Cp}^*]$

(176.0°)³⁸ and in stark contrast with that found in $[\{\text{Ta}(\text{CH}_2^t\text{Bu})_3\}\{\text{IrH}_2(\text{Cp}^*)\}]$ (151.3(4)°),²⁴ which features two terminal Ir-H moieties or that found in $[\text{Cp}^*\text{IrH}_3\text{Al}^t\text{Bu}(\text{OAr})]$ (143.8°),²⁷ which features one terminal and two bridging hydrides. The Hf-C bond distances (on average 2.19 Å) are in the expected range for hafnium neopentyl groups.^{39,40} The Hf-Ir separation of 2.6773(4) Å in **2** is 0.02 Å shorter than the sum of metallic radii of hafnium (1.442 Å) and iridium (1.260 Å),⁴¹ which translates in a formal shortness ratio very close to unity (FSR=0.991).⁴² This Hf-Ir distance is significantly longer than that of the sole structurally characterized molecular species containing a definitive Ir-Hf bond, $\text{Cp}^*\text{Ir}(\mu\text{-N}^t\text{Bu})\text{HfCp}_2$ (2.5689(9) Å),⁴³ but shorter than that calculated for some Hf-Ir complexes featuring unsupported metal-metal bonds (2.882 Å),^{44,45} and shorter than that found in $[\text{Cp}^*\text{Ir}(\mu\text{-H})_3\text{Hf}(\text{CH}_2\text{TMS})_2\text{Cp}^*]$ (2.7257(3) Å),³⁸ containing three bridging hydrides. Therefore, although a direct metal-metal interaction cannot be excluded, the close proximity between Hf1 and Ir1 is most likely the result of the presence of the bridging hydrides. DFT calculations were performed on compound **2** (see SI) and confirmed the bridging nature of the 3 hydrides. Furthermore, compared to compound **1**, which features clear metal-metal bonding (HOMO and HOMO-1), there is no clear Hf/Ir orbital overlap in complex **2**.

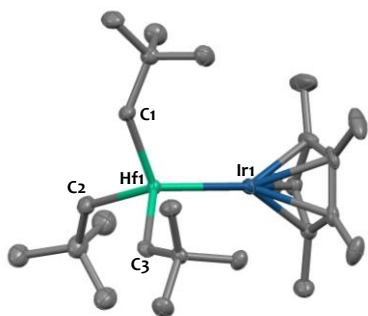


Figure 1. Solid-state molecular structure of **2** (30% probability ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Hf1-Ir1 2.6773(4), Hf1-C1 2.177(9), Hf1-C2 2.190(8), Hf1-C3 2.214(9), Ir1-Cp*_{centroid} 1.845(5), Hf1-Ir1-Cp*_{centroid} 179.2(3).

While a double deprotonation of Cp^*IrH_4 is observed with Ta, resulting in a multiple metal-metal bond, in the case of Hf a single deprotonation is observed (Scheme 4). This could be due to the fact that group 5 elements tend to form more covalent interactions than group 4 metals, and engage more easily in multiple bonding. Note however that the alkyl/alkylidene moieties from $\text{Ta}(\text{CH}^t\text{Bu})(\text{CH}_3^t\text{Bu})_3$ might be more basic than the Hf-alkyl bonds in $\text{Hf}(\text{CH}_3^t\text{Bu})_4$ and could also account for the differences in reactivity. Compounds **1** and **2** thus feature very different geometries and bonding situations, which should result in altered reactivity. Both **1** and **2** exhibit various possible sites of reactivity with alkali metal alkyl reagents (Figure 2): α -H abstraction at the early metal neopentyl moiety, hydride deprotonation or nucleophilic addition onto the electrophilic early metal center. The

purpose of the experiments described below is to delineate which, among these possibilities, is the preferred reactivity behavior, and compare the reactivity profile of the Ta/Ir derivative, **1**, with that of the Hf/Ir species, **2**.

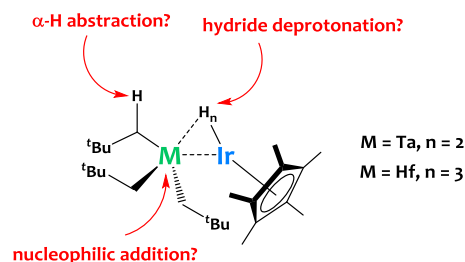
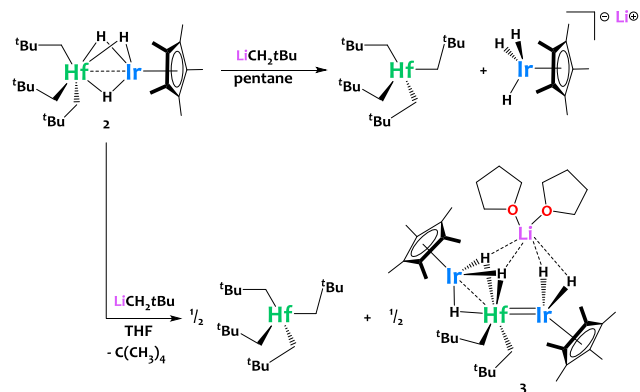


Figure 2. Possible sites of reactivity of the heterobimetallic M/Ir (M = Ta, Hf) complexes.

Treatment of **2** with 1 equiv. of NpLi in pentane at room temperature, leads to the formation of a pyrophoric yellow precipitate. ¹H NMR analysis of the latter after solubilization in deuterated THF shows two resonances at 2.13 and -19.86 ppm integrating respectively for 15H and 3H and corresponding to compound $\text{LiCp}^*\text{IrH}_3$ (Scheme 5), already reported in the literature.^{46,47} The ¹H NMR spectrum of the filtrate from the crude reaction shows characteristic resonances for HfNp_4 .⁴⁰ This reaction supports the idea that nucleophilic addition of NpLi occurs initially at the early metal, and displaces the iridate moiety.



