ORGANOMETALLICS

Early–Late Heterobimetallic Complexes with a Ta–Ir Multiple Bond: Bimetallic Oxidative Additions of C-H, N-H, and O-H Bonds

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S Supporting Information

ABSTRACT: A heterobinuclear transition metal complex with a Ta–Ir multiple bond, $Cp^*(Me_3SiCH_2)_2Ta-IrCp^*(H)_2$ (1), was synthesized using a salt elimination reaction. The isolable complex was characterized by NMR, IR, UV-vis spectroscopy, and X-ray crystallography. Compound 1 features an exceptionally short intermetallic distance (Ta-Ir 2.4457(3) Å). DFT calculation for 1 revealed the presence of a highly covalent bonding nature in spite of the involvement of such disparate d elements. Oxidative additions of C-H, N-H, and O-H bonds to 1 were also investigated.



C tudies of the electronic structures and properties of metal-O metal bonds are of particular importance in fundamental chemistry.¹ Among a number of directly metal-metal-bonded complexes, early-late heterobimetallic compounds have attracted considerable attention with regard to synergetic effects in their reactivity.² Much effort has also been devoted to studying higher bond orders (especially, higher than triple bonds) of homobinuclear complexes such as K₂[Re₂Cl₈]·H₂O³ and [ArCrCrAr] (Ar = $C_6H_3-2,6(C_6H_3-2,6-Pr_2)_2)$,⁴ but there are still few studies of heterobinuclear analogues, and such studies are limited to direct bonds between transition metals close to each other in the d block^{2b,d} or complexes stabilized using rigid hard-soft spectator ligand linkages.^{5,6} An example of the latter case is the report by Wolczanski's group on the heterobimetallic complex $[Ti(\mu:\eta^1,\eta^1-OCMe_2CH_2PPh_2)_3Rh]$, which possesses a cylindrically symmetric triple bond that is suggested to arise from one $Ti(d_{\sigma})-Rh(d_{\sigma})$ and two dative $Rh(d_{\pi}) \rightarrow Ti(d/p_{\pi})$ interactions.^{5b} Very recently, Thomas and co-workers investigated [ClZr(μ : η^1 , η^1 -NR'PR₂)₃CoI] and its application in redox chemistry and catalysis.^{6b,c}

We have previously reported that $[(L_2ZrPh)(Cp*Ir)(\mu-H)_3]$ (L = Cp derivative) enables aromatic C-H(D) activation. Reversible ligand exchange is thought to proceed through a transient Zr–Ir-bonded intermediate $[(L_2Zr)(Cp*IrH_2)]$, which ultimately results in dimerization to $[(L_2Zr)_2(Cp^*Ir)_2(\mu_3-H)_4]$ as stable and isolable complexes. However, isolation and characterization of such highly reactive intermediates with interactions between vastly different metal centers have not been successful. Here we describe the synthesis of a multiply bonded Ta-Ir complex and bimetallic oxidative addition of C-H(D), N-H, and O-H bonds.

In a glovebox, to a toluene solution of [Cp*Ta(Cl)- (CH_2SiMe_3) (=CHSiMe_3)], which was prepared from a 1:3 mixture of [Cp*TaCl₄] and LiCH₂SiMe₃, was added an

equimolar amount of powdery Li[Cp*IrH₃] at 25 °C. The resulting slurry was then stirred for 15 h. After workup, a crude product was obtained as a brown solid (ca. 90% yield),⁸ which was purified by recrystallization from pentane at -30 °C, giving reddish-brown crystals of [{Cp*Ta(CH₂SiMe₃)₂}(Cp*IrH₂)] (1) (Scheme 1).





Structure of diamagnetic 1 was identified by both spectroscopy and crystallography. The ¹H NMR spectrum in C₆D₆ solvent shows the characteristic upfield resonance of Ir-bound hydride at $\delta = -9.68$ ppm as well as signals for other hydrocarbyl ligands in typical chemical shift region. The spinlattice relaxation time (T_1) for the Ir–H resonance in 1 $(T_{1 \text{ min}})$ = 0.30 s) suggests that 1 is a classical hydrido complex. Furthermore, the IR spectrum of 1 shows a distinct absorption at 2154 cm⁻¹, which is assignable to the terminal Ir-H stretching vibration.9

