

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/49797831>

Manganese Alkane Complexes: An IR and NMR Spectroscopic Investigation

ARTICLE *in* JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · FEBRUARY 2011

Impact Factor: 12.11 · DOI: 10.1021/ja110451k · Source: PubMed

CITATIONS

36

READS

55

7 AUTHORS, INCLUDING:



[Simon B Duckett](#)

The University of York

140 PUBLICATIONS 3,448 CITATIONS

[SEE PROFILE](#)



[Khuong Vuong](#)

Institute of Chemical and Engineering Sciences

27 PUBLICATIONS 628 CITATIONS

[SEE PROFILE](#)

Manganese Alkane Complexes: An IR and NMR Spectroscopic Investigation

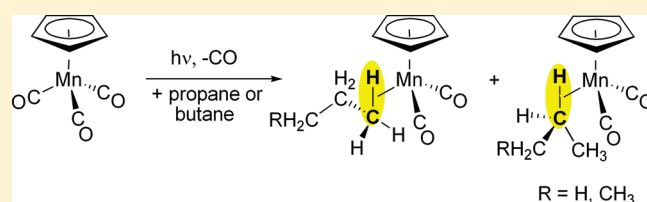
James A. Calladine,[†] Simon B. Duckett,[†] Michael W. George,^{*,†} Steven L. Matthews,[‡] Robin N. Perutz,^{*,†} Olga Torres,[‡] and Khuong Q. Vuong[†]

[†]School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, United Kingdom

[‡]Department of Chemistry, University of York, Heslington, York YO10 5DD, United Kingdom

 Supporting Information

ABSTRACT: Manganese propane and manganese butane complexes derived from $\text{CpMn}(\text{CO})_3$ were generated photochemically at 130–136 K with the alkane as solvent and characterized by FTIR spectroscopy and by ^1H NMR spectroscopy with in situ laser photolysis. Time-resolved IR spectroscopic measurements were performed at room temperature with the same laser wavelength. The $\nu(\text{CO})$ bands in the IR spectra of the photoproducts in propane



are shifted to low frequency with respect to $\text{CpMn}(\text{CO})_3$, consistent with formation of $\text{CpMn}(\text{CO})_2(\text{propane})$. The ^1H NMR spectra conform to the criteria for alkane complexes: a high-field resonance for the $\eta^2\text{-CH}$ protons that shifts substantially on partial deuteration of the alkane and exhibits a coupling constant $J_{\text{C-H}}$ on ^{13}C -labeling of ca. 120 Hz. The NMR spectrum of each system exhibits two diagnostic product resonances in the high-field region for the $\eta^2\text{-CH}$ protons, corresponding to $\text{CpMn}(\text{CO})_2(\eta^2\text{-C1-H-alkane})$ and $\text{CpMn}(\text{CO})_2(\eta^2\text{-C2-H-alkane})$ isomers. Partial deuteration of the alkane at C1 results in characteristic strong isotopic perturbation of equilibrium of the $\eta^2\text{-CH}$ resonance of $\text{CpMn}(\text{CO})_2(\eta^2\text{-C1-H-alkane})$. With propane- $^{13}\text{C}_1$, the $\eta^2\text{-CH}$ resonance of $\text{CpMn}(\text{CO})_2(\eta^2\text{-C1-H-alkane})$ isomer exhibits ^{13}C satellites with $J_{\text{C-H}} = 119$ Hz. The corresponding resonance of $\text{CpMn}(\text{CO})_2(\eta^2\text{-C2-H-alkane})$ is identified by use of propane-2,2- d_2 . The lifetimes of the ($\eta^2\text{-C1-H-alkane}$) isomers of the manganese complexes were determined by NMR spectroscopy as 22 ± 2 min at 134 K (propane) and 5.5 min at 136 K (butane). The corresponding spectra and lifetimes of the $\text{CpRe}(\text{CO})_2(\text{alkane})$ complexes were measured for reference ($\text{CpRe}(\text{CO})_2(\text{propane})$ lifetime ca. 60 min at 161 K; $\text{CpRe}(\text{CO})_2(\text{butane})$ 13 min at 171 K). The lifetimes determined by IR spectroscopy were similar to those determined by NMR spectroscopy, thereby supporting the assignments. These measurements extend the range of alkane complexes characterized by NMR spectroscopy from rhenium and rhodium derivatives to include less stable manganese derivatives.

INTRODUCTION

Coordination complexes in which an alkane is bound to a metal were first identified in the 1970s,^{1–8} even before the more stable dihydrogen complexes were discovered. It is now recognized that they form one member of the class of σ -complexes or σ -bond complexes, $\text{M}(\sigma\text{-E-H})$ ($\text{E} = \text{H}, \text{C}, \text{B}, \text{Si}$, and others), in which the bonding and antibonding orbitals of a saturated E–H σ -bond interact with the metal orbitals (Scheme 1).⁹ The σ -alkane complexes represent the intermolecular analogues of agostic complexes in which the saturated C–H bond that interacts with the metal is bound as a chelate with the support of more conventional metal–ligand interactions.¹⁰

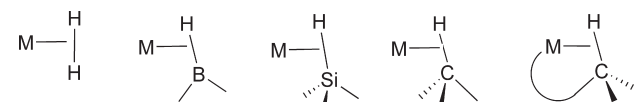
There are numerous mechanistic studies that implicate alkane complexes as reaction intermediates in processes such as C–H oxidative addition and reductive elimination,^{3,4,11–14} metathesis processes especially σ -CAM,^{15–17} protonation of metal alkyls,^{18,19} simple ligand substitution processes,^{3,4,20,21} and alkane adsorption on metal surfaces.²² Recent examples include borylation of alkanes (a σ -CAM mechanism),^{15,16} equilibrium isotope effects,²³ isotope exchange and chain walking at rhodium alkyl

hydrides,²⁴ and C–H activation at platinum.^{11,12} It follows that alkane complexes may be formed in a variety of ways including reaction with an alkane, reductive coupling of a metal alkyl hydride, and protonation of a metal alkyl. These experimental studies are accompanied by extensive computational studies of reaction mechanisms.^{25,26} Many of the reaction steps mentioned above play an important role in catalysis.

