

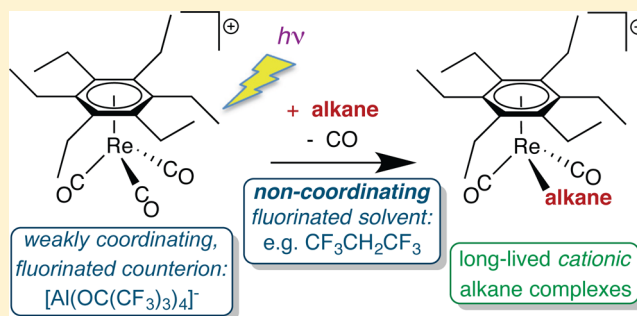
Observation of Cationic Transition Metal–Alkane Complexes with Moderate Stability in Hydrofluorocarbon Solution

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S Supporting Information

ABSTRACT: In seeking to create more-stable transition metal–alkane complexes, we generated cationic alkane complexes of the type $[(\text{HEB})\text{Re}(\text{CO})_2(\text{alkane})][\text{Al}(\text{OR}^f)_4]^+$ (HEB = η^6 -hexaethylbenzene; alkane = cyclopentane (**16**) or pentane (**17–19**); OR^f = perfluoro-*tert*-butoxy) via photolysis of the precursor complex $[(\text{HEB})\text{Re}(\text{CO})_3][\text{Al}(\text{OR}^f)_4]$ (**15**) in the presence of the added alkane. The alkane complexes were generated in a hydrofluorocarbon (HFC) solvent, most often $\text{CF}_3\text{CH}_2\text{CF}_3$, which is capable of simultaneously dissolving the ionic complex **15** and a small amount of alkane at low temperature (183 K). Use of the HFC solvent in tandem with the highly fluorinated, solubilizing, weakly coordinating $[\text{Al}(\text{OR}^f)_4]^-$ anion overcomes the technical difficulty of combining ionic species with alkanes in solution without the solvent molecules rapidly displacing the bound alkane ligand, as the alkanes bind in preference to the HFCs to the organometallic fragments employed in this study. The $[(\text{HEB})\text{Re}(\text{CO})_2(\text{alkane})]^+$ complexes are more long-lived than the corresponding neutral alkane complexes $[(\text{HEB})\text{W}(\text{CO})_2(\text{alkane})]$ and $[\text{CpRe}(\text{CO})_2(\text{alkane})]$ (Cp = η^5 -cyclopentadienyl), with samples of $[\text{CpRe}(\text{CO})_2(\text{cyclopentane})]$ decaying significantly more rapidly than $[(\text{HEB})\text{Re}(\text{CO})_2(\text{alkane})]^+$ when present in the same solution. Intramolecular exchange of the methylene group bound to the metal within the cyclopentane ligand in **16** was observed at 212 K, with the 1,2 shifts appearing to be faster than 1,3 shifts.



INTRODUCTION

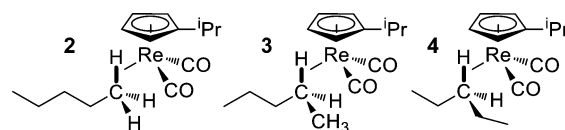
The basis of the petrochemical industry is the large-scale conversion of petroleum into useful chemical products, ranging from low-complexity fuel products to compounds that can be used in the manufacture of sophisticated materials and pharmaceuticals. Alkanes are a major component (typically 30%) of petroleum and natural gas reserves but are notoriously difficult to modify, because they are solely composed of strong, unreactive C–H and C–C bonds. Functionalization of alkanes to create more-valuable compounds, catalyzed by transition metal complexes in homogeneous processes, has therefore been an intense area of research over the past 30 years.^{1–12}

It is widely accepted that key intermediates in C–H activation processes, which can proceed via a manifold of mechanistic pathways,^{1,13,14} are σ -alkane complexes that contain an essentially intact alkane weakly bound to a metal center.^{15–18} An in-depth understanding of the coordination in σ -alkane complexes should aid in the design of next-generation catalysts for alkane functionalizations.

σ -Alkane complexes are also of great interest in terms of fundamental coordination chemistry. Devoid of lone pairs, alkanes interact with a metal center via the electron pair associated with a C–H σ bond, and this interaction is the genesis of the term σ -alkane complex. The C–H–metal interaction, frequently referred to as an agostic interaction,¹⁹

is weak, even when compared to interactions of related σ complexes, e.g., where H–H or Si–H moieties are coordinated to the metal center, resulting in low stability of σ -alkane complexes.^{20,21} Currently known σ -alkane complexes are all unstable in solution; therefore, new alkane complexes are targets for observation, mechanistic study, and isolation.

Previous work by our group in this area involved the NMR-spectroscopic observation of rhenium–alkane complexes, including the cyclopentane complex $[\text{CpRe}(\text{CO})_2(\text{c-C}_5\text{H}_{10})]$ ²² (**1**) and three isomeric rhenium–pentane complexes $[\text{iPrCpRe}(\text{CO})_2(n\text{-C}_5\text{H}_{12})]$ (**2–4**) (Cp = η^5 -cyclopentadienyl).²³



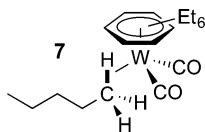
n-Pentane shows a slight preference for binding via the CH_2 over the CH_3 group in $[\text{iPrCpRe}(\text{CO})_2(n\text{-pentane})]$. There is little preference for binding CH_2 vs CH_3 groups in the complexes $[\text{CpMn}(\text{CO})_2(\text{butane})]$ (**5**) and $[\text{CpMn}(\text{CO})_2$

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(propane)] (6). 5 and 6 are significant as they are alkane complexes of a first-row transition metal.^{24,25} Alkane serves as both solvent and ligand in all these studies.

More recently, we reported the NMR spectroscopic observation of a group 6 σ -alkane complex [(HEB)W(CO)₂-(pentane)] (7) (HEB = η^6 -hexaethylbenzene).²⁶ Binding of

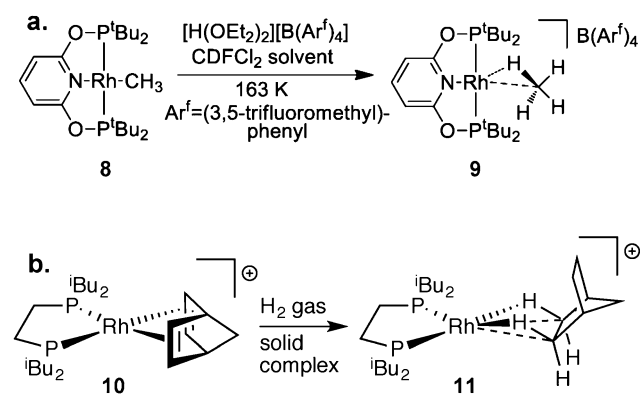


pentane to the tungsten fragment shows the *opposite* binding preference to the rhenium case; i.e., only binding of the CH₃ group was detected. This illustrates the potential for the metal–ligand combination to be tailored to manipulate the site of binding within the alkane, which may ultimately promote regioselective alkane functionalization in the future.