Scheme 5. Solvent-dependent reactivity of **2** towards neopentyl lithium

To avoid precipitation of $\text{LiCp}^*\text{IrH}_3$, which is insoluble in pentane, and attempt to shift the equilibrium of the reaction, the same reaction was repeated in THF (Scheme 5). After addition of one equivalent of NpLi to a colorless solution of **2** in THF, the solution immediately turns yellow. The volatile species are removed under dynamic vacuum and the crude product is crystallized from pentane, affording yellow crystals (56% isolated yield) of a new polynuclear compound, $[\text{Li}(\text{THF})_2]\{\{\text{Cp}^*\text{IrH}_2\}\{\text{Hf}(\text{CH}_2^t\text{Bu})_2\}\{\mu\text{-H}\}_3\text{Ir}(\text{Cp}^*)\}$, **3**. ¹H NMR analysis of the filtrate highlights the presence of HfNp_4 as co-product.⁴⁰ The NMR data for **3** are in agreement with the proposed structure. In particular, two hydride resonances at -12.61 and -15.81 ppm integrating for 3H and 2H respectively are observed in the ¹H NMR spec-

trum of **3**, recorded in deuterated THF at room temperature. This confirms the two inequivalent hydride environments, most probably in interaction with the lithium cation which reduces fluxionality during the NMR acquisition time at room temperature. Indeed, a single hydride signal integrating for 5H is found in the tantalum analogue, $[\{\text{Cp}^*\text{IrH}_2\}\{\text{Ta}(\text{CH}_2^t\text{Bu})_2\}\{\mu\text{-H}\}_3\text{Ir}(\text{Cp}^*)\}]$,²⁵ due to rapid exchange on the NMR timescale in the absence of such Li^+ cation. The ^7Li NMR of compound **3** shows a broad singlet at 4.1 ppm and coupling to the hydrides is not seen (Figure S9). Confirmation of the structure of complex **3** is provided by analysis of the solid state structure obtained by X-ray diffraction (Figure 3), in which the two Ir atoms are in distinct environments as evidenced by the strong disparity in the intermetallic distances and geometries. The Hf1-Ir1 distance (2.7742(2) Å) is more than 0.2 Å longer than the Hf1-Ir2 distance (2.5218(6) Å). The latter is 0.18 Å shorter than the sum of the respective metallic radii (Hf: 1.442 Å; Ir: 1.260 Å; sum = 2.702 Å)⁴¹ and displays a FSR of 0.94 which suggests a strong metal-metal interaction with a multiple bond order as observed in **2**. This is the shortest Hf-Ir distance reported to date to our knowledge.⁴³ On the contrary, the FSR for Hf1-Ir1 is slightly higher than unity (1.03) and although a direct metal-metal interaction cannot be excluded (the rare examples of reported Hf-Ir single bond distances span the range 2.57–2.93 Å),^{43–45,48,49} the close proximity between Hf1 and Ir1 is most likely the result of the presence of bridging hydrides. This is further supported by the approximately linear $\text{Cp}^*_{\text{centroid}}\text{-Ir1-Hf1}$ angle (175.2(1)°), which suggests the presence of 3 bridging hydrides across the two metals, arranged to favor a three-legged piano stool coordination geometry around the $\{\text{Cp}^*\text{Ir}\}$ core. In contrast, the clear tilting of the Cp^* ligand with respect to the Hf1-Ir2 bond ($\text{Cp}^*_{\text{centroid}}\text{-Ir2-Hf1}$ angle of 141.9(1)°) suggests two terminal hydrides. Note that a similar bonding situation is found in the tantalum analogue, $[\{\text{Cp}^*\text{IrH}_2\}\{\text{Ta}(\text{CH}_2^t\text{Bu})_2\}\{\mu\text{-H}\}_3\text{Ir}(\text{Cp}^*)\}]$.²⁵ The hydrides locations were also supported by DFT (see SI). The hafnium-carbon bond lengths (2.246(3) Å on average) are in agreement with neopentyl ligands.^{50,51} The proximity of Li to both Ir1 and Ir2 in the solid state structure of **3** ($\text{Li}^+\text{-Ir1} = 2.72(2)$ Å; $\text{Li}^+\text{-Ir2} = 3.12(3)$ Å) suggests the interaction of the lithium cation with the hydrides. It is possible that 3-center-2-electron bonding occurs to some extent in these Ir-H-Li fragments, as was recently disclosed by Carmona and coworkers in dimolybdenum hydride lithiates derivatives (Scheme 3b).^{20,52}

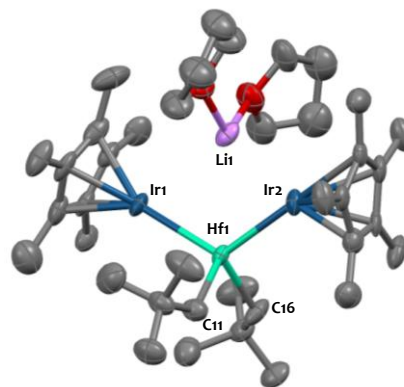


Figure 3. Solid-state molecular structure of compound **3**. Ellipsoids are represented with 30% probability. Hydrogen atoms and disorder have been omitted for clarity. Selected bond distances (Å) and angles (°): Hf1-Ir1 2.7742(2); Hf1-Ir2 2.5218(6); Hf1-C11 2.25(1); Hf1-C16 2.24(1); Ir1⁺-Li 2.72(2); Ir2⁺-Li 3.12(3); Hf1-Ir1-Cp*_{centroid} 175.2(1); Hf1-Ir2-Cp*_{centroid} 141.9(1).

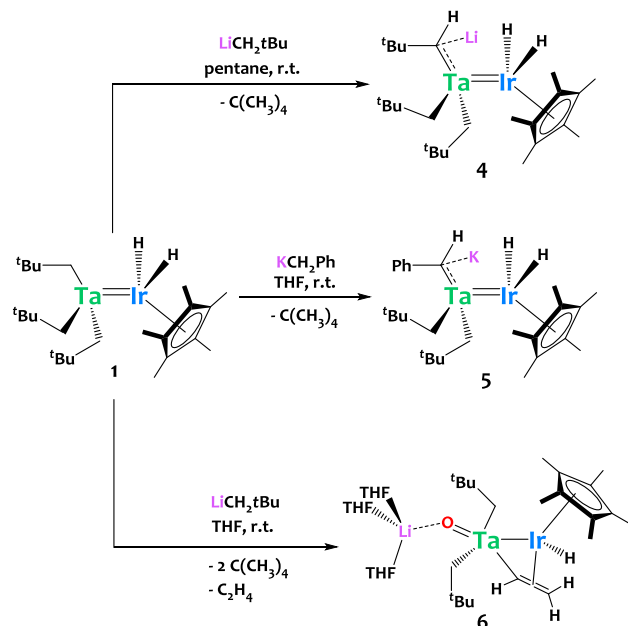
The formation of **3** probably results from the breakup of the heterobimetallic complex **2** through nucleophilic attack of NpLi on Hf to form HfNp_4 and $\text{LiCp}^*\text{IrH}_3$, as observed in pentane. The use of THF allows the solubilization of the latter which reacts with the residual complex **2** via a protonolysis reaction to form the polynuclear complex **3** together with the removal of one equivalent of neopentane. To support this hypothesis, we investigated the reaction between $\text{LiCp}^*\text{IrH}_3$ (prepared upon treating Cp^*IrH_4 with NpLi)^{46,47} and complex **2** in THF- d_8 . This resulted in the formation of **3** as major product (assessed spectroscopically, by ^1H NMR), therefore in agreement with this mechanism.

