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# Direct Observation of a Transition Metal Alkane Complex, CpRe(CO)$_2$(cyclopentane), Using NMR Spectroscopy

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There is already a considerable body of experimental and theoretical data indicating that simple alkanes can act as ligands in transition metal complexes.[1] As a result, the isolation of the first true alkane complex remains a key objective of organometallic chemistry.[2]

Experimentally, the existence of short-lived alkane complexes has been inferred from detailed studies of C−H activation processes with metals such as Rh[3] and related hydrogen isotope scrambling experiments with Ir.[4] After alkane coordination, the C−H bond-breaking step is generally very rapid and irreversible in systems where the alkyl hydride is the thermodynamically favored product. It is not always the case that the alkane complex is thermodynamically unstable with respect to the C−H activation product, however. For example, complexes of the type W(CO)$_5$(alkane) have long been known in matrix-isolated, solution, and gas phases.[5] Alkane complexes of iridium have also been inferred in studies of dihydrogen substitution reactions.[6] Until now, infrared spectroscopy has proven the most valuable tool in these investigations. Unfortunately, in all cases, these studies give scant information about the nature of these weak interactions with alkanes with little information about the bonding or the on/off rates of the alkane.

Recently, George et al. reported that CpRe(CO)$_2$(*n*-heptane), photolytically produced by irradiation of the parent tricarbonyl in heptane, has the longest lifetime measured of any known alkane complex.[7] Under the conditions employed, at 298 K, the decay rate in the absence of added ligand was only 40 s$^{-1}$. This observation prompted us into this investigation since at ~180 K, assuming reasonable activation parameters for the decay process, we expected the chemical lifetime of this and related species to be sufficient for an NMR study.

First, we built apparatus to allow a sample to be continuously irradiated with UV light while in the NMR spectrometer and at lower temperature. Broad-spectrum UV/visible light is delivered directly to the inside of the 5-mm NMR tube using a 2-m-long, single-core, 1-mm-outside diameter, fiber optic cable. This connects to a 100-W mercury arc lamp (Oriel) fitted with a standard fiber optic coupling device located ~1 m from the magnet. When a supersaturated solution of CpRe(CO)$_3$ ($\sim 4 \times 10^{-3}$ M) in neat cyclopentane is cooled to −80 °C or below and photolyzed using this equipment, a new singlet peak at $\delta$ 4.920 in the Cp region of the $^1$H NMR spectrum appears at the expense of the peak due to the starting complex ($\delta$ 5.23). Concomitant with the growth of the new Cp peak, another highly shielded resonance at $\delta$ −2.32 grows in a previously blank region of the spectrum, and a fixed integral ratio of close to 5:2 of $\delta$ 4.920:$\delta$ −2.32 resonances is maintained (Figure 1a). We attribute these new peaks to the alkane complex CpRe(CO)$_2$(cyclopentane) (**1**) with the peak at $\delta$ −2.32 due to one methylene unit of the cyclopentane ring being coordinated to the metal center. After a period of typically 15−30 min of irradiation, the concentration of the new peaks reaches a maximum without complete disappearance of the starting complex. After this, both starting and new complexes lose intensity slowly and a brown precipitate forms if the irradiation is continued. If the irradiation is discontinued at this point, the concentration of the parent tricarbonyl does not change noticeably but the alkane complex **1** still disappears at a rate similar to that under photolytic conditions. These observations are consistent with competition from liberated CO preventing full conversion via reaction reversal, and the formation of an insoluble dimer, presumably Cp$_2$Re$_2$(CO)$_5$,[7] being the ultimate metal-containing product. This is in agreement with the observations of the IR study.[7] Complete disappearance takes several hours (typically ~1 h), allowing a significant amount of time to perform other NMR experiments. The shielded peak has a multiplet structure, appearing as a first-order quintet with $^3J_{\mathrm{HH}} = 6.6$ Hz, consistent with four similar couplings to protons on adjacent carbons. Proton−proton coupling constants are similar to those in uncomplexed cyclopentane (a similar, second-order splitting pattern is visible in the $^{13}$C satellites of the free alkane), suggesting little perturbation from its uncomplexed geometry. These data indicate that both protons attached to the same carbon are each involved in binding to the metal center. Possibilities for the mode of binding in **1** are shown in Chart 1.