Furthering the comparison of alkane versus dihydrogen complexes,^{27,28} it is noteworthy that, while the first dihydrogen complexes observed were neutral complexes, reviews indicate that many cationic dihydrogen complexes are now known,^{29,30} outnumbering neutral variants. Therefore, it is possible that cationic alkane complexes may ultimately prove to be more accessible than neutral alkane complexes, *but only if* suitable conditions for their generation can be accessed.

In terms of observation of cationic alkane complexes, the two studies shown in Scheme 1 stand out. Scheme 1a shows the

Scheme 1. Generation of Cationic Alkane Complexes



breakthrough observation of a σ -complex of methane, [(PONOP)Rh(CH₄)]⁺ (9), PONOP = 2,6-(^tBu₂PO)₂C₅H₃N, using NMR spectroscopy.³¹ 9 is generated in solution via protonation of the metal–alkyl precursor [(PONOP)Rh(CH₃)] (8). The corresponding ethane complex, [(PONOP)Rh(CH₃CH₃)]⁺ (12), has likewise been prepared and characterized at 130 K.³² Both studies make use of the weakly coordinating [BAr^F₄][−] anion to reduce the chance of the counterion displacing the bound alkane.

Two points of significance to the study presented here arise from this work. First, a cationic metal center was employed to stabilize the metal–alkane interaction. Second, the rhodium(I)–methane complex decayed with a half-life of ~83 min at a temperature of only 186 K. The decay was proposed to be due to substitution of methane by the CDCl₂F solvent to form [(PONOP)Rh(CDCl₂F)]⁺ (13), despite CDCl₂F being considered a relatively poor ligand for transition metal species. The ethane complex is even less stable than the methane complex,

with the decreased stability attributed to steric interactions of the larger ethane ligand and the sterically demanding −CMe₃ groups of the PONOP ligand. Again, the final product is proposed to be the solvent complex 13. Hence, identifying solvents that can dissolve cationic alkane complexes but do not lead to the displacement of weakly bound alkane ligands is key to the development of the chemistry of cationic alkane complexes.

Scheme 1b shows the second notable observation of a cationic alkane complex, which was the crystallographic characterization of [Rh(^tBu₂PCH₂CH₂P^tBu₂)(η^2,η^2 -C₇H₁₂)]-[BAr^F₄][−] (11),³³ which shows a bidentate interaction of norbornane with a rhodium center. This complex is prepared via hydrogenation of the precursor norbornadiene complex, [Rh(^tBu₂PCH₂CH₂P^tBu₂)(η^2,η^2 -C₇H₈)] [BAr^F₄][−] (10), *in the solid state*. This demonstrates a radically different solution to the problem of reactions of alkane complexes with solvent by circumventing the use of solvent altogether.

The ability to generate alkane complexes in the solid state does not diminish the need to develop the chemistry of alkane complexes in the solution state, as the latter is the more convenient phase for reactivity studies. The norbornane ligand in the rhodium complex is readily displaced by a solvent molecule when dissolved in CDCl₂F, even at temperatures as low as 133 K, precluding its characterization using NMR experiments in this solvent. Hence, the synthesis of an alkane complex that is stable at or near room temperature in solution is a key goal that still remains unfulfilled.

Theory also supports the concept that cationic alkane complexes are potentially more stable. A DFT study found that the calculated binding energy for methane is ~55% larger in the case of binding to cationic [CpRe(CO)(NO)⁺] compared to binding to isoelectronic, neutral [CpRe(CO)₂].³⁴ This is logical, given that the binding interaction in compounds of this class is primarily one of charge transfer, mostly from the alkane to the metal.^{35,36} Other calculations have revealed that the electron-deficient nature of the cationic [RhP₂]⁺ fragment is an important factor in stabilizing the alkane binding in the rhodium–norbornane complexes,³⁷ and that methane should be bound more strongly in [(PONOP)Pd(CH₄)]²⁺ (14) compared to [(PONOP)Rh(CH₄)]⁺ (9).³⁸

In view of all of the above, while it appears logical to attempt the synthesis of cationic alkane complexes, an empirical roadblock is that displacement of bound alkanes from the metal center by either the solvent or the counterion is facile. Essentially all common solvents that are used to dissolve pairs of ions contain atoms such as O, N, and Cl, which all contain lone pairs capable of binding to metal centers more strongly than alkanes and can displace them from a coordination sphere. For example, attempts to prepare [(PONOP)Pd(CH₄)]²⁺ (14) in (CF₃SO₂)₂O at 193 K were unsuccessful, as a solvent-coordinated species was formed before the methane complex could be observed.³⁹

While fluorine atoms also contain lone pairs, the unique properties of the fluorine atom make it an extremely reluctant donor atom when it is found in highly fluorinated species. For example, cyclopentane bonds to the neutral, 16-electron species W(CO)₅ with a binding energy of 43 ± 13 kJ mol^{−1},⁴⁰ slightly lower than that of CH₃F (47 ± 13 kJ mol^{−1}), which likely binds via a lone pair on the fluorine.⁴¹ However, increasing the number of geminal fluorines from CH₃F through to CF₄ progressively lowers the electron density on each fluorine atom and significantly reduces its propensity to act as a donor

atom, evident from experimental binding energies of <21 kJ mol⁻¹ for CHF₃ and CH₃CF₃ with W(CO)₅.⁴⁰

RESULTS AND DISCUSSION

In this work we have employed highly fluorinated hydrofluorocarbon (HFC) solvents, most frequently 1,1,1,3,3,3-hexafluoropropane, CF₃CH₂CF₃. This HFC was calculated to bind less favorably than alkanes to specified transition-metal centers (Table 1). Through calculations of binding energies using two

Table 1. Calculated Binding Energies (kJ mol⁻¹) of Cyclopentane, CHFCl₂, and CF₃CH₂CF₃ Ligands Bound to Assorted Metal Fragments

fragment	ligand	binding energy (kJ mol ⁻¹)	
		B3PW91-D3BJ	ωB97X-D
$[(\eta^6\text{-C}_6\text{H}_6)\text{Re}(\text{CO})_2]^+$	cyclopentane	120	109
$[(\eta^6\text{-C}_6\text{H}_6)\text{Re}(\text{CO})_2]^+$	CHFCl ₂ ^a	138	119
$[(\eta^6\text{-C}_6\text{H}_6)\text{Re}(\text{CO})_2]^+$	CF ₃ CH ₂ CF ₃ ^b	65	68
$[(\eta^6\text{-C}_6\text{H}_6)\text{Re}(\text{CO})_2]^+$	CF ₃ CH ₂ CF ₃ ^c	39	37
[CpRe(CO) ₂]	cyclopentane	87	80
$[(\eta^6\text{-C}_6\text{H}_6)\text{W}(\text{CO})_2]$	cyclopentane	75	66
$[(\text{HEB})\text{Re}(\text{CO})_2]^+$	cyclopentane	109	103
$[(\text{HEB})\text{W}(\text{CO})_2]$	cyclopentane	80	74

^aBound to metal via Cl group. ^bBound to metal via CF₃ group. ^cBound to metal via CH₂ group. Binding energies calculated with the B3PW91-D3BJ/def2-TZVP and ωB97X-D/def2-TZVP methods using geometries and ZPVE corrections calculated at the B3PW91/6-31G(d,p);SDD+f (rhenium, tungsten) level of theory. See Supporting Information for details.

dispersion-corrected DFT methods that have been found to perform well in previous benchmark studies,³⁸ Table 1 illustrates two main points.