These reactions show that the Hf center in **2** is Lewis acidic, and that the $[\text{Cp}^*\text{IrH}_3]$ moiety is labile and is easily displaced by the incoming nucleophilic lithium neopentyl moiety. This is reminiscent of the chemistry of aluminium-iridium polyhydride clusters recently described by our group,⁵³ in which we have shown that $[\text{Cp}^*\text{IrH}_3]$ and aluminium-isobutyl units are labile and can be redistributed reversibly.

The Ta/Ir heterobimetallic complex **1**, on the other hand, exhibits a different reactivity with lithium neopentyl (Scheme 6). Treatment of the tantalum-iridium species **1** with 1 equivalent of neopentyl lithium in pentane at room temperature triggers the α -hydrogen abstraction at a Ta-neopentyl moiety and leads to the formation of the alkylidene *-ate* complex $[\text{Li}][\{\text{Ta}(\text{CH}^t\text{Bu})(\text{CH}_2^t\text{Bu})_2\}\{\text{IrH}_2\text{Cp}^*\}]$, **4** in 63% isolated yield (Scheme 6). The ^1H NMR spectrum for **4** displays a singlet at +0.98 ppm attributed to the Ta neopentylidene α -H. This signal correlates in the ^1H - ^{13}C HSQC NMR experiment to the characteristic neopentylidene ^{13}C resonance found at +239.7 ppm; this highly deshielded value is typical of Ta(V) neopentylidenes.^{54–56} The loss of symmetry of compound **4** in solution results in the presence of two diastereotopic doublets corresponding to the

Ta-CH₂ fragments, each integrating for 2H with a strong coupling constant (²J_{HH} = 13.0 Hz).

The solid-state structure of **4**, determined by X-ray diffraction, is reproduced in Figure 4-top. The Ta=Ir distance in **4** is elongated compared to **1** (2.4533(9) Å in **4** vs 2.3559(6) Å in **1**)²⁴ but the formal shortness ratio⁴² (FSR = 0.94) is still below unity, in agreement with multiple metal-metal bonding. The weakening of the metal-metal bonding in **4**, which is quite polarized (Ir→Ta), suggests that the electron density at the Ta center increases upon deprotonation, as expected due to the formation of the alkylidene moiety. DFT computations support σ and π metal-metal bonding in compound **4** (HOMO and HOMO-5, see SI). The presence of the hydrides is indicated by the strong tilting of the Cp* ligand with respect to the Ta=Ir bond (Ta-Ir-Cp*_{centroid} = 139(2)°), to satisfy a classical piano-stool coordination geometry around the Ir center. The Ta-C_{alkylidene} bond length (1.93(2) Å) is significantly shorter than the Ta-C_{alkyl} distances (avg. 2.18(4) Å), and falls in the expected range for tantalum-carbon double bonds.^{54-55,57} The Ta-C π-bond is also corroborated by DFT (HOMO-2, see SI). In the solid-state structure, the Li cation interacts with the neopentylidene carbon (Li-C_{alkylidene} distance = 2.25(4) Å) and points towards the hydrides of an adjacent complex (Ir[⋯]Li separation = 2.63(3) Å). The distance between the alkylidene carbon and the lithium center is compatible with a covalent bond.^{58,59}



Scheme 6. Reactivity of [Ta(CH₂tBu)₃IrH₂(Cp*)], **1**, with alkali metal alkyls.

We note that a single example of a tantalum-lithium alkylidene was described in the literature by Arnold and coworkers, featuring very similar metrical parameters (Ta-C_{alkylidene} bond length of 1.93(3) Å, Li-C_{alkylidene} distance of 2.23(6) Å).⁵⁷ Schrock also reported a tantalum lithium neopentylidyne (Scheme 1b) in which the lithium cation interacts with the nucleophilic carbyne carbon,⁸ which is

also reminiscent of the bonding situation in **4**. As in complex **3**, the interaction of the Li cation with the hydrides of an adjacent complex might further stabilize these assemblies.^{20,52}

The heterobimetallic complex **1** also reacts *via* α-hydrogen abstraction with benzyl potassium (KCH₂Ph) to give the benzylidene complex [K][Ta(CHPh)(CH₂tBu)₂IrH₂Cp*], **5**, as shown in Scheme 6. This reaction is conducted in THF instead of pentane for solubility reasons, and the product is crystallized in a pentane:THF (10:1) mixture. The presence of the benzylidene group is confirmed by NMR spectroscopy with a typical ¹³C resonance at +220.5 ppm and a ¹H signal at +3.66 ppm, integrating for 1H and corresponding to the alkylidene α-H. The iridium hydrides are observed by ¹H NMR as a singlet at -14.61 ppm integrating for 2H, confirming that the deprotonation reaction does not affect them.