As seen in Figure 1, single-crystal X-ray analysis of 1 shows a three-legged piano stool geometry for both Ta and Ir centers. The intermetallic distance $(2.4457(3) \text{ Å})^{10}$ is exceptionally short in comparison to those in other known complexes with a Ta-Ir single bond, e.g., $[(indenyl)(Cp)Ta(\mu-CH_2)_2Ir(CO)_2]$ $(2.858(1) \text{ Å})_{11a,b} [Cp_2Ta(\mu-CH_2)_2Ir(CO)_2(PEt_3)] (2.881(1))$

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Figure 1. X-ray structure of **1** (hydrogen atoms except for IrH are omitted for clarity; thermal ellipsoids are drawn at 50% probability level). Selected bond distances (Å) and angles (deg): Ta1–Ir1 2.4457(3), Ta1–C11 2.194(5), Ta1–C15 2.173(5), Ta1–Ir1–Cp*-(cent) 163.7, C11–Ta1–C15 103.2(2), Cp*(cent)–Ta1–Ir1–Cp*-(cent) 71.0.

Å),^{11b} and $[Cp_2Ta(\mu-CH_2)_2Ir(Cp^*)(H)]$ (2.776(1) Å).^{11c} The bitetrahedral Ta and Ir centers in 1 are twisted with respect to each other (torsion angle Cp*(cent)–Ta1–Ir1– Cp*(cent) = 71.0°). Although this solid-state structure shows the two alkyl groups on the Ta and the two hydride ligands as nonequivalent, variable temperature ¹H NMR measurements at 163–298 K indicated that each ligand set is equivalent in solution, implying a weak secondary Ta–Ir bonding interaction.

We performed a DFT calculation at the B3LYP level on the geometrical and electronic structures of 1. The DFT-optimized structure of 1 has good agreement with the experimental data, especially in terms of the Ta-Ir distance (2.4303 Å), Ta-Ir- $Cp^{*}(cent)$ angle (158.3°), and $Cp^{*}(cent)-Ta-Ir-Cp^{*}(cent)$ torsion angle (75.2°). According to the calculated M-H and H-H distances (Ta-H = 2.21, 2.47 Å; Ir-H = 1.62, 1.63 Å, H-H = 2.23 Å), 1 can best be described as having a terminal dihydride structure.¹² NBO analysis indicated a positively charged Ta center (natural charge = +1.273) but a less polarized Ta-Ir bonding interaction [Cp*Ta(CH₂SiMe₃)₂ fragment = +0.254, Cp*IrH₂ fragment = -0.254]. In addition, the Wiberg index, Ta-Ir = 1.210, is decisive evidence of a relatively high covalent bonding interaction between Ta and Ir although it is still less than that for a formal covalent double bond.¹³ Molecular orbitals 130 (HOMO) and 121 (HOMO-9) are depicted in Figure 2. The energetically low-lying HOMO-9 explicitly represents the $Ta(d_{\sigma})$ -Ir(d_{σ}) bonding interaction, while the HOMO includes not only an indistinct π -interaction

between the two metal atomic orbitals but also antibonding interactions between the Ir orbital and p-orbitals of the three Cp*-ring carbon atoms. The former bonding interaction might reflect less restricted Ta–Ir bond rotation, as suggested by the variable temperature NMR result.

The NBO orbital can account for the metal orbital contributions in more detail (Ta: 37%, Ir: 63%), and Ta has a higher d character in the hybridized orbital than does Ir (Ta: sd^{6.47}, Ir: sd²). The UV–vis spectra of 1 have an absorption band as a shoulder in the visible-light region ($\lambda_{max} = 503 \text{ nm}, \varepsilon = 729 \text{ mol}^{-1} \text{ L cm}^{-1}$), which is obviously of much smaller energy than the ground state HOMO–LUMO gap of optimized-1 (3.74 eV). A time-dependent DFT calculation on 1 was therefore carried out, and the HOMO–LUMO transition was found to be the major component (90.4%) of the least energetic excitement (2.85 eV, i.e. 436 nm) with an oscillator strength (f) = 0.0137. This estimation has better consistency with the experimental data.

