Communication

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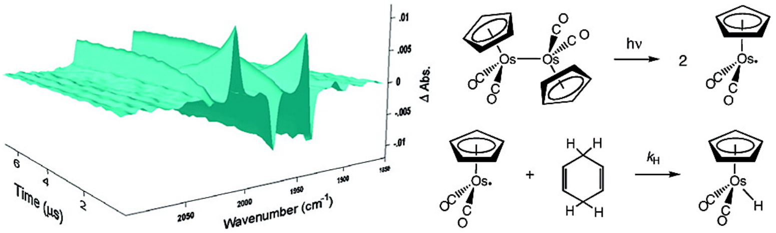

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# Carbon-to-Metal Hydrogen Atom Transfer: Direct Observation Using Time-Resolved Infrared Spectroscopy

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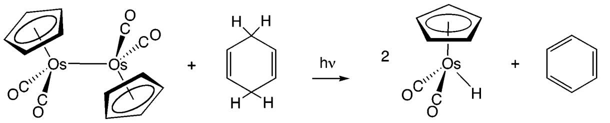
Reactions that cleave C−H bonds are a requisite step in the conversion of hydrocarbons to higher-value chemicals or fuels.[1] The most commonly encountered metal-mediated pathways are oxidative addition of a C−H bond to a low-valent metal complex and $\sigma$-bond metathesis reactions. An alternative mechanism involves breaking C−H bonds with metal radicals. Wayland and co-workers have reported remarkable results in which C−H bonds can be cleaved by rhodium complexes that have bulky porphyrin ligands.[2] Since two rhodium radicals react with the hydrocarbon, the rates are hampered by the entropic constraints of properly assembling a termolecular transition state.

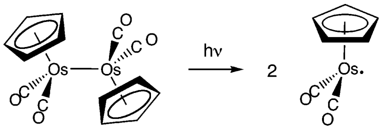
Hydrogen atom transfers are fundamentally important in many chemical and biological processes.[3] Metal-to-carbon hydrogen atom transfer[4] occurs in certain types of hydrogenations,[5] hydroformylations,[6] and radical polymerizations of C═C bonds.[7] Such reactions often involve reversible equilibria,[5,8] but the reverse reaction (carbon-to-metal hydrogen atom transfer) has, to our knowledge, never been directly observed. We report here the direct spectroscopic observation of hydrogen atom transfer reactions from carbon to metals, in which homolytic cleavage of a C−H bond is accomplished at a single metal center.

Laser flash photolysis (355 nm) of a hexane solution of $[Cp(CO)_2Os]_2$ leads to an instantaneous bleaching of the $\nu$(CO) IR bands of the dimer and appearance of two new $\nu$(CO) bands at 2003 and 1938 $cm^{-1}$, as observed by nanosecond time-resolved infrared (TRIR) spectroscopy using a step-scan FTIR spectrometer. The new bands are assigned to the osmium-centered radical $Cp(CO)_2Os^{\bullet}$; DFT (B3LYP)[9] computations predict $\nu$(CO) IR bands at 2008 and 1955 $cm^{-1}$, thus supporting the assignment of the transient species as $Cp(CO)_2Os^{\bullet}$. In contrast to nearly all other known metal carbonyl radicals,[10] this metal-centered radical does not cleanly dimerize back to the metal−metal bonded complex, but instead undergoes other reactions that appear to involve a C−H bond of the Cp ring.[11]

When continuous photolysis ($\lambda > 300$ nm) of $[Cp(CO)_2Os]_2$ is carried out in $C_6D_6$ or THF-$d_8$ in the presence of excess 1,4-cyclohexadiene, the osmium hydride $Cp(CO)_2OsH$ forms in 83−88% yield, together with benzene (eq 1). Photochemical homolysis of the Os−Os bond provides $Cp(CO)_2Os^{\bullet}$ (eq 2), an osmium-centered radical that abstracts a hydrogen atom from cyclohexadiene, giving $Cp(CO)_2OsH$ and the cyclohexadienyl radical (eq 3). The second equivalent of $Cp(CO)_2OsH$ could be formed by hydrogen atom transfer from another 1,4-cyclohexadiene or from the cyclohexadienyl radical, which would produce benzene. Disproportionation of cyclohexadienyl radicals is known to give benzene and 1,4-cyclohexadiene.[12]