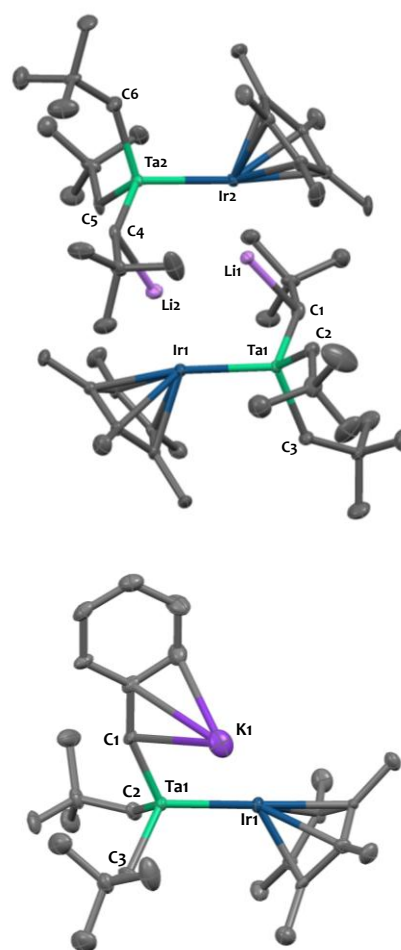
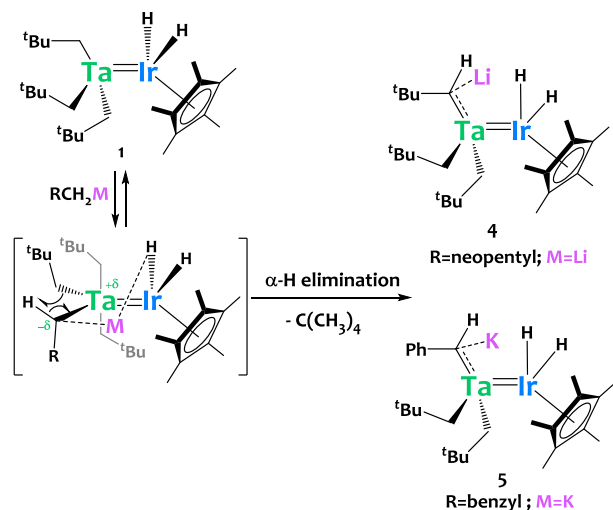


Figure 4. Solid-state molecular structures of complexes **4** (top) and **5** (bottom). Ellipsoids are represented with 30% probability. Hydrogen atoms have been omitted for clarity. Two independent complexes are found in the asymmetric unit for **4**. Two disordered potassium cations are found in the asymmetric unit for **5**, only one is represented for clarity. Selected bond distances (Å) and angles (°) for **4**: Ta1-Ir1 2.4535(9); Ta2-Ir2 2.4531(9); Ta1-C1 1.94(2); Ta2-C4 1.91(2); Ta1-C2 2.15(2); Ta1-C3 2.18(2); Ta2-C5 2.16(2); Ta5-C6 2.22(2);

Ir1-Cp*_{centroid} 1.92(1); Ir2-Cp*_{centroid} 1.92(1); C1-Li1 2.24(4); C4-Li2 2.25(4); Li1...Ir1 3.35(3); Li1...Ir2 2.61(3); Li2...Ir1 2.66(3); Li2...Ir2 3.36(3); Ta1-Ir1-Cp*_{centroid} 137(1); Ta2-Ir2-Cp*_{centroid} 141(1); for **5**: Ta1-Ir1 2.411(7); Ta1-C1 1.97(1); Ta1-C2 2.18(1); Ta1-C3 2.20(1); Ir1-Cp*_{centroid} 1.94(1); Ta1-Ir1-Cp*_{centroid} 144(1).

The solid state structure of complex **5**, obtained by X-ray diffraction, is shown in Figure 4-bottom. Complex **5** shares similar structural characteristics than **4**, with a short Ta=Ir bond (2.411(7) Å, FSR of 0.93), a Ta1-Ir1-Cp*_{centroid} angle of 144(1)° typical of a piano stool geometry around Ir and a pseudo-tetrahedral geometry around Ta (C-Ta-C angles from 105.0(1)° to 110.7(1)°; Ir-Ta-C angles from 108.7(4)° to 113.1(3)°). The K⁺ cation is disordered across two positions in the crystal structure, both sites revealing a strong interaction with the C1 benzylidene carbon (3.32(1) and 3.34(1) Å). The K⁺...Ir1 distances are also relatively short (3.61(1) and 3.92(1) Å), and may suggest an interaction of the K⁺ center with the hydride ligands. The Ta1-C1 bond length of 1.97(1) Å is clearly shorter than those of the Ta-C2 and Ta-C3 bonds (2.18(1) and 2.20(1) Å respectively), reflecting a multiple bond order between Ta1 and C1, consistent with a benzylidene moiety.^{60,61}



Scheme 7. Proposed mechanism for the formation of complexes **4** and **5**.

These experiments demonstrate that the base-promoted α-H abstraction at the tantalum alkyl is more favorable than deprotonation of the iridium hydride in **1**. A plausible mechanism to explain the reaction of complex **1** with NpLi and BnK is shown in Scheme 7. At first, the nucleophilic addition of the external alkyl reagent onto tantalum is proposed. This leads to a sterically hindered reaction intermediate, with a possible interaction of the Li⁺ or K⁺ cation with the hydrides, as observed on the solid state structures. Such nucleophilic addition onto the early metal is observed experimentally in the case of the hafnium-iridium analogue (Scheme 5), which adds credibility to the proposed mechanism for tantalum. The presence of the alkali metal cation on the C1 carbon increases the relative acidity of the C1-H proton, making it more reactive towards α-H abstraction. Furthermore, Copéret,

Eisenstein, Andersen and coworkers demonstrated that the intramolecular α-H abstraction reaction requires a bis-alkyl complex with a vacant orbital on the metal oriented in the plane of the M-Cα and M-Cα' bonds, and that this reaction is more favorable for neopentyl ligands: both conditions are present here.¹ Such mechanism also explains why the benzylidene species, **5**, is formed quantitatively. However, the monitoring of these reactions by NMR spectroscopy did not allow the identification of a reaction intermediate, and it is possible that a direct α-H elimination occurs first, or that a more complex mechanism involving iridium hydrides takes place here. In the case of Hf, the α-H abstraction does not occur probably due to the lower stability of Hf alkylidenes, which are rare.^{51,62,63}