The most likely explanation for the equivalence of the two protons of the methylene group is a rapid exchange of the two different C−H bonds interacting individually and alternately with the metal in an $\eta^2$-C,H $\sigma$-type interaction (structures **2** and **4**). Alternatively, an $\eta^2$-H,H interaction (structure **3**) with a symmetry element or exchange process/rapid rotation rendering the two bound H's equivalent is a possibility.[8] Theoretical studies on the related alkane complex W(CO)$_5$(propane) suggested that with the central methylene unit bound, the lowest energy form was the $\eta^2$-C,H option.[9] Hence **3** may be a ground-state structure or, more likely, may act as a low-energy transition state for interconversion of **2** and **4**. Further NMR experiments are underway which should distinguish these two cases.

The NMR experiments are performed using the WATERGATE sequence[10] to suppress the ~10$^5$ times more intense free cyclopentane peak and run without lock when no deuterated solvent is present. We assume that the other protons not directly attached to the metal in the coordinated cyclopentane of **1** are close in frequency to those of free cyclopentane and hence suppressed in the 1D spectra. Our current photolysis setup has allowed only a maximum of 20% conversion of CpRe(CO)$_3$ to occur resulting in $<10^{-3}$ M concentration of **1**. As a result, to rule out the possibility of trace impurities being responsible for the formation of **1**, further experiments were performed (Figure 1b−e).

Repeating the experiment with cyclopentane-$d_{10}$ (Isotec) in place of perprotiocyclopentane (C$_5$H$_{10}$) results in the observation of an isotopically shifted Cp resonance at $\delta$ 4.911 (Figure 1b) but no multiplet at $\delta$ −2.32 due to the formation of **1**-$d_{10}$. Use of 1:1 v/v C$_5$H$_{10}$/C$_5$D$_{10}$ as solvent results in the observation of two close Cp resonances (Figure 1c) with the high-field resonance due to **1**-$d_{10}$ and the low-field Cp resonance due to **1**, which

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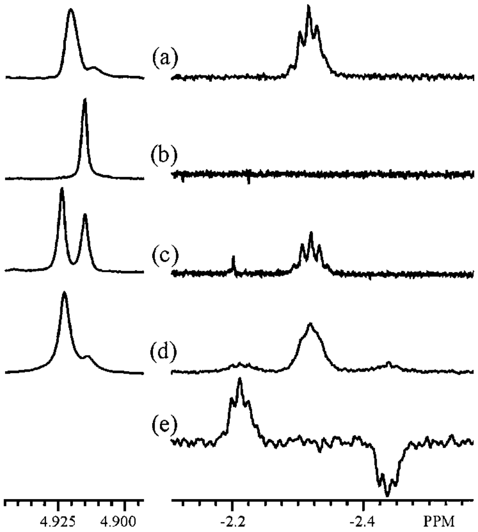
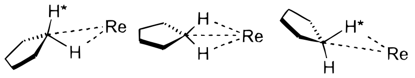


**Figure 1.** 500-MHz 1D $^1$H NMR spectra at 180 K of photolysis products formed from CpRe(CO)$_3$ in various mixtures of cyclopentane and its isotopomers. All regions shown contain no resonances prior to irradiation. Spectra in the right column are scaled 8 times larger than the adjacent left column spectra: (a) spectrum in 95:5% $C_5H_{10}/C_5D_{10}$; (b) in 100% $C_5D_{10}$; (c) in 50:50% $C_5H_{10}/C_5D_{10}$; (d) $^{13}$C-labeled sample, 85:15% $C_5H_{10}$-$^{13}C_1/C_5D_{10}$; (e) same sample as (d) $^{13}$C edited experiment showing $^1J_{CH}$ in the coordinated cyclopentane ligand of 112.9 Hz.

**Chart 1**



**2** η$^2$-C,H **3** η$^2$-H,H **4** η$^2$-C,H*

integrates 4.6:2 with respect to the expected multiplet at $\delta$ −2.32. Integration of these Cp resonances shows that the $C_5H_{10}$ ligand is preferentially bound in the ratio of 1.33:1. Hence, a small equilibrium isotope effect *opposite* in sense to the large effect seen by Moore and Bergman et al. in Cp*Rh(alkane) complexes[3b,c] is observed.