(1)



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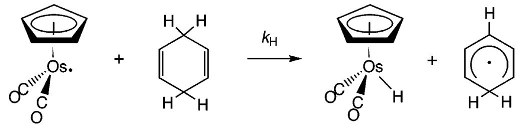

(3)

TRIR monitoring (Figure 1) at 23 °C following flash photolysis (355 nm) of a hexane solution containing 0.50 mM $[Cp(CO)_2Os]_2$ and excess 1,4-cyclohexadiene (250 mM) reveals a first-order decay of the $\nu$(CO) bands due to $Cp(CO)_2Os^{\bullet}$, together with the simultaneous formation of two new bands at 2021 and 1960 $cm^{-1}$, assigned to $Cp(CO)_2OsH$, which grows at a rate identical to the rate of decay of the osmium radical. A plot of pseudo-first-order rate constants for the osmium radical decay as a function of [1,4-cyclohexadiene] gives a straight line (see Supporting Information), the slope of which provides the second-order rate constant, $k_H = (2.1 \pm 0.2) \times 10^6\ M^{-1}\ s^{-1}$, for carbon-to-metal hydrogen atom transfer (eq 3). Similar experiments using the partially deuterated 1,4-cyclohexadiene-1,2,3,4,5,6-$d_6$ gave $k_{HD} = (1.1 \pm 0.2) \times 10^6\ M^{-1}\ s^{-1}$. These experiments are consistent with a large isotope effect for hydrogen atom transfer. However, the experimental uncertainties are too high to allow an accurate estimate of the isotope effect (see Supporting Information).

Carbon-to-metal hydrogen atom transfers are often thermodynamically unfavorable since C−H bonds are generally much stronger than M−H bonds. The C−H bond of 1,4-cyclohexadiene is weak, being reported as 73 kcal/mol[13] but later revised to 77 kcal/mol.[14] The facility of this hydrogen atom abstraction suggests that it does not have a large thermochemical or kinetic barrier. We sought to determine the Os−H bond dissociation energy (BDE) to assess the thermodynamics of the hydrogen atom transfer. The p$K_a$ of $Cp(CO)_2OsH$ was determined as 32.7 by equilibration in $CD_3CN$

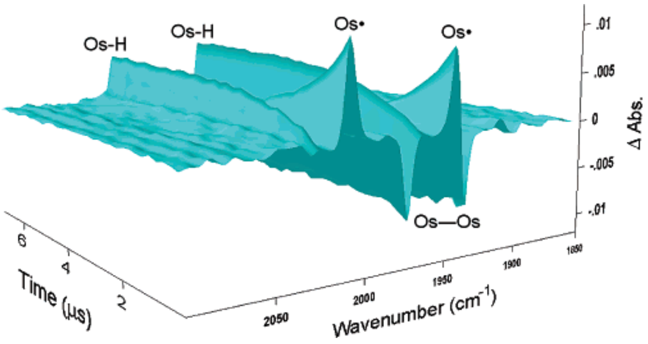

***Figure 1.*** Time-resolved infrared spectra obtained following 355-nm laser flash photolysis of $[Cp(CO)_2Os]_2$ (0.50 mM) and 1,4-cyclohexadiene (0.25 M) in hexane.

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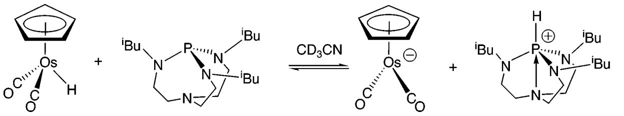
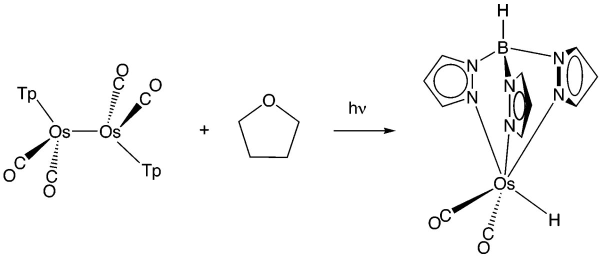
with the tri-isobutyl version of Verkade's superbase[15] (eq 4; the p$K_a$ of the protonated form of this superbase is 33.53).[16]