Interestingly, when treatment of complex **1** with neopentyl lithium is performed in THF instead of pentane, THF fragmentation occurs, resulting in a new complex **6** which was isolated in 48% yield (Scheme 6). The ether oxygen atom is excavated and trapped in the form of a terminal oxo dianion (O²⁻) moiety, capping the oxophilic Ta metallic site. The C-C ring bonds as well as C-H bonds from THF are also cleaved to give a vinyl anion (CH₂=CH⁻) fragment which is captured by bimetallic chelation. The structure of **6** was elucidated *via* multinuclei NMR spectroscopy as well as single crystal X-ray diffraction (Figure 5). The ¹H NMR spectrum of **6** displays deshielded resonances typical of a vinyl ligand at 5.26 (t, ³J_{HH} = 10 Hz, 1H), 3.43 (dd, ²J_{HH} = 3 Hz, ³J_{HH} = 10 Hz, 1H) and 2.98 (t, ³J_{HH} = 10 Hz, 1H) ppm. The low field chemical shift for the Ta-bound methyne carbon of 145.1 ppm is also characteristic of σ,π-vinyl ligands.^{64,65} The iridium hydride ¹H NMR resonance is found at -15.51 ppm and integrates for 1H, in agreement with the proposed formula. The presence of the hydride ligand is further established by DRIFT spectroscopy, displaying a typical ν_{Ir-H} signal at 2068 cm⁻¹. The original μ-κ¹:η² vinyl coordination is confirmed by XRD. Both carbon atoms from the vinyl anion are bound in an η²-fashion to the Ir site, while Ta is bound to the deprotonated C-terminus. The short C1-C2 bond distance (1.429(6) Å) is intermediate between typical C-C single and C=C double bonds, in agreement with an unsaturated C₂ unit, and compares well with that found in related vinyl complexes.⁶⁴⁻⁶⁷ The π-system of the vinyl anion is bound symmetrically to the iridium center: the Ir-C1 (2.128(4) Å) and Ir-C2 (2.1287(4) Å) distances are almost identical and lie well within the range for bond lengths between Ir and π-bonded carbons.^{67,68} The Ta-C1 distance (2.141(4) Å) is in the expected range for a single bond, and is slightly shorter than the Ta-C_{neopentyl} bond lengths (Ta1-C13 = 2.206(4) Å; Ta1-C16 = 2.232(4) Å). The tantalum-iridium distance of 2.6586(2) Å is considerably elongated in comparison to that in **1** (2.3559(6) Å),²⁴ but remains in the range of the sum of the respective metallic radii (Ta: 1.343 Å; Ir: 1.260 Å; sum = 2.603 Å)⁴¹ and falls in the range of the few reported Ta-Ir single bonds (2.43-2.85 Å).^{26,69-72} The short Ta-O distance (1.764(3) Å) is consistent with a multiple metal oxygen bond and falls in the expected range for mono-oxo complexes of Ta.^{63,73-75}

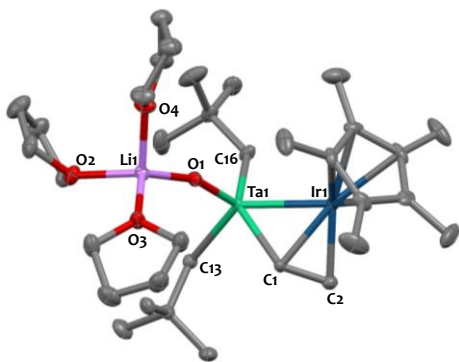


Figure 5. Solid-state molecular structure of complex **6**. Ellipsoids are represented with 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ta1-Ir1 2.6586(2); Ta1-O1 1.764(3); Ta1-C1 2.141(4); Ta1-C13 2.206(4); Ta1-C16 2.232(4); Ir1-C1 2.128(4); Ir1-C2 2.127(4); Ir1-Cp*_{centroid} 1.875(3); C1-C2 1.429(6); Ta1-Ir1-Cp*_{centroid} 139(1); Ir-C1-Ta1 77.0(1); C2-C1-Ir1 70.3(2).

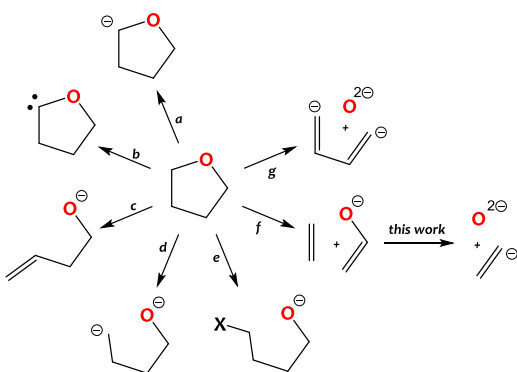
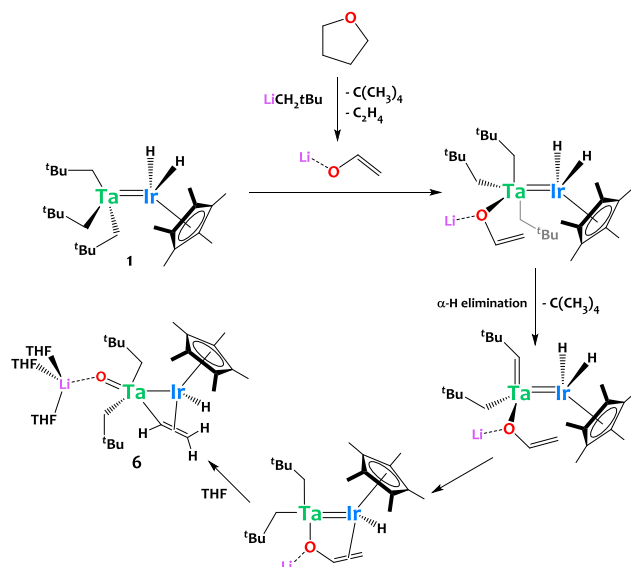


Figure 6. The reactivity of THF with metallic species. *a* (TMEDA)Na(TMP)(R)Zn(R) R = CH₂SiMe₃,⁷⁶ *b* Ir⁷⁷⁻⁸¹ and Os⁸²⁻⁸⁴ complexes; *c* *t*-BuLi-HMPA;⁸⁵ *d* Low-valent An,⁸⁶ Ln,⁸⁷ Group 4⁸⁸⁻⁹³ and Group 5^{94,95} species; *e* Lewis Acids^{96,97,106,107,98-105}; *f* RLi (R = Me, *t*-Bu, *n*-Bu)^{108,109} *g* (TMEDA)Na(TMP)(R)M(TMP) R = CH₂SiMe₃, M = Mg or Mn.¹¹⁰

From the perspective of THF, the formation of **6** implies the rupture of at least one C–C, one C–H and two C–O bonds. Such a multiple bond breaking process, leading to complete fragmentation of THF is unprecedented and presumably involves a highly complex mechanism that is hard to establish. Still, organometallic species are known to activate THF in multiple pathways (Figure 6). In particular, the cleavage of THF by organolithium reagents is well documented, and typically leads to ethylene and ethenolate species (Figure 6-f).^{108,109,111} Mulvey and coworkers also demonstrated that the synergy between two different metals can promote the dramatic breakdown of THF, leading to the excision of the ether oxygen and the formation of a butadiene dianion (Figure 6-g).¹¹⁰



Scheme 8. Proposed pathway for the formation of complex **6**.