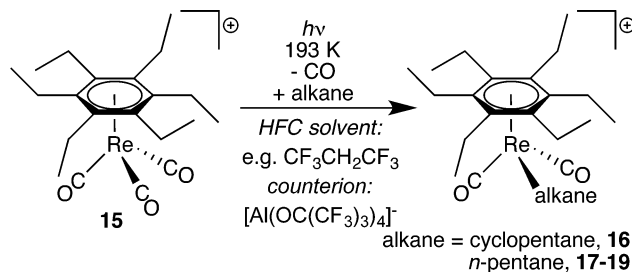
First, cyclopentane is calculated to have a significantly higher binding energy when bound to $[(\eta^6\text{-C}_6\text{H}_6)\text{Re}(\text{CO})_2]^+$ than does CF₃CH₂CF₃, irrespective of whether the CF₃CH₂CF₃ binds via hydrogen or fluorine atoms. In contrast, CHFCl₂, the solvent frequently employed in the recent literature examples described above, is predicted to bind more strongly than cyclopentane in this case.

Second, the predicted binding energies of alkanes to specified model cationic fragments is higher than binding to related, isoelectronic neutral fragments that are known to form alkane complexes, specifically [CpRe(CO)₂] and [(HEB)W(CO)₂] (HEB = η⁶-hexaethylbenzene). This applies whether the charge is introduced by changing the half-sandwich ligand (C₃H₅⁻ vs C₆H₆ in [CpRe(CO)₂] vs $[(\eta^6\text{-C}_6\text{H}_6)\text{Re}(\text{CO})_2]^+$) or by changing the metal (W⁰ vs Re⁺ in $[(\eta^6\text{-C}_6\text{H}_6)\text{W}(\text{CO})_2]$ vs $[(\eta^6\text{-C}_6\text{H}_6)\text{Re}(\text{CO})_2]^+$).

In tandem, the extremely weakly coordinating anion [Al(OR^f)₄]⁻ (OR^f = perfluoro-*tert*-butoxy), introduced by Krossing and co-workers,⁴² was employed as a counterion. It was envisaged that, since the surface of this counterion resembles a perfluorocarbon and contains a single negative charge distributed equally between 36 fluorine atoms, all in CF₃ groups, it too may have an extremely low predisposition toward binding in the vacant sites of the coordinatively unsaturated fragments designed to bind alkanes. This anion has been employed previously in numerous situations that involve stabilization of complexes that contain very weakly bound ligands.⁴³

Taking all of the above into consideration, we therefore sought to generate complexes of the type $[(\text{HEB})\text{Re}(\text{CO})_2(\text{alkane})]^+$ using a photochemical approach, starting from $[(\text{HEB})\text{Re}(\text{CO})_3]^+$, using a HFC solvent and employing the $[\text{Al}(\text{OR}^f)_4]^-$ counterion (Scheme 2). The precursor $[(\text{HEB})\text{Re}(\text{CO})_3][\text{Al}(\text{OR}^f)_4]$ (15) was prepared from the known complex $[(\text{HEB})\text{Re}(\text{CO})_3][\text{PF}_6]$ described by Sweigart,⁴⁴ via an anion exchange reaction with Li[Al(OR^f)₄] in Et₂O to afford the desired rhenium(I) complex 15.

Scheme 2. Route to $[(\text{HEB})\text{Re}(\text{CO})_2(\text{alkane})]^+$ Complexes



The structure of 15 was confirmed using X-ray crystallography. Slow evaporation of a dichloromethane solution of 15 afforded crystalline 15 as colorless plates. The solid-state structure of the cation (Figure 1) largely resembles that of the corresponding complex with the $[\text{PF}_6]^-$ anion, $[(\text{HEB})\text{Re}(\text{CO})_3][\text{PF}_6]$.⁴⁴

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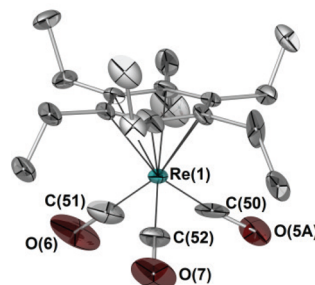


Figure 1. Solid-state structure of the $[(\text{HEB})\text{Re}(\text{CO})_3]^+$ ion of 15 (50% thermal ellipsoids). Hydrogen atoms and the $[\text{Al}(\text{OR}^f)_4]^-$ ion are omitted for clarity, as are lower-occupancy disordered atoms. Selected bond length [Å] and angles [°]: Re(1)–C(50) 1.935(12), Re(1)–C(51) 1.926(11), Re(1)–C(52) 1.897(10), C(50)–O(5A) 1.20(6), C(51)–O(6) 1.127(13), C(52)–O(7) 1.147(13), C(50)–Re(1)–C(51) 88.0(7), C(51)–Re(1)–C(52) 85.4(4), C(50)–Re(1)–C(52) 89.5(6). The average M–C(arene) bond length is 2.34(2) Å.

Observation of the Cyclopentane Complex, $[(\text{HEB})\text{Re}(\text{CO})_2(\text{c-C}_5\text{H}_{10})]^+$ (16). $[(\text{HEB})\text{Re}(\text{CO})_3][\text{Al}(\text{OR}^f)_4]$ (15) was found to be sufficiently soluble (at least 2 mg in ~0.7 mL) in CF₃CH₂CF₃ to perform NMR experiments at temperatures of 183 K. Unlike corresponding alkanes or perfluorocarbons, CF₃CH₂CF₃ is moderately polar (dipole moment 1.98 D,⁴⁵ cf. dichloromethane, 1.14 D), which assists in dissolving ionic compounds. CF₃CH₂CF₃ is a gas at room temperature (bp ≈ 272 K; mp ≈ 180 K), so precautions must be taken to mitigate the risk of explosion at room temperature. A small amount of alkane solvent was found to be soluble in CF₃CH₂CF₃ at 193 K, e.g., 2% v/v cyclopentane in CF₃CH₂CF₃. The NMR spectra of higher concentrations of cyclopentane (10% v/v) in CF₃CH₂CF₃ at 193 K show the presence of two resonances

for the cyclopentane moiety (see Supporting Information). We ascribe the two separate signals to the presence of two phases in the mixture at low temperature; i.e., some cyclopentane is dissolved in the HFC solvent phase, and after the HFC is saturated with alkane, a separate alkane phase forms as droplets. The signal from the separate alkane phase slowly decreases in intensity, presumably as the alkane droplets, which have a different density than the HFC phase, slowly separate out and move to the top of the NMR sample, away from the central, detected region of the sample.