It is intriguing to explore the reactivities of M–M' multiple bonds. Complex 1 is air- and moisture-sensitive and reacts readily with excess H_2O ,¹⁴ affording the oxo complex [{Cp*Ta(O)(CH₂SiMe₃)}(Cp*Ir)(μ -H)₃] (2).¹⁵ The terminal Ta oxo structure was confirmed by NMR, X-ray, and IR analyses.^{16–18} Treatment of 1 with D₂O yielded a mixture of isotopomers [{Cp*Ta(O)(CH₂SiMe₃)}(Cp*Ir)(μ -D)_n(μ -H)_{3-n}] (2- d_n) in a ratio of $d_0/d_1/d_2/d_3 = 6:26:63:4$ (~55% total D incorporation) and Me₃SiCH_{2.7}D_{0.3}. The ratio was independent of both the reaction time and the amount of D₂O employed. It therefore seems reasonable to suggest that the formation of 2 does not proceed simply via σ -bond metathesis on the Ta side alone but involves initial bimetallic oxidative addition of H₂O into the Ta–Ir double bond, followed by reductive elimination of Me₄Si from an intermediate, i.e., [{Cp*Ta(OH)(CH₂SiMe₃)₂}(Cp*Ir)(μ -H)₃].^{15a}

With the above finding in hand, we investigated the oxidative addition of various substrates to complex 1. Thermolysis of 1 in C_6D_6 solvent at 60–80 °C was reluctant to eliminate or exchange the hydrocarbyl ligands but slowly promoted H/D exchange of the methylene and methyl protons of the Me_3SiCH_2 group as well as of Ir-bound hydrides with C_6D_6 (80 °C, 24 h; D incorporations into IrH_2 , $TaCH_2$, and $SiMe_3$ were 25%, 33%, and <4%, respectively). As shown in Scheme 2

Scheme 2. Formation of 1- d_n and 3 through Possible Oxidative Addition Intermediate A



Figure 2. Depictions of the molecular orbitals 130 (HOMO) and 121 (HOMO-9) of DFT-optimized 1 (left) and schematic metal atomic orbital interactions (right).



(top), this observation would imply occurrence of inter- and intramolecular C-H(D) cleavages via oxidative addition followed by α -elimination (A \rightarrow B) and successive deuteride shifts to the alkylidene α -carbon. The related intramolecular exchange between the bridging CH₂ proton and Ir-bound D in $[Cp_2Ta(\mu-CH_2)_2Ir(Cp^*)(D)]$ has been reported.^{11c} In an attempted preparation of $[{Cp*Ta(CH_2SiMe_3)(CHDSiMe_3)}]$ $(Cp*IrD_2)$] (1- d_3) using Li[Cp*IrD_3] (>99% D-enriched), faster intramolecular H/D exchange took place at 25 °C, resulting in lower D incorporation on the Ir and higher D incorporation into Ta methylene moieties than would be expected based on the starting materials. On the other hand, exposure of 1 to 1 atm of H₂ caused elimination of Me₄Si (2 equiv), leading to clean formation of a tetranuclear complex [(Cp*TaH)₂(Cp*IrH)₂] (3) (>99% NMR yield, 62% isolated yield), presumably through intermediates A and C (bottom of Scheme 2).^{19,20}

Activation of the ammonia N–H bond is challenging because the presence of the nitrogen lone pair usually enables facile formation of Lewis acid–base adducts for the majority of transition metal complexes, and the N–H bond has a relatively high bond dissociation energy (108.2 ± 0.3 kcal mol⁻¹).^{21,22} We therefore examined reactions between 1 and primary amines as well as ammonia. These results are summarized in Scheme 3. The reactions with the primary amines were greatly

Scheme 3. NMR-Scale Reaction of 1 with Ammines



accelerated upon addition of H₂ (1 atm) under mild conditions, yielding yellow imido complexes 4a–d, whose structures were identified using NMR and X-ray analyses. As shown in Figure S4 (Supporting Information) (R = C₆H₄-4-Br), the preferred imido structure of 4d, with sp² \rightarrow sp hybridization of a π donating nitrogen, features Ta(V) Lewis acid, even with an electron-deficient substituent (Ta–N (av) = 1.808 Å, Ta–N– C(Ar_{ipso}) (av) = 165.7°).²³ When excess ammonia was reacted with 1 in the presence of H₂, imide 4e and amide 5e were formed. The structure of 5e was identified on the basis of the similarity of the NMR and IR spectral data to those of 1 (see Supporting Information). 4e and 5e are analogous to structures B and C (Scheme 1), respectively.