Metal–dihydrogen, metal–borane, and metal–silane complexes have been studied very extensively by a range of spectroscopic and diffraction methods and have also been the target of many computational investigations.^{9,27–31} Information about alkane complexes has been much harder to acquire because of their lability and the relative lack of crystallographic information. The principal sources of spectroscopic and kinetic information that target the metal–alkane complex have originated from (a) UV/vis and IR absorption studies in low-temperature matrices,^{1–3} (b) room temperature time-resolved UV/vis and IR spectroscopy,^{6,32–41} (c)

Received: November 20, 2010

Published: January 31, 2011

Scheme 1. Metal σ -Bond and Agostic Complexes

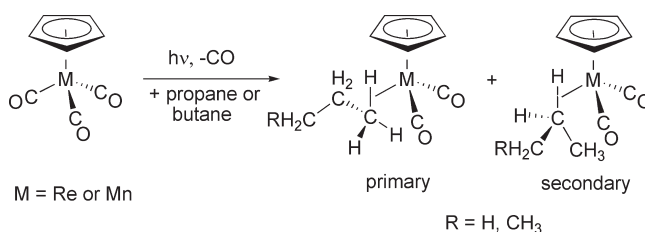
low-temperature solution NMR spectroscopy,^{42–47} and (d) mass spectrometry.^{48–50} Examples of alkane complexes concern metals predominantly in d^4 , d^6 , and d^8 configurations with ligands that provide a covalent environment, especially carbonyls, phosphines, alkyls, etc.

The strength of the NMR studies of alkane complexes is that they are conducted in solution and probe the coordinated C–H bond directly. Their weakness is that so far they are limited to a small range of examples (see below). In contrast, the IR and UV/vis studies are applicable to a wider range of complexes because they can be employed for much more labile complexes, but they probe alkane coordination indirectly via its effect on other molecular properties such as $\nu(\text{CO})$. Structural and bonding information on alkane complexes has also come from computational studies, which have often shown alkane complexes as well-defined minima.^{25,26,51,52} The only examples of crystal structures that show alkane coordination concern metal–ligand environments that are very different from those studied by other methods. One crystal structure shows an iron porphyrin coordinated to heptane, while the others are uranium derivatives.⁵³

Time-resolved IR studies have shown that many coordinatively unsaturated metal carbonyls interact with alkanes and that the least labile of them derive from $[\text{CpRe}(\text{CO})_2]$. The longest lived alkane complexes at room temperature are $\text{CpRe}(\text{CO})_2$ -(cyclopentane) and $\text{CpRe}(\text{CO})_2$ -(heptane), which react with CO with rate constants of 1.1×10^3 and $2.5 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively, leading to lifetimes of ca. 25–50 ms. Activation energies for reaction with CO provide an estimate of the minimum interaction energy between the alkane and the metal fragment. The value for $\text{CpRe}(\text{CO})_2$ -(heptane) is ca. $49 \pm 2 \text{ kJ mol}^{-1}$.³⁸

Ball's pioneering NMR studies of alkane complexes targeted the $[\text{CpRe}(\text{CO})_2]$ fragment (and its derivatives) because previous TRIR work had shown them to be “remarkably stable”.^{42–45} These alkane complexes were generated by in situ photolysis of the parent metal carbonyls (or more recently metal dinitrogen complexes) in alkane solvents at low temperature. Through these studies, some characteristic features of alkane complexes were demonstrated: (a) the ^1H resonance of the coordinated C–H group lies in the negative δ region, similar to those found for metal hydrides; (b) there is a large isotopic shift of ca. 0.5–2 ppm on partial deuteration (isotopic perturbation of equilibrium, IPE); (c) the value of $J_{\text{C-H}}$ is ca. 100–120 Hz; and (d) the ^{13}C chemical shift of the coordinated C–H is found at ca. $\delta -30$. The IPE arises because of fast interconversion of the coordinated and geminal C–H bonds, with a preference for deuterium to occupy the geminal position and hydrogen to occupy the coordinated position.⁵⁴ These last three features can be used to distinguish an alkane complex from a metal alkyl hydride unambiguously.^{42–44}

Recently, Brookhart and co-workers have made a major advance by generating a rhodium methane complex via protonation of a rhodium methyl precursor. This work provided the first NMR data for a metal–methane complex and showed that its characteristics matched those of other reported alkane

Scheme 2. Photolysis of $\text{CpM}(\text{CO})_3$ in Liquid Propane or Butane ($\text{M} = \text{Mn}$ or Re)

complexes.¹⁸ This study also showed the importance of protonation and demonstrated that cationic alkane complexes are accessible.