In the present case, we noticed that the contact time between neopentyl lithium and THF, before the addition onto compound **1**, had an impact on the selectivity of the reaction. Indeed, when NpLi is added to a THF solution of **1**, a subsequent amount of **4** is formed, along with **6**. Conversely, compound **6** is obtained selectively when NpLi is stirred for 1 hour in THF at room temperature before addition onto **1**. Note that the isolated neopentylidene complex, **4**, prepared in pentane, is stable in THF solution. This suggests that NpLi first activates THF, most probably to form ethylene and the lithium enolate of acetaldehyde (Figure 6),^{108,109} which then reacts with **1** to form **6**. A possible reaction pathway is proposed in Scheme 8. By analogy with the alkylidene formation described above (Scheme 7), the enolate coordination to the Lewis acidic Ta center might trigger α -H elimination, releasing neopentane. Interestingly, a single hydride ligand remains on the Ir center, which indicates that under certain conditions these hydrides can be activated. This suggests that the reaction of **1** with the enolate triggers intramolecular migration of an Ir–H to form a monohydride, as proposed in Scheme 8, before C–O bond cleavage leading to the oxo and vinyl anion.

CONCLUSION

This study underlines the diversity of reactivity that can occur at heterobimetallic alkyl hydride species. The nature of the early metal (Hf versus Ta) has a strong impact, not only on the structure of the M/Ir heterobimetallic complexes, but also on their reactivity. The protonolysis of Hf(Np)₄ with Cp*IrH₄ leads to a novel Hf/Ir alkyl hydride complex, **2**, where the two metals are held together by bridging hydrides, with little to no metal-metal interaction. Treatment of **2** with NpLi in pentane results in the nucleophilic addition of a neopentyl moiety onto the Hf center. This results in the breakup of the Hf/Ir dinuclear assembly, restoring Hf(Np)₄ and displacing the Cp*IrH₃[−] iridate moiety. When the same reaction is carried out in

THF, a polynuclear aggregate is formed, most likely as a result of the reactivity of $\text{Cp}^*\text{IrH}_3^-$ with **2**. Ta is more prone to multiple covalent bonding. Indeed, the Ta/Ir analogue, **1**, features a robust multiple metal-metal bond, and leads to alkylidenes when treated by NpLi of BnK. The proposed mechanism likely involves first addition of the alkali alkyl onto Ta, as observed for Hf, but is then followed by rapid α -H elimination. When **1** is treated with NpLi in THF instead of pentane, THF fragmentation occurs leading to an original oxo vinyl Ta/Ir/Li trimetallic species, **6**. Future studies will be devoted in the deeper understanding of the structure and reactivity of these alkylidene -ate species, featuring original M-C and M-H contacts (M = Li, K).

EXPERIMENTAL SECTION

General considerations. Unless otherwise noted, all reactions were performed either using standard Schlenk line techniques or in an MBraun inert atmosphere glovebox under an atmosphere of purified argon (<1 ppm $\text{O}_2/\text{H}_2\text{O}$). Glassware and cannulae were stored in an oven at $\sim 100^\circ\text{C}$ for at least 12 h prior to use. Tetrahydrofuran, toluene and *n*-pentane were purified by passage through a column of activated alumina, dried over Na/benzophenone, vacuum-transferred to a storage flask and freeze-pump-thaw degassed prior to use. Deuterated solvents (THF- d_8 and C_6D_6), were dried over Na/benzophenone vacuum-transferred to a storage flask and freeze-pump-thaw degassed prior to use. NpLi,¹¹² benzyl potassium¹¹³ and $[\text{Ta}(\text{CH}_2^t\text{Bu})_3\text{IrH}_2(\text{Cp}^*)]^{24}$ were prepared using literature procedures. All other reagents were acquired from commercial sources and used as received.

Liquid state NMR spectra were recorded on Bruker AV-300, AVQ-400 and AV-500 spectrometers. Chemical shifts were measured relative to residual solvent peaks, which were assigned relative to an external TMS standard set at 0.00 ppm. ^1H and ^{13}C NMR assignments were routinely confirmed by ^1H - ^1H COSY and ^1H - ^{13}C HSQC and HMBC experiments. ^7Li NMR is calibrated using LiCl in D_2O (resonance set to 0.0 ppm). Samples for Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) were prepared in a glovebox (diluted in KBr powder), sealed under argon in a cell equipped with KBr windows and analyzed on a Nicolet 670 FT-IR spectrometer. Elemental analyses were performed under inert atmosphere either at the School of Human Sciences, Science Center, London Metropolitan University or at Mikroanalytisches Labor Pascher, Germany. Experimental details regarding the X-ray structural determinations are provided in SI. CCDC 2116171, 2149832, 2149835, 2149836 and 2149838

contain the supplementary crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Centre.