A mixture of $[(\text{HEB})\text{Re}(\text{CO})_3][\text{Al}(\text{OR}^f)_4]$ (**15**) (2 mg) and cyclopentane (15 μL) was dissolved in $\text{CF}_3\text{CH}_2\text{CF}_3$ (~ 0.7 mL). The result of photolyzing this mixture at 193 K using light from a mercury arc lamp, administered via an optical fiber, to the NMR tube²² is shown in Figure 2. ^1H NMR spectra monitoring the photolysis were recorded unlocked. The intense signal due to $\text{CF}_3\text{CH}_2\text{CF}_3$ was suppressed using the method of excitation sculpting.⁴⁶

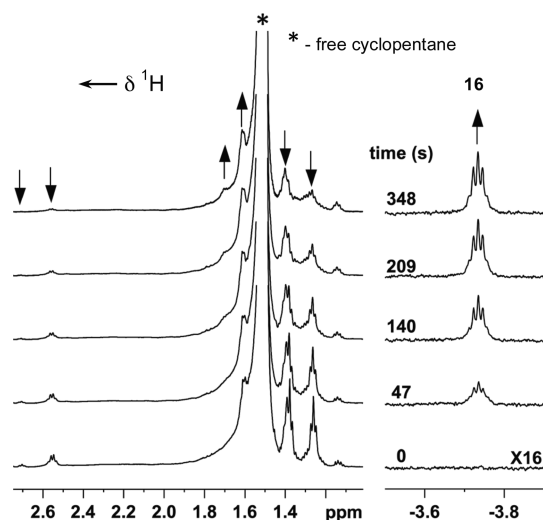


Figure 2. 600 MHz ^1H NMR spectra monitoring the photolysis of $[(\text{HEB})\text{Re}(\text{CO})_3][\text{Al}(\text{OR}^f)_4]$ (**15**) and excess cyclopentane in $\text{CF}_3\text{CH}_2\text{CF}_3$ at 193 K. Decreasing signals (\downarrow) are due to the HEB ligand of the starting complex. Increasing signals (\uparrow) are due to the cyclopentane ligand of the product $[(\text{HEB})\text{Re}(\text{CO})_2(\text{C}-\text{C}_5\text{H}_{10})]^+$ (**16**). Signals close to the $\text{CF}_3\text{CH}_2\text{CF}_3$ solvent resonance (δ 2.91) are reduced in intensity due to the suppression method employed. The right-hand region (δ -3.5 to -3.9) is expanded vertically by a factor of 16.

At 193 K, two different ethyl groups (CH_2 δ 2.71 and 2.56; CH_3 δ 1.38 and 1.26) are observed in the ^1H NMR spectra of the precursor complex **15** due to slowed rotation around the C–C bond between the aromatic and CH_2 carbons and the adoption of the conformation with alternating distal and proximal methyl groups of the HEB ligand seen in the crystal structure (Figure 1). Upon UV irradiation, the signals due to the two types of ethyl groups in **15** decrease in intensity. At the same time, new signals grow into other regions of the spectrum, most significantly an apparent quintet at δ -3.74 . The quintet splitting pattern, $J_{\text{HH}} = 6.7$ Hz, is consistent with the presence of four vicinal hydrogens creating the splitting, suggesting the presence of a cyclopentane complex product, $[(\text{HEB})\text{Re}(\text{CO})_2(\text{C}-\text{C}_5\text{H}_{10})]^+$ (**16**). Resonances in the ^1H NMR spectra that can be ascribed to the HEB ligand of **16** are difficult to see in Figure 2. Not only are the intensities of the resonances

apparently reduced due to the lower symmetry of the product (six types of methylene proton and four types of methyl proton are expected in complex **16**, assuming the alkane ligand is free to rotate) but also the signals appear to be broad, likely due to fluxional processes involving the HEB ligand, overlapped, and, in the case of some of the CH_2 resonances, significantly suppressed.

The product **16** was found to be moderately stable at 193 K, losing only $\sim 22\%$ of its concentration in a 13 h period in one sample, during which several 2D NMR experiments were acquired (see below). Signals due to **16** were visible in ^1H NMR spectra recorded at temperatures of up to 226 K over a period of several minutes prior to complete decomposition upon warming to 236 K.

New peaks in the ^1H NMR spectra ascribable to decomposition products were not observed, and the fate of the alkane complex **16** could not be determined. An increase in the amount of starting material **15** upon decomposition of alkane complex **16** was not observed, indicating that the major route of decomposition is not simply a recombination of the alkane complex **16** with CO that was photochemically liberated earlier.

The presence of a cyclopentane complex was confirmed from a natural-abundance ^1H – ^{13}C HSQC experiment (Figure 3),

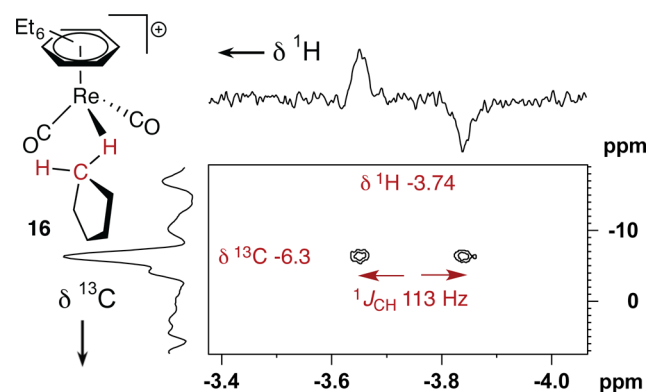


Figure 3. Expansion of the 600 MHz ^1H – ^{13}C HSQC spectrum of the shielded resonance due to $[(\text{HEB})\text{Re}(\text{CO})_2(\text{C}-\text{C}_5\text{H}_{10})]^+$ (**16**) at 193 K, produced via photolysis of a solution of $[(\text{HEB})\text{Re}(\text{CO})_3][\text{Al}(\text{OR}^f)_4]$ (**15**) and excess $\text{C}-\text{C}_5\text{H}_{10}$ in $\text{CF}_3\text{CH}_2\text{CF}_3$ solvent. The spectrum was recorded with retention of coupling to the ^{13}C nucleus in f_2 . The spectrum is annotated in f_1 and f_2 with slices extracted through the cross peaks in the spectrum.

and coupling to the ^{13}C nucleus on the cyclopentane fragment was retained in f_2 .²³ This experiment reveals that the proton(s) at δ -3.74 are attached to a carbon at δ ^{13}C -6.3 with $^1J_{\text{CH}} = 112.7 \pm 2.5$ Hz. This value of $^1J_{\text{CH}}$ is slightly reduced from that in free cyclopentane (128 Hz), diagnostic for an alkane complex.

Other resonances due to the protons in the cyclopentane ligand that are not directly interacting with the rhenium center are visible at δ 1.70 (apparent quintet) and 1.61 (multiplet, overlapped) as shoulders next to the intense signal of free cyclopentane. 2D TOCSY experiments (10–60 ms mixing times, 60 ms shown in Figure 4) confirm the assignment of these resonances to the cyclopentane ligand.