This Os hydride is more than 12 p$K_a$ units less acidic than its first and second row congeners Cp(CO)$_2$FeH (p$K_a$ = 19.4 in $CH_3CN$) or Cp(CO)$_2$RuH (p$K_a$ = 20.2 in $CH_3CN$).[17] Electrochemical oxidation of $[Cp(CO)_2Os]^-Li^+(DME)$ in $CH_3CN$ (0.1 M $Bu_4N^+PF_6^-$) using cyclic voltammetry gave an irreversible wave at $E_{ox}° > -0.945$ V (versus Fc/Fc$^+$; see Supporting Information). Application of a well-known thermochemical cycle[18] to these data provides an estimated lower limit of the Os−H BDE as 82 kcal/mol. The Os−H bond is exceptionally strong, greatly exceeding those of Cp(CO)$_2$FeH (BDE = 58 kcal/mol) and Cp(CO)$_2$RuH (BDE = 65 kcal/mol) and being substantially higher than those reported for other third-row metal carbonyl hydrides such as (CO)$_5$ReH (BDE = 75 kcal/mol) or Cp(CO)$_3$WH (BDE = 72 kcal/mol).[18] Our DFT computations provide a BDE of 80 kcal/mol for Cp(CO)$_2$OsH and 69 kcal/mol for Cp(CO)$_2$RuH. The Os−H bond appears to be the strongest M−H yet determined for a metal carbonyl complex and is among the strongest of any transition metal hydride bond (cf. 81.0 kcal/mol average Hf−H BDE for Cp*$_2$HfH$_2$[19]).

Continuous photolysis of [Cp*(CO)$_2$Os]$_2$ in the presence of 1,4-cyclohexadiene also proceeds cleanly to give Cp*(CO)$_2$OsH and benzene. [Cp*(CO)$_2$Os]$_2$ is surprisingly much less soluble than [Cp(CO)$_2$Os]$_2$ and has insufficient solubility in hexane to allow TRIR kinetics to be measured. Other potentially suitable solvents that dissolve this dimer absorb too strongly in the appropriate region of the IR spectrum. We are attempting to prepare more soluble derivatives with longer chain alkyl groups on the Cp ring to improve the solubility.

Photolysis of an osmium dimer with tris(pyrazolyl)borate ligands, [Tp(CO)$_2$Os]$_2$, results in carbon-to-metal hydrogen atom transfers from even stronger C−H bonds (eq 5). Photolysis ($\lambda > 300$ nm) in THF results in carbon-to-osmium hydrogen atom transfer, and this reaction can be used synthetically as a route to Tp(CO)$_2$OsH (68% isolated yield). The osmium deuteride, Tp(CO)$_2$OsD, results from photolysis of [Tp(CO)$_2$Os]$_2$ in toluene-$d_8$. The C−H BDEs of THF (92 kcal/mol)[14] and toluene (90 kcal/mol)[20] show that this method can be used to cleave C−H bonds that are much stronger than those of 1,4-cyclohexadiene.



Along with seeking to determine how strong of a C−H bond can be ruptured by this method, we wondered if formation of a very strong Os−H bond is actually required. Photolysis of the ruthenium dimer [Cp*(CO)$_2$Ru]$_2$ in THF-$d_8$ in the presence of 1,4-cyclohexadiene produced Cp*(CO)$_2$RuH and benzene, indicating that a carbon-to-metal hydrogen atom transfer does not require the formation of an unusually strong M−H bond. The reactions of [Cp*(CO)$_2$Ru]$_2$ and [Tp(CO)$_2$Os]$_2$ all involve carbon-to-metal hydrogen atom transfers that are thermodynamically unfavorable. We have not yet studied the kinetics of these reactions, and we cannot rule out the possibility that more complex mechanisms are involved compared to the [Cp(CO)$_2$Os]$_2$ reaction (eqs 1−3).

We have shown that carbon-to-metal hydrogen atom transfers to photochemically generated metal radicals can be directly observed and that C−H bonds as strong as 92 kcal/mol can be cleaved in this manner. Future research will seek to determine further mechanistic details and to measure the rate constants and isotope effects for a range of metal complexes and organic substrates.

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**Supporting Information Available:** Experimental procedures, characterization of new complexes, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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