Synthesis of $[\text{Hf}(\text{CH}_2^t\text{Bu})_3(\mu\text{-H})_2\text{IrCp}^*]_2$, **2**

A colorless pentane solution (10 mL) of Cp^*IrH_4 (423.4 mg, 1.28 mmol, 1.0 equiv.) was added dropwise to a colorless pentane solution (10 mL) of $\text{Hf}(\text{CH}_2^t\text{Bu})_4$ (591.3 mg, 1.28 mmol, 1.0 equiv.). The reaction mixture was stirred at room temperature for 2 hours and remained colorless. Volatiles were removed under vacuum affording a white powder. The crude product was dissolved in the minimum amount of pentane and stored at -40°C overnight to yield colorless crystals of $[\text{Hf}(\text{CH}_2^t\text{Bu})_3(\mu\text{-H})_2\text{IrCp}^*]_2$ (**2**) (859 mg, 1.19 mmol, 93%). Single crystals suitable for X-ray diffraction were obtained similarly. ^1H NMR (400 MHz, 293K , C_6D_6) δ 1.93 (s, 15H, Cp*), 1.33 (s, 27H, ^tBu), 0.79 (s, 6H, Ta-CH₂), -11.10 (s, 2H, Ir-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, 293K , C_6D_6) δ 109.98 (Hf-CH₂), 92.00 (C_5Me_5), 36.12 ($\text{C}(\text{CH}_3)_3$), 35.92 ($\text{C}(\text{CH}_3)_3$), 10.69

(C_5Me_5). DRIFT (293K , cm^{-1}) ν 2950 (s, $\nu_{\text{C-H}}$), 2896 (s, $\nu_{\text{C-H}}$), 2859 (s, $\nu_{\text{C-H}}$), 2793 (w, $\nu_{\text{C-H}}$), 2771 (w, $\nu_{\text{C-H}}$), 2744 (w, $\nu_{\text{C-H}}$), 2699 (w, $\nu_{\text{C-H}}$), 1982 (s, $\nu_{\text{M-H}}$), 1461 (m), 1383 (m), 1358 (m), 1228 (m), 1032 (m), 748 (m). Elemental analysis calcd (%) for $\text{C}_{25}\text{H}_{51}\text{HfIr}_2$: C 41.57, H 7.12; found: C 41.37, H 6.98.

Reaction of **2** with NpLi.

a) Reactivity in pentane: A colorless pentane solution (10 mL) of neopentyl lithium (20 mg, 0.25 mmol, 1 equiv.) was added to a colorless pentane (25 mL) solution of complex **2** (183 mg, 0.25 mmol, 1 equiv.) at ca. 25°C . The reaction mixture was stirred 1 hour at ca. 25°C . A yellow precipitate formed during the reaction and was collected by filtration and identified as $\text{LiCp}^*\text{IrH}_3$ ^{46,47} (68 mg, 0.20 mmol, 84%) ^1H NMR (300 MHz, 293K , THF- d_8) δ 2.13 (s, 15H, Cp*), -19.86 (s, 3H, Ir-H). The colorless filtrate was analyzed by ^1H NMR spectroscopy and was only composed of HfNp_4 according to literature data.⁴⁰ ^1H NMR (300 MHz, 293K , C_6D_6) δ 1.18 (s, 36H, ^tBu), 0.94 (s, 8H, Hf-CH₂).

b) Reactivity in THF: A colorless THF solution (10 mL) of neopentyl lithium (14.4 mg, 0.18 mmol, 1 equiv.) was added to a colorless THF solution (10 mL) of complex **2** (133 mg, 0.18 mmol, 1 equiv.) at ca. 25°C . The solution turned from colorless to an intense yellow color. The reaction mixture was stirred 2 hours at ca. 25°C and the volatiles were removed under vacuum. The resulting oily crude material was triturated in pentane (3 mL) and the volatiles were removed under vacuum, affording a yellow powder. Cold recrystallization (-40°C) from a pentane saturated solution afforded compound $[\text{Li}\{\text{Hf}(\text{CH}_2^t\text{Bu})_2\text{Ir}_2\text{H}_5(\text{Cp}^*)_2\}]_2$, **3** as yellow crystals (51 mg, 0.05 mmol, 56%). ^1H NMR (400 MHz, 293K , THF- d_8) δ 2.14 (s, 30H, Cp*), 1.01 (s, 18H, ^tBu), 0.11 (d, $^2J_{\text{HH}} = 11\text{Hz}$, 2H, Hf-CH₂), -0.42 (d, $^2J_{\text{HH}} = 11\text{Hz}$, 2H, Hf-CH₂), -12.61 (s, 3H, Ir-H), -15.81 (s, 2H, Ir-H). ^{13}C NMR (101 MHz, 293K , THF- d_8) δ 99.79 (Hf-CH₂), 90.53 (C_5Me_5), 89.89 (C_5Me_5), 36.46 ($\text{C}(\text{CH}_3)_3$), 35.39 ($\text{C}(\text{CH}_3)_3$), 11.92 (C_5Me_5), 11.03 (C_5Me_5). ^7Li NMR (194.4 MHz, 300K , THF- d_8) δ 4.1. Elemental analysis calcd (%) for $\text{Li}_2\text{C}_{38}\text{H}_{73}\text{O}_2\text{Hf}_2\text{Ir}_2$: C 40.32, H 6.50; found: C 40.66, H 6.55.

$[\text{Li}\{\text{Ta}(\text{CH}^t\text{Bu})(\text{CH}_2^t\text{Bu})_2\text{IrH}_2(\text{Cp}^*)\}]_4$, **4**

A colorless pentane solution (6 mL) of neopentyl lithium (23.6 mg, 0.30 mmol, 1 equiv.) was added dropwise to a red pentane solution of complex $[\text{Ta}(\text{CH}_2^t\text{Bu})_3\text{IrH}_2(\text{Cp}^*)]_2$ **1** (218.2 mg, 0.30 mmol, 1 equiv.) under vigorous stirring at ca. 25°C . After 5 minutes, the formation of a yellow precipitate was observed. The reaction mixture was stirred 1 hour at ca. 25°C . The yellow solid was removed by filtration on a glass microfiber filter, and the yellow filtrate was concentrated by half and stored 3 days at -40°C to yield compound $[\text{Li}\{\text{Ta}(\text{CH}^t\text{Bu})(\text{CH}_2^t\text{Bu})_2\text{IrH}_2(\text{Cp}^*)\}]_4$, **4**, as yellow crystals which were recovered by filtration and dried in vacuum (138 mg, 0.19 mmol, 63 % yield). ^1H NMR (400 MHz, 293K , THF- d_8) δ 2.16 (s, 15H, Cp*), 1.28 (s, 9H, ^tBu), 1.16 (s, 18H, ^tBu), 0.98 (s, 1H, Ta=CH), 0.34 (d, $^2J_{\text{HH}} = 13\text{Hz}$, 2H, Ta-CH₂), -0.56 (d, $^2J_{\text{HH}} = 13\text{Hz}$, 2H, Ta-CH₂), -15.06 (s, 2H, Ir-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, 293K , THF- d_8) δ 239.72 (Ta= $\text{C}_{\text{sp}2}$), 98.71 (Ta- $\text{C}_{\text{sp}2}$), 93.69 (C_5Me_5), 46.42 ($\text{CHC}(\text{CH}_3)_3$), 39.53 ($\text{CHC}(\text{CH}_3)_3$), 38.77 ($\text{CH}_2\text{C}(\text{CH}_3)_3$), 36.53 ($\text{CH}_2\text{C}(\text{CH}_3)_3$), 14.79 (C_5Me_5). DRIFT (293K , cm^{-1}) ν 2953 (s, $\nu_{\text{C-H}}$), 2895 (s, $\nu_{\text{C-H}}$), 2850 (s, $\nu_{\text{C-H}}$), 2027-1991 (s, $\nu_{\text{Ir-H}}$), 1468 (m), 1361 (m), 1084 (m), 789 (m). Elemental analysis calcd (%) for $\text{Li}_4\text{C}_{25}\text{H}_{49}\text{Ta}_4\text{Ir}_4$: C 41.15, H 6.77; found: C 42.02, H 6.94. Despite multiple attempts, the value for carbon was consistently found to be higher than the theoretical value. We attribute this to residual pentane.