To demonstrate equilibrium between 4e and 5e, we carried out a spin-saturation transfer (SST) experiment. Although the ratio of [5e]/[4e] did not greatly change in the temperature range 298–353 K ($[5e]/[4e] = 0.97 \pm 0.07$), irradiation of hydride resonance of 4e ($\delta = -13.18$ ppm) at 353 K substantially decreased the hydride integration of 5e (47% decrease at $\delta = -10.85$ ppm). The observed SST process unequivocally indicates hydride-assisted interconversion between Ta–N and Ta–Ir multiple bonds, as described by eq 1. In other words, intramolecular bimetallic oxidative addition and reductive elimination of the N–H bond take place in the Ta–Ir system.

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Bimetallic oxidative additions of alcohols to $[{Ti(NMe_2)_3}]$ - $\{CpRu(CO)_2\}\]$ and $[(Cp_2Zr)(Cp^*Ir)(\mu-N^tBu)]$ have been reported.^{24,25} The entire regioselective scission of the M_{early} - M_{late} direct bond to $M_{early}OR$ (R = ^tBu, aryl) and $M_{late}H$ is apparently the result of the high oxophilicity of group IV metals and basicities of the *d*-electron-rich late metals. The attempted alcoholysis of 1 with MeOH and PrOH (excess) disappointingly brought about disruption of the Ta-Ir bimetallic structure, whereas ^tBuOH reacted with 1 at 25 °C in the presence of H_2 (1 atm), giving rise to a monoalkoxide $[{Cp*Ta(O^tBu)(CH_2SiMe_3)}(Cp*IrH_2)]$ (6) and unreacted ^tBuOH, leaving the Ta–Ir bond intact (Ta–Ir = 2.450(1) Å). Unlike the reaction of 1 with amines and the bulky alcohol, reaction with 2 equiv of a phenol does not necessarily require H₂, leading to selective formation of $[{Cp*Ta(OR)_2}]$ - $(Cp*IrH_2)$ (7) (Scheme 4). The Ta-Ir distance in the solid-state structure of 7b still shows the presence of a direct Ta–Ir bond (Ta–Ir (av) = 2.456 Å).

Scheme 4. NMR-Scale Reaction of 1 with Phenols



The mechanism of hydrocarbyl/aryloxy ligand exchange was preliminarily studied by a labeling experiment using **1** and 4-^tBuC₆H₄OD (~2 equiv), resulting in 55% D incorporation into the Ir hydride moiety of 7a- d_n (91% conversion of **1**, 86% yield of 7a- d_n : $d_0/d_1/d_2 = 24:42:34$). This observation rules out a mechanism via σ -bond metathesis on the Ta center only, but reasonably supports occurrence of oxidative addition/reductive elimination sequences.²⁶ More importantly, oxidative addition of a third equivalent of a phenol to the Ta–Ir bond in 7 proceeded to afford triaryloxides [{Cp*Ta(OR)₃}(Cp*Ir)(μ -H)₃] (8). Furthermore, treatment of **8a** with Me₃SiCH₂Li or KN(TMS)₂ as a base smoothly regenerated 7**a** in 70% and 85% yields, respectively. Therefore, thanks to the multiple interactions, the Ta–Ir species appeared to be stable during the course of the oxidative addition and reductive eliminations of phenols.

In summary, we have demonstrated that the new hydride 1 with a direct multiple bond between Ta and Ir can be formed via the salt elimination route. In oxidative addition reactions, the bonding nature of the Ta–Ir system was found to alter, depending, in principle, on the facility of the early metal–ligand multiple bonds, i.e., H_2O and primary amines prefer oxo and imide trihydride structures with no direct metal–metal covalent bond [formal shortness ratio (FSR) = 1.022 (2) and 1.025–1.033 (4)], whereas two hydrocarbyl or alkoxy ligands on the Ta preserve multiple bonds between disparate d elements (1, 6,

and 7). Furthermore, the present Ta–Ir system gave reversible reactions of 7 and phenols without extensive decomposition of the bimetallic complex. Applications of these fundamental but unique M-M'–ligand conjugations and bimetallic oxidative additions of protic substrates are currently under investigation.

ASSOCIATED CONTENT

Supporting Information

Experimental and computational details of new complexes as well as X-ray crystallographic files (CIF) for $[Cp*Ta(Cl)-(CH_2SiMe_3)(=CHSiMe_3)]$, 1–3, 4a, 4c, 4d, 6, and 7b. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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