The fact that only one shielded ^1H NMR resonance and only two other resonances were located for the cyclopentane ring is consistent with a rapid exchange between the two hydrogens in the bound CH_2 unit that is directly interacting with the metal

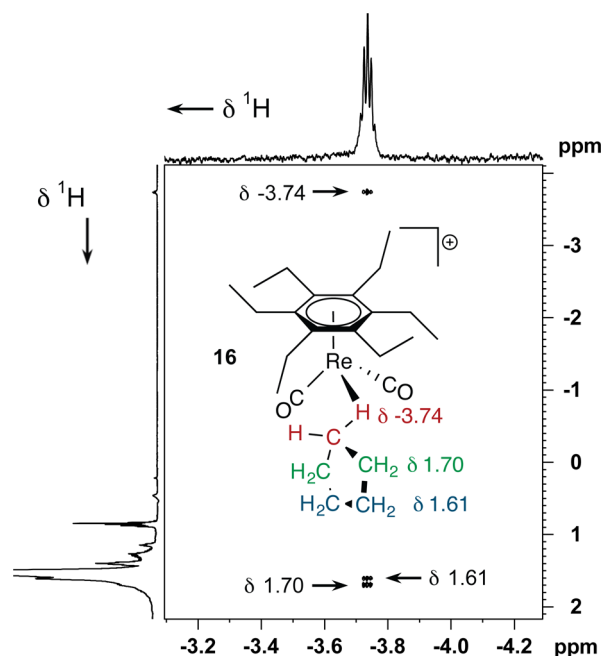


Figure 4. Expansion of the 600 MHz ^1H 2D TOCSY spectrum (60 ms mixing time) of $[(\text{HEB})\text{Re}(\text{CO})_2(\text{c}\text{-C}_5\text{H}_{10})]^+$ (**16**) at 193 K. The sample is the same as that used in Figure 3. The spectrum is annotated in f_1 and f_2 with the solvent-suppressed ^1H NMR spectrum. Assignments are indicated.

center at any instant (Figure 5a). This has been observed for all alkane complexes characterized using NMR spectroscopy so far.¹⁵

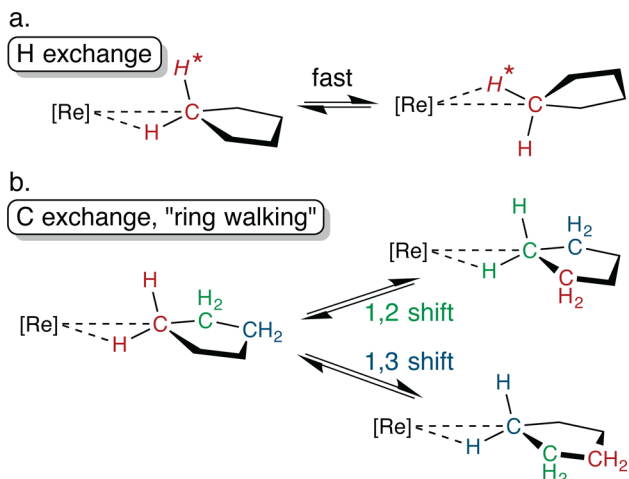


Figure 5. Possible intramolecular dynamic processes for the cyclopentane ligand in $[(\text{HEB})\text{Re}(\text{CO})_2(\text{c}\text{-C}_5\text{H}_{10})]^+$ (**16**).

Neither intramolecular exchange between the different methylene sites in the cyclopentane ligand (at δ ^1H -3.74 , 1.61 , and 1.70) nor intermolecular exchange with free cyclopentane (at δ ^1H 1.51) is detected in NOESY or ROESY spectra at 193 K. NOESY spectra recorded at 213 K (see Supporting Information, Figure S5) indicate that intramolecular exchange is occurring and detectable at this higher temperature, at a rate of $\sim 2 \text{ s}^{-1}$, corresponding to an activation barrier of $\sim 50 \text{ kJ mol}^{-1}$. At this temperature, decomposition of the sample prevents extended acquisition times, leading to 2D

NMR spectra with lower than ideal resolution in the indirect dimension, making discrimination of the rates of exchange into the two sites at δ ^1H 1.61 and δ ^1H 1.70 difficult in the 2D spectrum.

We have attempted to measure the rates of 1,2 and 1,3 shifts shown in Figure 5b that can occur in **16** using a series of selective 1D EXSY experiments performed on a sample at 211.6 K (Figure 6). The sample containing **16** was produced as

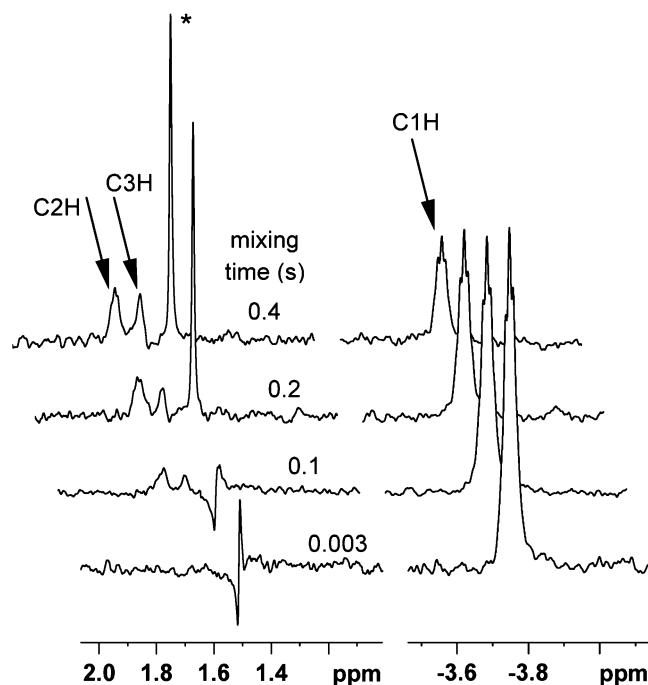


Figure 6. 600 MHz selective 1D ^1H EXSY NMR spectra of $[(\text{HEB})\text{Re}(\text{CO})_2(\text{c}\text{-C}_5\text{H}_{10})]^+$ (**16**) at various mixing times (0.003–0.4 s) at 211.6 K. * marks peaks due to residual signal from the intense free cyclopentane peak. Noise levels vary in the different spectra due to different numbers of scans, NS, being recorded at different mixing times, t_m , specifically $t_m = 0.003$, NS = 256; $t_m = 0.1$, NS = 768; $t_m = 0.2$, 0.4 , NS = 128. Spectra have been scaled to allow direct comparison based upon the number of scans collected and the time at which they were collected to correct for decay of the sample (see text).

above via the photolysis of **15** ($\sim 2 \text{ mg}$) and excess cyclopentane ($\sim 15 \mu\text{L}$) in $\text{CF}_3\text{CH}_2\text{CF}_3$ ($\sim 700 \mu\text{L}$) at 193 K. This sample decayed with a half-life of 88 min at 211.6 K, resulting in decreasing signal intensities over time. Spectral intensities were multiplied by a scaling factor to counter the effect of the decay, resulting in varying amounts of noise in the spectra, which is also scaled by this process.