We have developed an approach to widen the scope of NMR studies of alkane complexes through targeted combination of time-resolved IR spectroscopy and laser photochemistry within the NMR probehead of an NMR spectrometer.^{46,47} Our aim is to use the same precursors, solvents, temperatures, and laser wavelengths for both the IR and the NMR studies. Room-temperature TRIR or low-temperature FTIR spectroscopic studies provide information regarding the reactivity of the alkane complexes and their lifetime. NMR spectroscopy is used to provide direct evidence for the coordination of the alkane and to distinguish between different isomeric forms. This methodology has already been successfully used by us to identify two new alkane complexes, $\text{TpRe}(\text{CO})_2$ -(cyclopentane) and $\text{Cp}^{\ddagger}\text{Re}(\text{CO})_2$ -(cyclopentane) ($\text{Tp} = \text{tris}(\text{pyrazolyl})\text{borate}$, $\text{Cp}^{\ddagger} = 1,2\text{-C}_5\text{H}_3(\text{tBu})_2$).^{46,47}

Our previous TRIR investigations indicated that $[\text{CpMn}(\text{CO})_2(\text{alkane})]$ complexes were possible candidates for observation by NMR spectroscopy, but their reactivity is approximately 300 times greater than that for the analogous rhenium complexes (measured by the rate constant for reaction with CO, k_{CO}).³⁷ With the aim of characterizing a manganese alkane complex by NMR spectroscopy, we selected liquid propane as a suitable solvent. Liquid propane has a very low freezing point (85 K), exists as a liquid at room temperature under modest pressures (ca. 125 psi), and possesses two closely spaced ^1H NMR resonances, allowing for easy suppression of the solvent signal. Liquid butane was also considered as a candidate for similar reasons. We have previously reported an IR spectroscopic investigation into the formation of $\text{CpRe}(\text{CO})_2(\text{C}_3\text{H}_8)$ at room temperature and 160 K.³⁶ This Article builds on our earlier work and extends it to the formation of the more reactive Mn analogue. Here, we report both IR and NMR evidence for the formation of the rhenium and manganese propane complexes and NMR evidence for the analogous butane complexes (Scheme 2).

RESULTS AND DISCUSSION

TRIR Spectroscopy in Liquid Propane at Room Temperature. TRIR spectroscopy has been used to characterize and monitor the reactivity of the propane complexes of Mn and Re following photolysis of the precursor $\text{CpM}(\text{CO})_3$ ($\text{M} = \text{Mn}, \text{Re}$) in liquid propane at 298 K. Photolysis of $\text{CpMn}(\text{CO})_3$ with 355 nm radiation leads to bleaching of the parent $\nu(\text{CO})$ bands ($2031, 1950 \text{ cm}^{-1}$) and formation of two new bands at 1965 and 1899 cm^{-1} , which are assigned to the propane complex, $\text{CpMn}(\text{CO})_2(\text{C}_3\text{H}_8)$. The IR spectrum does not indicate whether the metal is coordinated to a primary or secondary C–H bond.

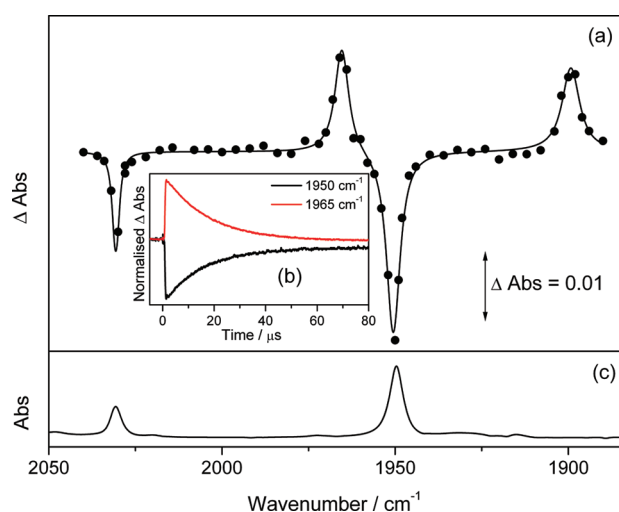


Figure 1. (a) TRIR difference spectrum 2 μ s after UV photolysis (355 nm) of CpMn(CO)_3 in liquid propane (150 psi) in the presence of CO (15 psi) at 298 K, showing the formation of $\text{CpMn(CO)}_2(\text{C}_3\text{H}_8)$. The solid line is a Lorentzian curve fit. (b) Kinetic traces showing decay of $\text{CpMn(CO)}_2(\text{C}_3\text{H}_8)$ at 1950 cm^{-1} and the recovery of CpMn(CO)_3 at 1965 cm^{-1} . (c) FTIR spectrum before photolysis.

Table 1. $\nu(\text{CO})/\text{cm}^{-1}$ Bands for CpM(CO)_3 and $\text{CpM(CO)}_2(\text{propane})$ in Liquid Propane ($\text{M} = \text{Mn, Re}$)

complex	$\nu(\text{CO})/\text{cm}^{-1}$	T/K
CpMn(CO)_3	2031, 1950	298
	2028, 1945	130
$\text{CpMn(CO)}_2(\text{propane})$	1965, 1899	298
	1960, 1893	130
CpRe(CO)_3^a	2033, 1944	298
	2032, 1940	160
$\text{CpRe(CO)}_2(\text{propane})^a$	1956, 1892	298
	1951, 1886	160

^a Reference 36.

Figure 1a shows the TRIR difference spectrum 2 μ s after photolysis of CpMn(CO)_3 at 355 nm in liquid propane (150 psi) and in the presence of CO (15 psi). Similar experiments were performed with CpRe(CO)_3 for reference (Table 1). These bands are very close to those observed previously in other alkane solvents.³⁶

The bands of $\text{CpMn(CO)}_2(\text{C}_3\text{H}_8)$ decay in the presence of CO at 298 K at the same rate as the parent recovers ($k_{\text{obs}} = 1.0 (\pm 0.1) \times 10^5 \text{ s}^{-1}$) (Figure 1b). The estimated k_{CO} value of $2.4 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ($[\text{CO}] = 41 \text{ mM}$) is 3 times faster than the rate of reaction for the *n*-heptane analogue³⁸ and is comparable to that of the ethane analogue⁴⁴ (Table 2). The value of k_{CO} for the Mn–propane complex is ca. 430 times faster than that for the Re–propane complex (Table 2), a ratio similar to those measured for other alkane complexes of Mn and Re.^{38,44,47} As previously demonstrated, shorter chain alkanes tend to give more reactive complexes than do longer chain alkanes.^{40,41,44}