Due to the low concentrations of **1** accessible and its limited lifetime, measurement of $^{13}$C NMR parameters at natural abundance was not viable. A labeled sample using [$^{13}C_1$]cyclopentane (Isotec) plus ~15% cyclopentane-$d_{10}$ for deuterium lock purposes as NMR solvent was prepared. Photolysis of this sample resulted in the expected pattern for the resonance at $\delta$ −2.32 with 20% $^{13}$C labeling (Figure 1d). A $^{13}$C edited 1D $^1$H spectrum (Figure 1e) confirmed $^1J_{CH}$ to be 112.9 Hz compared with 129.4 Hz in free cyclopentane. A fast HSQC experiment[11] indicates a $^{13}$C chemical shift of $\delta$ −31.2 (Figure 2).

This small reduction of $^1J_{CH}$ and significant shielding of both $^1$H and $^{13}$C NMR resonances is fully consistent with a weakly bound alkane complex. These results may be compared with NMR data available concerning $\beta$-agostic bonded and related bound C−H moieties, which may be considered to be tethered model complexes for alkane complexes.[12] If **1** is indeed an $\eta^2$-C,H $\sigma$-type complex, the observed $^1J_{CH}$ value represents the average value from one coordinated and one unbound C−H bond, allowing estimation of $^1J_{CH}$ in the coordinated moiety to be ~96 Hz. Such a value is consistent with a relatively weak interaction with the metal center, since typical agostic interactions result in $^1J_{CH}$ values between 60 and 90 Hz, indicative of a weaker C−H bond and correspondingly stronger metal−ligand bond strengths.[12a] The change in $^{13}$C shift is large compared with typical values observed in $\beta$-agostic complexes, but highly pertinent data for rhenium are lacking. It is possible that, to some extent, this reflects a shorter metal−carbon distance in the alkane complex compared with those found in typical $\beta$-agostic complexes. This may be due to steric factors. The bound carbon in **1** is not constrained by any tether, and the other group attached to it that is syn to the metal is a hydrogen atom rather than a bulkier group.

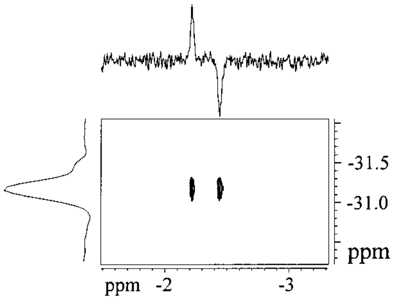


**Figure 2.** 500-MHz 2D $^1$H−$^{13}$C FHSQC of **1**-$^{13}C_1$ at 180 K without F$_2$ decoupling showing $\delta$ $^{13}C = -31.2$ ppm and $^1J_{CH} = 112.9$ Hz in the coordinated cyclopentane ligand. Annotated with slices through the cross-peak in both dimensions.

Presaturation of the free cyclopentane resonance for 6 s prior to acquisition of a 1D WATERGATE spectrum results in disappearance of the signal at $\delta$ −2.32. Most likely, this indicates that free cyclopentane is exchanging slowly with the bound protons. Alternatively, protons in the coordinated cyclopentane involved in an intramolecular exchange process (or a negative NOE) could be responsible for the observed saturation transfer. The bound protons leave their site between 2 and 20 s$^{-1}$ at −80 °C, leading to an estimated free energy of activation, $\Delta G^{\ddagger}_{193K} = 10.3^{-1} \pm 0.5$ kcal mol$^{-1}$.

Initial results of a wider survey of ligands show that both *n*-pentane and tetramethylsilane form complexes in slow exchange with free ligand. Three high-field resonances are observed with *n*-pentane which we tentatively ascribe to the three possible binding sites in this ligand and relative intensities suggest only a small preference between sites.

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**Note Added in Proof.** Further studies indicate that further photolysis of solutions containing **1** results in the formation of small amounts of hydride species. It is unclear at present whether these hydrides are produced directly from C−H activation of **1** or from trace impurities.

**Supporting Information Available:** Stacked $^1$H NMR plot monitoring photolytic production and decay of **1** vs time (1 page, print/PDF). See any current masthead page for ordering information and Web access instructions.

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