The selective 1D EXSY experiment employed was set up to selectively excite the proton resonance of the bound methylene group (C1H) at δ ^1H -3.74 . The gradient spin echo in the selective excitation element destroys the magnetization at all the other sites.⁴⁷ This significantly aids the suppression of the large peak due to free cyclopentane at δ ^1H 1.51 which is approaching 1000 times more intense than the other resonances of the cyclopentane ligand, which are very close at δ ^1H 1.70 (C2H) and δ ^1H 1.61 (C3H) (see Figure 2). All of the 1D EXSY spectra contain a residual signal from the free cyclopentane due to imperfect suppression rather than intermolecular exchange, which is not detected in the full 2D NOESY.

The appearance of exchange peaks at short mixing times (0.1, 0.2 s) at both δ ^1H 1.70 (C2H) and δ ^1H 1.61 (C3H) suggests that the

bound methylene (C1) of the cyclopentane ring is undergoing 1,2 and 1,3 shifts. If only 1,2 shifts were occurring, for example, significant transfer of magnetization from the C1H site into the C3H site would only occur if two successive 1,2 shifts had occurred, meaning there would be a lag in the appearance of magnetization at the C3H site at short mixing times, which is not what is observed. Integrations of the exchange peaks indicate that the rate of exchange of C1H into the broader C2H resonance is faster than that into the sharper C3H resonance, suggesting that the 1,2 shift is about 2.2 times the rate of the 1,3 shift. The measured rates of exchange are $1.03 \pm 0.2 \text{ s}^{-1}$ for the 1,2 shift and $0.48 \pm 0.31 \text{ s}^{-1}$ for the 1,3 shift (see Supporting Information for details), corresponding to activation barriers of 51.2 and 52.5 kJ mol^{-1} , respectively. We note that these measurements may be subject to some systematic errors. A positive NOE between C1H and C2H, masked by the exchange, is likely to be present which will reduce the observed rate of exchange for the 1,2 shift. The peaks at δ 1.70 and 1.61 are separated by slightly less than 10 times the coupling constant, meaning that a small amount of strong coupling will exist between the protons on C2 and C3 in the bound cyclopentane ring. Finally, the suppression sequence employed to remove the $\text{CF}_3\text{CH}_2\text{CF}_3$ solvent resonance may perturb relative intensities by a small amount. These effects may slightly distort the measured rates, which already have high uncertainties due to the poor signal-to-noise ratio, driven by sample decomposition, but this is not expected to affect the overall conclusion that both 1,2 and 1,3 shifts are occurring directly and the former is (slightly) faster. Using ^{13}C NMR spectroscopy to study the exchange in this system would be preferable but was not possible because of insufficient sensitivity.

The activation barrier for migration of the cyclopentane ligand via 1,2 or 1,3 shifts of $\sim 50 \text{ kJ mol}^{-1}$ is higher than that observed in other known alkane complexes where “chain walking”, or in this case “ring walking”, has been measured (or calculated³⁶). This is not surprising, given the increased binding energy of the alkane in this system. For example, the lowest activation barrier for intramolecular carbon migration is ~ 38 – 42 kJ mol^{-1} for $[\text{iPrCpRe}(\text{CO})_2(n\text{-pentane})]^+$ (2–4),²³ $\sim 37 \text{ kJ mol}^{-1}$ for $[(\text{HEB})\text{W}(\text{CO})_2(1\text{-pentane})]^+$ (7),²⁶ and 30 kJ mol^{-1} for $[(\text{PONOP})\text{Rh}(\text{CH}_3\text{CH}_3)]^+$ (12).³²

Observation of the Pentane Complexes, $[(\text{HEB})\text{Re}(\text{CO})_2(n\text{-C}_5\text{H}_{12})]^+$ (17–19). The photolysis experiments were repeated using *n*-pentane in place of cyclopentane and then photolyzing at 178 K. Again, new peaks appeared in the shielded region of the spectrum ($\delta < 0$), and the photolysis was ceased after typically 17 min. Three new species assigned as alkane complexes were observed in the ^1H NMR spectrum, with resonances at δ -2.60 , -4.00 , and -4.11 and relative areas of 45.2:1.0:6.4, respectively (Figure 7).

The largest signal, at δ -2.60 (triplet), is consistent with a bound methyl group of an $n\text{-C}_5\text{H}_{12}\text{-}\eta^2\text{-C}^1\text{H}^1$ ligand in $[(\text{HEB})\text{Re}(\text{CO})_2(1\text{-pentane})]^+$ (17), with $^3J_{\text{HH}} = 6.7 \text{ Hz}$ couplings to two adjacent methylene protons. Again, a ^1H – ^{13}C HSQC experiment that retains coupling to ^{13}C (see Supporting Information) confirms that this signal is an alkane complex with $^1J_{\text{CH}} = 119.8 \pm 1.5 \text{ Hz}$ and δ $^{13}\text{C} = -23.7$. The signals at δ -4.00 and -4.11 are broad and too low in intensity to generate cross peaks in the natural abundance HSQC spectrum, but they are assigned as methylene-bound alkane complexes, either $[(\text{HEB})\text{Re}(\text{CO})_2(2\text{-pentane})]^+$ (18) or $[(\text{HEB})\text{Re}(\text{CO})_2(3\text{-pentane})]^+$ (19), containing $n\text{-C}_5\text{H}_{12}\text{-}\eta^2\text{-}$

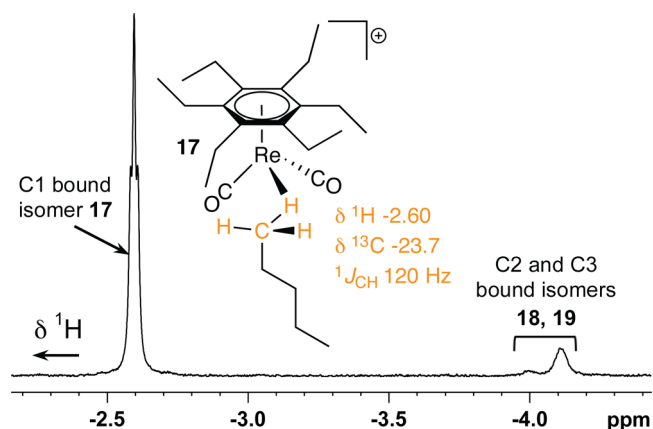


Figure 7. Shielded region of the ^1H NMR spectrum at 178 K of a mixture of isomers of $[(\text{HEB})\text{Re}(\text{CO})_2(n\text{-C}_5\text{H}_{12})]^+$ (17–19) produced via photolysis of $[(\text{HEB})\text{Re}(\text{CO})_3][\text{Al}(\text{OR}^t)_4]$ (15) and excess *n*-pentane dissolved in $\text{CF}_3\text{CH}_2\text{CF}_3$.