The activation energies (E_a) for the reaction of $\text{CpM(CO)}_2(\text{C}_3\text{H}_8)$ with CO to reform CpM(CO)_3 were obtained by measuring the rate of decay of the propane complex, as a function of temperature (Figure 2 and Table 2), yielding

Table 2. Second-Order Rate Constants at 298 K and Activation Energies for the Reaction of $\text{CpM(CO)}_2(\text{alkane})$ with CO in Liquid Alkane Solution ($\text{M} = \text{Mn, Re}$)

complex	$k_{\text{CO}}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$E_a/\text{kJ mol}^{-1}$
$\text{CpMn(CO)}_2(n\text{-C}_7\text{H}_{16})^a$	$(8.0 \pm 0.6) \times 10^5$	38.7 ± 2
$\text{CpMn(CO)}_2(c\text{-C}_5\text{H}_{10})^a$	$(2.5 \pm 0.4) \times 10^5$	26.2 ± 2
$\text{CpMn(CO)}_2(\text{C}_3\text{H}_8)^b$	2.4×10^6	33 ± 3
$\text{CpRe(CO)}_2(n\text{-C}_7\text{H}_{16})^a$	$(2.5 \pm 0.2) \times 10^3$	48.7 ± 2
$\text{CpRe(CO)}_2(c\text{-C}_5\text{H}_{10})^a$	$(1.1 \pm 0.2) \times 10^3$	34.8 ± 2
$\text{CpRe(CO)}_2(\text{C}_3\text{H}_8)^{b,c}$	5.6×10^3	52 ± 4

^a Reference 38. ^b Estimated from a single concentration of CO.

^c Reference 36.

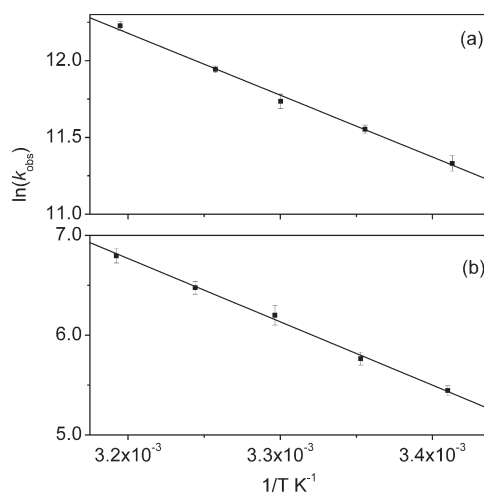


Figure 2. Arrhenius plots for the reaction of $\text{CpM(CO)}_2(\text{C}_3\text{H}_8)$ with CO (15 psi) in liquid propane (150 psi) at $T = 293\text{--}318 \text{ K}$: (a) $\text{M} = \text{Mn}$ and (b) $\text{M} = \text{Re}$.

values of 52 ± 4 and $33 \pm 3 \text{ kJ mol}^{-1}$ for $\text{M} = \text{Re}$ and Mn , respectively.

FTIR Spectroscopy at Low Temperature. The activation parameters measured above can be used to estimate the lifetime of these propane complexes at low temperature by extrapolation of the Arrhenius equation. The resulting lifetime for $\text{CpMn(CO)}_2(\text{propane})$ is estimated as several minutes at 130 K, while that for $\text{CpRe(CO)}_2(\text{propane})$ is a few hours at 160 K. Because these values have large uncertainties, we studied the propane complexes by FTIR spectroscopy at low temperature to test their viability as targets for NMR spectroscopy. A solution of CpMn(CO)_3 in propane at 130 K was photolyzed for 90 s using a broad-band UV source (125 W Hg-arc lamp). The parent $\nu(\text{CO})$ bands at 2028 and 1945 cm^{-1} decreased in intensity at the same time as two new bands were formed at 1960 and 1893 cm^{-1} (Figure 3, Table 1). These new bands, assigned to $\text{CpMn(CO)}_2(\text{C}_3\text{H}_8)$ (Table 2),^{40,44,55} decay with a lifetime of 6.6 min ($k_{\text{obs}} = (2.5 \pm 0.2) \times 10^{-3} \text{ s}^{-1}$, Figure 3b). Similar experiments were performed with CpRe(CO)_3 in liquid propane at 160 K (Table 1). The bands due to $\text{CpRe(CO)}_2(\text{C}_3\text{H}_8)$ decay with a lifetime of 47 min ($k_{\text{obs}} = (3.5 \pm 0.3) \times 10^{-4} \text{ s}^{-1}$).

NMR Spectroscopy. We investigated the photochemistry of CpMn(CO)_3 in alkane solvents at low temperature employing a laser ($\lambda = 355 \text{ nm}$) that irradiates the sample within a high-pressure sapphire tube inside the probehead of a 600 MHz NMR spectrometer (see Experimental Section). For reference, we have

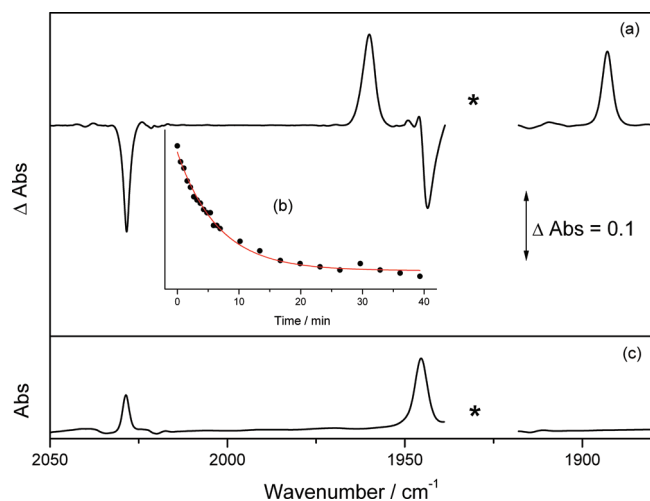


Figure 3. (a) FTIR difference spectrum showing formation of $\text{CpMn}(\text{CO})_2(\text{C}_3\text{H}_8)$ after UV irradiation (90 s broad-band) of $\text{CpMn}(\text{CO})_3$ in liquid propane at 130 K; (b) kinetic trace showing the decay of $\text{CpMn}(\text{CO})_2(\text{C}_3\text{H}_8)$; and (c) FTIR spectrum of the same sample before photolysis. Asterisk denotes a strong solvent absorption, which has been removed for clarity.