$[\text{K}\{\text{Ta}(\text{CHPh})(\text{CH}_2^t\text{Bu})_2\text{IrH}_2(\text{Cp}^*)\}]_5$, **5**

A red THF solution (6 mL) of benzyl potassium (9.0 mg, 0.07 mmol, 1 equiv.) was added dropwise to an orange solution (8 mL) of complex $[\text{Ta}(\text{CH}_2^t\text{Bu})_3\{\text{IrH}_2(\text{Cp}^*)\}]_2$ **1** (50 mg, 0.07 mmol, 1 equiv.) at ca. 25°C . The reaction mixture was stirred 4 hours at ca. 25°C leading to an orange solution. Volatiles were removed *in vacuo* to yield an orange solid. Recrystallization from a pentane/THF (20/1) saturated solution at -40°C yielded com-

plex **5** as yellow crystals (54 mg, 0.07 mmol, 99%). ¹H NMR (300 MHz, 293K, THF-*d*₈) δ 7.21 (d, ²J_{HH} = 7.5 Hz, 2H, C₆H₅-o), 6.95 (t, ²J_{HH} = 7.5 Hz, 2H, C₆H₅-m), 6.43 (t, ²J_{HH} = 7.5 Hz, 1H, C₆H₅-p), 3.66 (s, 1H, Ta=CH), 2.20 (s, 15H, Cp*), 1.02 (s, 18H, *t*Bu), 0.41 (d, ²J_{HH} = 13 Hz, 2H, Ta-CH₂), -0.30 (d, ²J_{HH} = 13 Hz, 2H, Ta-CH₂), -14.61 (s, 2H, Ir-H). ¹³C{¹H} NMR (75 MHz, 293K, THF) δ 220.50 (Ta=C_{sp2}H), 151.05 (C₆H₅-i), 128.13 (C₆H₅-m), 126.07 (C₆H₅-o), 118.47 (C₆H₅-p), 100.05 (Ta-CH₂), 92.36 (C₅Me₅), 35.72 (C(CH₃)₃), 34.15 (C(CH₃)₃), 11.52 (C₅Me₅). Elemental analysis calcd (%) for C₂₇H₄₅K₁Ta₁Ir₁: C 41.47, H 5.80; found: C 41.76, H 5.94.

[[Li(THF)₃Ta(O)(CH₂^tBu)₂{μ-C₂H₃}IrH(Cp*)], **6**

A colorless THF solution (4 mL) of neopentyl lithium (7.2 mg, 0.09 mmol, 1 equiv.) was prepared, kept 2h at 25°C and then added dropwise to an intense red THF solution of complex [Ta(CH₂^tBu)₃IrH₂(Cp*)], **1** (67.0 mg, 0.09 mmol, 1 equiv.) under vigorous stirring at ca. 25°C. The reaction mixture was stirred 12 hours at ca. 25°C to yield a yellow-orange solution which was concentrated by half and stored 3 days at -40°C to yield compound **6**, as orange crystals (41 mg, 0.045 mmol, 48 % yield). ¹H NMR (400 MHz, 293K, THF-*d*₈) δ 5.26 (t, ³J_{HH} = 10 Hz, 1H, Ta-CH=CH₂), 3.43 (dd, ²J_{HH} = 3 Hz, ³J_{HH} = 10 Hz, 1H, Ta-CH=CH₂), 2.98 (t, ³J_{HH} = 10 Hz, 1H, Ta-CH=CH₂), 2.01 (s, 15H, Cp*), 1.02 (s, 9H, ^tBu), 0.96 (s, 9H, ^tBu), 0.56 (d, ²J_{HH} = 13 Hz, 1H, Ta-CH₂), -0.10 (d, ²J_{HH} = 13 Hz, 1H, Ta-CH₂), -0.27 (d, ²J_{HH} = 13 Hz, 1H, Ta-CH₂), -0.38 (d, ²J_{HH} = 13 Hz, 1H, Ta-CH₂), -15.51 (s, 1H, Ir-H). ¹³C{¹H} NMR (101 MHz, 293K, THF-*d*₈) δ 145.10 (Ta-CH=CH₂), 89.16 (C₅Me₅), 88.94 (Ta-CH₂), 72.77 (Ta-CH₂), 35.40 (CH₂C(CH₃)₃), 34.38 (CH₂C(CH₃)₃), 34.22 (CH₂C(CH₃)₃), 33.15 (CH₂C(CH₃)₃), 21.49 (Ta-CH=CH₂), 9.84 (C₅Me₅). DRIFT (293K, cm⁻¹) ν 2948 (s, ν_{C-H}), 2896 (s, ν_{C-H}), 2849 (s, ν_{C-H}), 2068 (s, ν_{Ir-H}), 1468 (m), 1383 (m), 1355 (m), 1237(m), 1216 (m) 1051 (m), 882(m). Elemental analysis calcd (%) for Li₁C₃₄H₆₂O₄Ta₁Ir₁: C 44.63, H 6.82; found: C 44.70, H 7.05.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

NMR and IR spectroscopic data, X-ray crystallography data (PDF)

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