C^2H^2 and $n\text{-C}_5\text{H}_{12}\text{-}\eta^2\text{-C}^3\text{H}^3$ ligands, respectively. The assignments are based on the chemical shifts being similar to that observed for the bound methylene in the cyclopentane complex (δ -3.74). It is uncertain which of the two signals is due to which of the two isomers based on the available data.

Based on the integrals of the resonances, it is clear that binding of the methyl group is favored in this case, with an equilibrium constant of approximately 2.4 or 4.7, in favor of the methyl-bound isomer 17 over the isomer with the second largest intensity, 18 or 19. By comparison, when pentane binds to the $[\text{CpRe}(\text{CO})_2]$ fragment, a slight preference for binding of the methylene groups is observed ($K \approx 1.5$); when pentane binds to the $[(\text{HEB})\text{W}(\text{CO})_2]$ fragment, only binding of the methyl groups is observed experimentally, although it is known that CH_2 groups can also bind, since the cycloheptane complex $[(\text{HEB})\text{W}(\text{CO})_2(c\text{-C}_7\text{H}_{14})]^+$ (20) has been observed.²⁶

Stability of the Complex $[(\text{HEB})\text{Re}(\text{CO})_2(c\text{-C}_5\text{H}_{10})]^+$ (16). The stability of complex 16 relative to the corresponding neutral complex $[\text{CpRe}(\text{CO})_2(c\text{-C}_5\text{H}_{10})]$ (1) was tested by preparing mixtures of alkane complexes and monitoring their decay. Photolyzing a mixture of $[(\text{HEB})\text{Re}(\text{CO})_3][\text{Al}(\text{OR}^t)_4]$ (15) ($\sim 1 \text{ mg}$), $[\text{CpRe}(\text{CO})_3]$ (21) ($\sim 1 \text{ mg}$), and cyclopentane ($50 \mu\text{L}$) in $\text{CF}_3\text{CH}_2\text{CF}_3$ ($\sim 0.7 \text{ mL}$) for 17 min at 193 K resulted in a mixture of two alkane complexes, $[(\text{HEB})\text{Re}(\text{CO})_2(c\text{-C}_5\text{H}_{10})]^+$ (16) and $[\text{CpRe}(\text{CO})_2(c\text{-C}_5\text{H}_{10})]$ (1). The observation of 1 under these conditions confirms that the HFC solvents may be suitable for observing neutral as well as cationic complexes.

The decay of the complexes at 193 K was monitored and is shown in Figure 8. $[\text{CpRe}(\text{CO})_2(c\text{-C}_5\text{H}_{10})]$ (1) decays with an apparent first-order rate constant of $0.75 \pm 0.16 \text{ h}^{-1}$ (half-life $\sim 55 \text{ min}$) at 193 K, significantly faster than the rate of decay of $[(\text{HEB})\text{Re}(\text{CO})_2(c\text{-C}_5\text{H}_{10})]^+$ (16). When the solution was warmed to 213 K, the remaining 16 decayed with an apparent first-order rate constant of $1.87 \pm 0.30 \text{ h}^{-1}$ (half-life $\sim 22 \text{ min}$) (see Supporting Information for details).

Since $[(\text{HEB})\text{W}(\text{CO})_2(\text{alkane})]$ complexes are known to be significantly less stable than $[\text{CpRe}(\text{CO})_2(\text{alkane})]$ complexes,²⁶ it is apparent that the cationic complex $[(\text{HEB})\text{Re}(\text{CO})_2(c\text{-C}_5\text{H}_{10})]^+$ (16) displays greater stability than either of the two corresponding neutral analogues under typical preparation conditions.

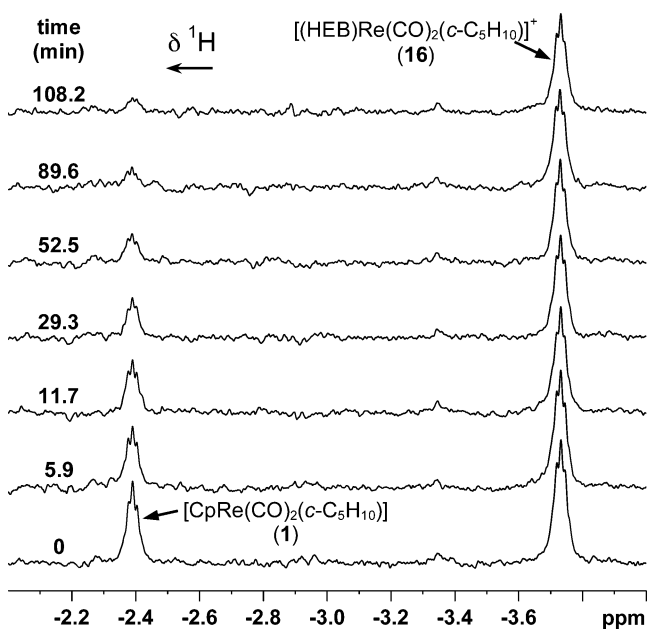


Figure 8. Decay of a mixture of $[(\text{HEB})\text{Re}(\text{CO})_2(c\text{-C}_5\text{H}_{10})]^+$ (**16**) and $[\text{CpRe}(\text{CO})_2(c\text{-C}_5\text{H}_{10})]$ (**1**) monitored using ^1H NMR at 193 K. Sample produced via photolysis of $[(\text{HEB})\text{Re}(\text{CO})_3][\text{Al}(\text{OR}^f)_4]$ (**15**), $[\text{CpRe}(\text{CO})_3]$ (**21**), and excess cyclopentane dissolved in $\text{CF}_3\text{CH}_2\text{CF}_3$. The UV lamp is off during the monitoring.

While the exact mode of the decomposition of the alkane complexes could not be determined using the data available to date, the temperature at which the complexes decompose in the absence of intentionally added reagents gives a measure of their stability in solution and an indication of the likelihood of being able to isolate these complexes.

Competitive Nature of Alkane Binding. The alkanes bind via a competitive process to the $[(\text{HEB})\text{Re}(\text{CO})_2]^+$ fragment; i.e., when a CO ligand is photochemically ejected from the coordination sphere of the tricarbonyl precursor, the solvent, counterion, adventitious impurities, other metal complex molecules, and alkane compete to fill the vacant coordination site produced. Binding of the alkane is observed despite the concentration of $\text{CF}_3\text{CH}_2\text{CF}_3$ being 30–65 times higher than that of the (cyclo)pentane in our experiments, so binding of $\text{CF}_3\text{CH}_2\text{CF}_3$ is statistically much more likely. The calculations suggest that this preference for binding of the alkane over $\text{CF}_3\text{CH}_2\text{CF}_3$ is thermodynamic.

Likewise, it is clear that the coordination of the $[\text{Al}(\text{OR}^f)_4]^-$ anion to the metal fragment is kinetically disfavored at least. In this case, the concentration of the alkane is much greater than that of the $[\text{Al}(\text{OR}^f)_4]^-$ anion, so initial binding of the alkane is, statistically, more likely than that of the anion.