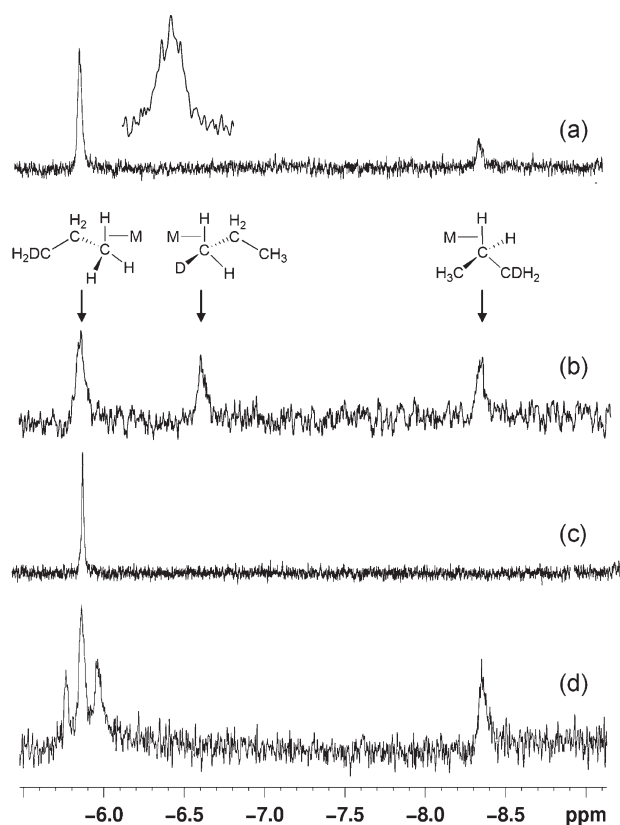


Figure 4. High-field region of ^1H NMR spectrum obtained at 133 K after 355 nm laser irradiation of $\text{CpMn}(\text{CO})_3$ in (a) propane (with resolution enhancement shown in inset); (b) propane-1- d_1 ; (c) propane-2,2- d_2 ; and (d) propane- $^{13}\text{C}_1$.

also studied $\text{CpRe}(\text{CO})_3$ in the same solvents, but with 266 nm irradiation. We have used protio solvents with the consequence that solvent suppression was required. Integrations were

measured relative to a reference, typically benzene or CH_2Cl_2 for the manganese samples or THF for the rhenium samples, which were added in trace amounts. Further details are given in the Experimental Section.

The photolysis at 355 nm (5 min) of a dilute solution (10–20 mmol dm^{−3}) of $\text{CpMn}(\text{CO})_3$ in propane at 133–136 K results in a 40–50% decrease in intensity of the Cp resonance at δ 4.58 (s) and the appearance of two new Cp resonances at δ 4.21 (shoulder) and 4.19 (s), together with two new resonances in the high-field region at δ −5.86 (t, J = 6.1 Hz) and δ −8.36 (m) with an integration ratio of 3:1, respectively (Figure 4a, Table 3). As a result of the solvent suppression, it is not possible to obtain a reliable integration of the Cp resonance relative to high-field resonances. The lifetime of the photoproduct was measured by integration of the resonance at δ −5.86 relative to that of CH_2Cl_2 added as a trace calibrant as ca. 22 ± 2 min at 134 K (Figure 5, laser off during decay). Comparisons with experiments without CH_2Cl_2 indicated that the dichloromethane did not affect the lifetime at these concentrations. The lifetime measured by following the decay of the resonance at δ −8.36 was ca. 15 min, but the error in the integration of this weaker resonance is substantial, and we cannot state that the lifetime is significantly different from that measured at δ −5.86.

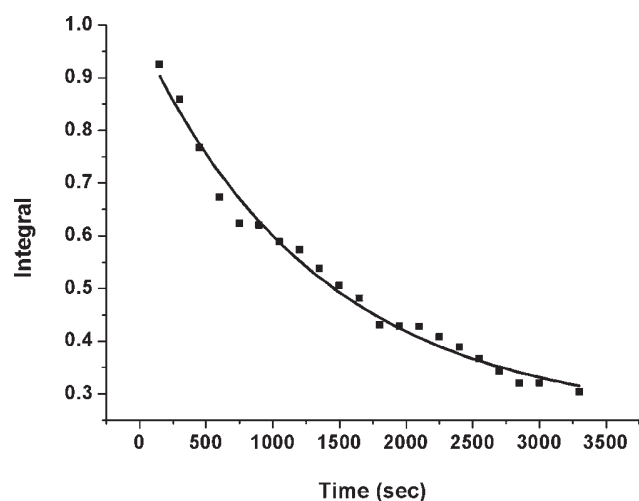
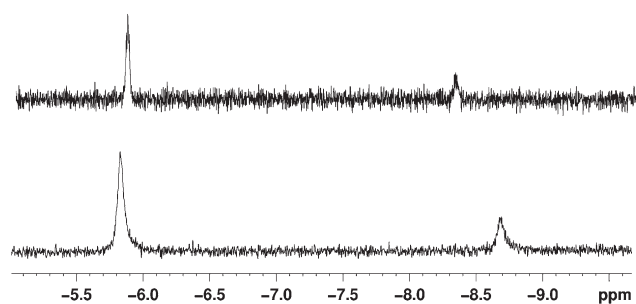
An analogous experiment using propane-1- d_1 resulted in the production of three resonances in the high-field region at δ −5.86, −6.60, and −8.36, with an intensity pattern of 3:2:2 (Figure 4b). An experiment using propane-2,2- d_2 generates just one narrow resonance after laser irradiation in the high-field region at δ −5.86 (Figure 4c). The ^1H NMR spectrum obtained after photolysis of $\text{CpMn}(\text{CO})_3$ in neat ^{13}C -1- C_3H_8 displays resonances for the Cp protons at δ 4.21 and 4.19 together with the η^2 -CH protons at δ −5.86 and δ −8.36, as expected. The δ −5.86 resonance is flanked by satellites with a large $^1J_{\text{C-H}}$ coupling of 119 Hz (Figure 4d). The presence of chemical impurities, notably ^{13}C -1-ethylene, in the ^{13}C -1- C_3H_8 reduced the lifetime of the product and prevented us from recording the ^{13}C – ^1H correlation spectrum. The experimental value of $^1J_{\text{C-H}}$ represents an average of the values for the coordinated C–H bond and the two geminal uncoordinated C–H bonds. Assuming that their value of $^1J_{\text{C-H}}$ is the same as that in free propane (124.5 Hz), we can deduce that the true value for the coordinated C–H bond is $J_{\text{C-H}}^{\eta^2}$ 108.4 Hz.

The high-field resonances could arise from metal hydride complexes or from metal alkane complexes. The effect of deuteration at C1 and the large value of $J_{\text{C-H}}$ provide conclusive evidence for assignment as alkane complexes.^{18,43–46} There are two possible sites for propane to coordinate to the $[\text{CpMn}(\text{CO})_2]$ fragment. On monodeuteration at C1, a new resonance is observed at δ −6.60 in addition to the resonance at δ −5.86 (Figure 4b). This extra resonance is consistent with an isotopic perturbation of equilibrium (IPE) in $\text{CpMn}(\text{CO})_2(\eta^2\text{-C1-H-propane})$ that arises if one coordinated C–H bond is undergoing rapid exchange with the unbound geminal proton of the methyl unit of the alkane. The shifted resonance at δ −6.60 (shift $\Delta\delta$ −0.75 ppm) can be assigned to the isotopomers with one deuterium on the coordinated carbon. The resonance at δ −5.86 is unshifted and corresponds to isotopomers with the three protons on the coordinated methyl and one deuterium on the uncoordinated methyl unit (Figure 4b). On deuteration at C2, the resonance at δ −8.36 disappears altogether, showing that it can be attributed to $\text{CpMn}(\text{CO})_2(\eta^2\text{-C2-H-propane})$ (Figure 4c). The changes in integration of the high-field resonances

Table 3. Observed ^1H NMR Chemical Shifts (δ /ppm) and Coupling Constants (J/Hz) for $\text{CpM}(\text{CO})_2(\text{alkane})$ Complexes in High-Field Region^a

	M = Mn (at 133–136 K)	M = Re (at 161–171 K)
$\text{CpM}(\text{CO})_2(\eta^2\text{-C1-H-propane})$	−5.86 (t, $J = 6.1$ Hz)	−2.09 (t, $J = 6.5$ Hz)
$\text{CpM}(\text{CO})_2(\eta^2\text{-C2-H-propane})$	−8.36 (m)	−2.75 (m)
$\text{CpM}(\text{CO})_2(\eta^2\text{-C1-D-propane})$	−6.60 ($\Delta\delta$ 0.75 ppm)	−2.75 ^b ($\Delta\delta$ 0.66 ppm)
$\text{CpM}(\text{CO})_2(\eta^2\text{-C1-H-butane})$	−5.83 (m)	−2.08 (m)
$\text{CpM}(\text{CO})_2(\eta^2\text{-C2-H-butane})$	−8.68 (m)	−3.22 (m)
$\text{CpM}(\text{CO})_2(\eta^2\text{-C1-D-butane})$	−6.58 ($\Delta\delta$ 0.77 ppm)	−2.76 ($\Delta\delta$ 0.67 ppm)
$\text{CpM}(\text{CO})_2(\eta^2\text{-cyclopentane})$	−7.53 ^c (m)	−2.32 (m) ^d

^a Note that all the resonances are observed under conditions of rapid exchange between geminal and coordinated C–H bonds. ^b The resonance of $\text{CpRe}(\text{CO})_2(\eta^2\text{-C1-D-propane})$ overlaps with that of $\text{CpRe}(\text{CO})_2(\eta^2\text{-C2-H-propane})$. ^c 5% cyclopentane in propane. ^d From ref 42.

**Figure 5.** Kinetics of decay of $\text{CpMn}(\text{CO})_2(\eta^2\text{-C1-H-propane})$ measured by NMR spectroscopy at 134 K.**Figure 6.** High-field region of ^1H NMR spectrum obtained after 355 nm laser irradiation of $\text{CpMn}(\text{CO})_3$ in butane (below) and in propane (above) at 136 and 134 K, respectively.

on partial deuteration are consistent with coordinated alkyl groups of the propane. The resonances of the uncoordinated alkyl groups of the propane are assumed to be hidden under the resonance of free propane. This deduction implies that chain walking is slow on the NMR time scale in contrast to the rapid geminal exchange. All of these characteristics, including the values of $\Delta\delta$ and of $J_{\text{C-H}}$, are consistent with previously characterized $\text{CpRe}(\text{CO})_2(\text{alkane})$ complexes.^{42–45} For a quantitative comparison of $\Delta\delta$, the best comparator is $\text{CpRe}(\text{CO})_2(\text{pentane})$.⁴³