Using Other Hydrofluorocarbons as Solvent. 1,1,1,2,2,3,3,4-Octafluorobutane, $\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2\text{F}$, was also successfully used as solvent to observe $[(\text{HEB})\text{Re}(\text{CO})_2(c\text{-C}_5\text{H}_{10})]^+$ (**2**). The observed yield was lower in this solvent than in 1,1,1,3,3,3-hexafluoropropane, so the latter solvent was employed for the majority of experiments in this study. 1,1,1,2,2,3,3,4-Octafluorobutane offers the benefits of being a liquid (just) at room temperature (bp \approx 298 K) and having a lower melting point (mp \approx 140 K). We also note that difluoromethane, CH_2F_2 , was present as an impurity in the $\text{CF}_3\text{CH}_2\text{CF}_3$ that was used, and CH_2F_2 is sufficiently highly fluorinated to have a lower bonding energy (82 kJ mol $^{-1}$,

B3PW91-D3BJ) than the cyclopentane (120 kJ mol $^{-1}$) with $(\text{C}_6\text{H}_6)\text{Re}(\text{CO})_2^+$.

CONCLUDING REMARKS

In this paper, we describe only the second class of cationic transition metal–alkane complex to be characterized in solution using NMR spectroscopy, $[(\text{HEB})\text{Re}(\text{CO})_2(\text{alkane})]^+$, where alkane = cyclopentane or pentane. $[(\text{HEB})\text{Re}(\text{CO})_2(c\text{-C}_5\text{H}_{10})]^+$ (**16**) shows greater stability than the corresponding neutral alkane complexes $[(\text{HEB})\text{W}(\text{CO})_2(\text{alkane})]$ and $[\text{CpRe}(\text{CO})_2(\text{alkane})]$. In the case of $[(\text{HEB})\text{Re}(\text{CO})_2(n\text{-C}_5\text{H}_{12})]^+$, the isomer with the CH_3 group bound to the metal fragment (**17**) is preferred but not exclusively so, as small amounts of the CH_2 -bound isomers (**18**, **19**) are observed.

More importantly, the use of HFC solvents and the extremely poorly coordinating $[\text{Al}(\text{OR}^f)_4]^-$ anion provides a template for observing numerous cationic alkane complexes in the future and assisting in their isolation, since, in this case at least, the cationic complex and alkane are solubilized by the HFC solvent and the alkane binds in preference to the HFC. This approach may be widely applicable to observing many other classes of complexes that contain weakly bound ligands in solution, and it should be possible to tailor the wide variety of HFC solvents that are available to specific situations. Ultimately, HFC solvents may prove useful as solvents to promote new transformations of alkanes, given that they may stabilize key intermediates such as cationic σ -alkane complexes.

EXPERIMENTAL SECTION

General Information. HFC solvents were purchased from SynQuest Laboratories, Alachua, FL. $\text{CF}_3\text{CH}_2\text{CF}_3$ was used without further purification and transferred using trap-to-trap methods on a Schlenk line. 1,1,1,2,2,3,3,4-Octafluorobutane was dried over phosphorus pentoxide prior to use.

Details of the X-ray structure of $[(\text{HEB})\text{Re}(\text{CO})_3][\text{Al}(\text{OR}^f)_4]$ (**15**) are given in the Supporting Information, including a CIF file.

Synthesis of $[(\text{HEB})\text{Re}(\text{CO})_3][\text{Al}(\text{OR}^f)_4]$ (15**).** In a typical preparation, a suspension of $[(\text{HEB})\text{Re}(\text{CO})_3][\text{PF}_6]^{44}$ (10.3 mg, 0.016 mmol) and lithium tetrakis(perfluoro-*tert*-butoxy)aluminate (19 mg, 0.020 mmol, 1.25 equiv) in diethyl ether was stirred in an oven-dried Schlenk tube under an argon atmosphere for 24 h. The supernatant was then collected by filter cannulation, and the solvent was removed under reduced pressure to give the desired product as an off-white solid (3.2 mg, 14%).

HRMS (FTMS, positive mode, m/z): calcd for $\text{C}_{21}\text{H}_{30}\text{O}_3\text{Re}$ $[\text{M}]^+$, 517.1753; found, 517.1744. HRMS (FTMS, negative mode, m/z): calcd for $\text{C}_{16}\text{O}_4\text{F}_{36}\text{Al}$ $[\text{M}]^-$, 966.9036; found, 966.9036. IR (CH_2Cl_2 , cm^{-1}): $\nu(\text{CO})$ 2062, 1993. ^1H NMR (CD_2Cl_2 , 600.2 MHz, 25 $^\circ\text{C}$): δ 1.38 (t, $^3J = 7.6$ Hz, 18 H), 2.66 (q, $^3J = 7.6$ Hz, 12 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 150.9 MHz, 25 $^\circ\text{C}$): δ 19.4 (br), 22.4 (s), 79.6 (br), 121.4 (br), 121.8 (q, $^1J_{\text{CF}} = 293.5$ Hz), 185.6 (s). ^{19}F NMR (CD_2Cl_2 , 564.7 MHz, 25 $^\circ\text{C}$): δ -75.8.

NMR Spectroscopy. NMR samples for photolysis were prepared under argon in screw-cap NMR tubes fitted with a Teflon/rubber septum. Samples in $\text{CF}_3\text{CH}_2\text{CF}_3$ (bp \approx 272 K) were kept below 273 K at all times when transferring samples to mitigate the risk of explosion. Samples were irradiated by means of an Oriel Q-series lamp housing fitted with a 100 W Hg arc lamp focused onto a 2.5 m long, 1.5 mm diameter single silica optical fiber (Spectran Speciality Optics). The optical fiber was guided through the pierced septum of the NMR tube, and the tip of the fiber was placed about 5 mm above the active region of the NMR coils in the NMR sample. Spectra were recorded on 600 or 500 MHz spectrometers fitted with inverse triple-resonance probes that were cooled to the temperature indicated. 1D ^1H NMR and homonuclear 2D experiments used standard Bruker pulse programs incorporating excitation sculpting (1D zgesgp; TOCSY dipsi2esgpph;

NOESY noesysegpph). The selective 1D EXSY experiments employed the selnogg program modified to include an excitation sculpting step at the end of the sequence to suppress the solvent. The pulse program for acquiring the ^1H - ^{13}C HSQC experiment with retention of coupling to the ^{13}C nucleus in f_2 is given in the [Supporting Information](#).

Spectra in CD_2Cl_2 were referenced by setting the ^1H NMR shift of CHDCl_2 to δ 5.320 and the ^{13}C NMR shift of CD_2Cl_2 to δ 54.00. ^1H NMR spectra in $\text{CF}_3\text{CH}_2\text{CF}_3$ and $\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2\text{F}$ solvents were referenced by setting the solvent resonance to δ 2.912 and 4.688, respectively.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/jacs.5b10583](https://doi.org/10.1021/jacs.5b10583).

X-ray crystallographic data for **15** (CIF)

Details of X-ray crystallography, NMR spectra, extraction of exchange rates from 1D EXSY, details of computed binding energies, and coordinates of calculated structures (PDF)

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Notes

The authors declare no competing financial interest.

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