The laser photochemistry of $\text{CpMn}(\text{CO})_3$ was also studied in liquid butane at 136 K. The ^1H NMR spectrum displays two

new high-field resonances for the products at $\delta = -5.83$ and -8.68 with relative integration 3:1 that can be attributed to the alkane complexes $\text{CpMn}(\text{CO})_2(\eta^2\text{-C1-H-butane})$ and $\text{CpMn}(\text{CO})_2(\eta^2\text{-C2-H-butane})$ by comparison with the previous photolysis in propane (Figure 6, Table 3). A single broad resonance in the Cp region was observed at δ 4.19 due to overlap of the two products. The estimated lifetime of $\text{CpMn}(\text{CO})_2(\eta^2\text{-C1-H-butane})$ complex is 5.5 min, while for $\text{CpMn}(\text{CO})_2(\eta^2\text{-C2-H-butane})$ complex it is approximately 3.5 min (error of about 20%, see Table 4). An experiment with butane- d_1 showed resonances at $\delta = -5.83$, -6.58 , and -8.68 . The upfield shift ($\Delta\delta = -0.77$) on deuteration confirms these assignments. The $\delta = -6.58$ resonance arises by IPE as described for the propane analogue.

The lability of the manganese propane and butane complexes indicates that the solvent must melt below 140 K to allow sufficient time for data collection in this type of experiment. Cyclopentane forms the most stable of the $\text{CpRe}(\text{CO})_2(\text{alkane})$ complexes but melts at 179 K. We therefore irradiated $\text{CpMn}(\text{CO})_3$ in liquid propane with 5% added cyclopentane at 133 K. In addition to the two resonances of $\text{CpMn}(\text{CO})_2(\eta^2\text{-C1-H-propane})$ and $\text{CpMn}(\text{CO})_2(\eta^2\text{-C2-H-propane})$, we observed a resonance at $\delta = -7.53$ consistent with $\text{CpMn}(\text{CO})_2(\eta^2\text{-cyclopentane})$. Notably, this species could still be detected 16 min after the laser had been turned off, while the signals of the propane complexes had disappeared.

Several alkane complexes of $[\text{CpRe}(\text{CO})_2]$ have already been reported by Ball et al., but no data are available for propane and butane. We therefore undertook laser photolysis experiments with these solvents at temperatures between 161 and 171 K and characterized the corresponding alkane complexes. The results are fully consistent with previous data for $\text{CpRe}(\text{CO})_2(\text{alkane})$ and are listed in Table 3 (see Supporting Information for figures). The relative integration of the two high-field resonances of the rhenium alkane complexes is unreliable because they are very close to the suppressed resonance of the free alkane.

The estimated lifetimes and free energies of activation obtained from transition state theory for both $\text{CpMn}(\text{CO})_2(\text{alkane})$ and $\text{CpRe}(\text{CO})_2(\text{alkane})$ are given in Table 4. These molecules decay in the NMR experiments by reaction either with expelled CO reforming starting material, or with $\text{CpM}(\text{CO})_3$ to form $\text{Cp}_2\text{M}_2(\text{CO})_5$, or with itself to form $\text{Cp}_2\text{M}_2(\text{CO})_4$, or with residual impurities to form $\text{CpM}(\text{CO})_2\text{L}$ ($\text{M} = \text{Mn}$ or Re).^{55–57} The rates of decay will depend linearly on the concentration of the incoming reagent if the reaction is associative. However, the same will also be true of a dissociative reaction because there will be competition with an extremely fast back reaction with

Table 4. Lifetime Data^a and Free Energies of Activation for Metal Alkane Complexes Derived from NMR Measurements

M:	lifetime (temp), min (K)		ΔG^\ddagger (kJ/mol) ^b	
	Mn	Re	Mn	Re
CpM(CO) ₂ (η^2 -C1-H-propane)	22 ± 2 (134)	60 (161)	39.9	50
CpM(CO) ₂ (η^2 -C2-H-propane)	15 (134)	50 (161)	39.5	49
CpM(CO) ₂ (η^2 -C1-H-butane)	5.5 (136)	13 (171)	39	51
CpM(CO) ₂ (η^2 -C2-H-butane)	3.5 (136)	18 (171)	39	51

^a Errors approximately 20% unless otherwise stated. ^b At the temperatures indicated in columns 2 and 3.

alkane.⁵⁸ Because the concentrations of the incoming reagents are different in the IR experiments from the NMR experiments, the lifetimes are not exactly the same for the two techniques. This analysis also explains why a trace of impurities such as alkenes affects the observed lifetimes. If the reactions are dissociative, we can regard the free energies of activation as lower limits for the free energies of dissociation of alkane.

The measurements of the lifetimes of the alkane complexes by NMR spectroscopy allow us to interrogate each of the two isomers independently. Although the measured lifetimes of the CpM(CO)₂(η^2 -C1-H-alkane) are slightly longer than those for CpM(CO)₂(η^2 -C2-H-alkane), we cannot state that the difference is significant and therefore that one isomer is more labile than the other. Indeed, the possibility remains that there is a dynamic equilibrium between them in which interchange occurs on a time scale of seconds or minutes that is too slow to affect the NMR spectra. Such exchange could occur by chain-walking or by a dissociative mechanism.

CONCLUSIONS

Our results demonstrate that manganese alkane complexes may be observed by both IR and NMR spectroscopy at low temperature with suitably chosen alkanes. The use of IR spectroscopy assists in the selection of suitable alkanes and provides kinetic information. Both propane and butane yield two isomers (Scheme 2), coordinated via a C–H bond of either the methyl or the methylene groups.⁵⁹ Their lifetimes are just sufficient for NMR spectroscopic measurement at 130–140 K. The NMR characteristics are similar to those of the rhenium analogues observed previously, but the ¹H resonances are found at considerably higher field.⁶⁰ The presence of the two isomers is revealed by NMR spectroscopy, but they are not distinguishable by IR spectroscopy. The observation of both isomers in approximately statistical proportions is consistent with previous measurements on CpRe(CO)₂ complexes. We may also compare with the indirect studies of alkanes coordination at Tp⁺Rh(CNR) in which a methylene group coordinates 1.5× faster than a methyl group, but C–H cleavage occurs only at the methyl group.¹³ The manganese alkane complexes and their analogues with other alkanes are likely to be formed as reaction intermediates in a variety of reactions of half sandwich manganese carbonyls. Our results extend the range of alkane complexes observable by NMR spectroscopy to the first row transition metals.

EXPERIMENTAL SECTION

Time-Resolved Infrared Spectroscopy. Room temperature TRIR measurements were made using the Nottingham point-by-point diode spectrometer, which has been discussed in detail elsewhere.⁶¹

Briefly, a continuous wave lead-salt diode laser is used to measure the change in IR transmission at a particular frequency following 266 or 355 nm irradiation by a frequency quadrupled/tripled Nd:YAG laser (Spectra Physics Quanta-Ray GCR-12). This measurement is repeated at different frequencies across the spectral region of interest such that a difference spectrum is constructed in a point-by-point manner. High pressure liquid propane experiments were conducted in a stainless-steel cell fitted with CaF₂ windows (15 × 10 mm).⁶² Fresh solutions of CpM(CO)₃ (M = Mn, Re) were flowed into the cell after each UV laser shot using a high pressure pump (MicroPump Corp.) and allowed to thermally equilibrate at 298 K before taking the next measurement.

Low-temperature spectroscopic measurements were performed in a high pressure-low temperature (HPLT) apparatus.⁶³ A few crystals of CpM(CO)₃ were placed in the cell, which was subsequently filled with liquid propane and cooled to 130 K (M = Mn) or 160 K (M = Re) and photolyzed with a broad-band medium-pressure mercury arc (Philips HPK, 125 W). The reaction was monitored using an FTIR spectrometer (Avatar 360, Nicolet) at 2 cm^{−1} resolution.

NMR Spectroscopy. We described our setup for in situ laser photolysis within an NMR spectrometer in recent papers.^{34,46} A diagram is shown in the Supporting Information of ref 46. The TRIR and the NMR photochemistry are based on a common pulsed laser operating at 355 or 266 nm. Very dilute samples of [Ru(CO)₂(Ph₂PCH₂CH₂-PPh₂)(PPh₃)] in C₆D₆ or [RuH₂(CO)(Ph₂PCH₂CH₂CH₂PPh₂)(PPh₃)] in CH₂Cl₂ were used for laser alignment at 355 or 266 nm, respectively, with *para*-hydrogen amplification in real time. NMR spectra were recorded on a Bruker Avance wide-bore 600 MHz spectrometer with solvent suppression achieved via a water suppression pulse program using excitation sculpting with gradients (zgpg30).⁶⁴ ¹H NMR spectra were calibrated by adding a trace of benzene, taken as resonating at δ 7.15, or CH₂Cl₂ at δ 5.32. Laser photolysis was carried out with a pulsed Nd:YAG laser (Continuum Surelite II) fitted with a frequency tripling crystal. Operating conditions were typically 10 Hz repetition rate, flash lamp voltage 1.49 kV, Q-switch delay increased from the standard to 320 μ s yielding a laser power of 85 mW when operating at 355 nm, and increased to 290 μ s yielding a laser power of 65 mW for 266 nm.

The samples of CpM(CO)₃ (M = Mn, Re, 1–2 mg, Strem) are contained in a sapphire high pressure NMR tube (IDEAS! Uva B.V.); approximately 0.4 mL of solvent was transferred either on a high pressure line or on a high vacuum line equipped with a mercury diffusion pump. For kinetics, the integration of the resonances at high-field region was measured relative to that of benzene or THF added as calibrants in trace quantities.

For NMR experiments, propane (BOC, instrument grade N2.5), butane (BOC, instrument grade N2.5), and propane-2,2-*d*₂ (98% atom D, Isotec TM) were used as received. Propane-1-¹³C (99% atom ¹³C) was obtained from Isotec TM and was purified before use. The gas was passed through a U-tube containing Pt (5%)/charcoal catalyst (Johnson Matthey) on a high vacuum line at 195 K to trap ethylene impurities.

Propane-1-*d*₁ was synthesized from the corresponding Grignard prepared by adding dropwise 17.6 mL (2 mol) of 1-chloropropane over

a boiling solution of magnesium turnings (5.35 g, 0.22 mol) in 100 mL of dry *n*-butyl ether under argon and refluxing the resulting gray solution for 2 h. The solution was cooled to 263 K, and the system was evacuated before the dropwise addition of 0.78 mL of D₂O. The propane-1-*d*₁ generated was passed through a trap at 227 K to remove *n*-butyl ether, collected in a trap cooled at 157 K (ether liquid nitrogen slush bath), and transferred into a glass bulb on a high vacuum line. The product was characterized by IR and NMR spectroscopy.⁶⁵ In the case of the experiments with CpRe(CO)₃, propane-1-*d*₁ was purified following the same method as for propane-1-¹³C purification. Butane-1-*d*₁ (98 atom %D) was obtained from CDN isotopes and purified before use. In this case, it was passed through a U-tube containing Pt/charcoal catalyst at 243 K. Cyclopentane was purified before use by stirring with concentrated H₂SO₄ overnight, washing with water and drying over MgSO₄, then storing over a potassium mirror.

■ ASSOCIATED CONTENT

S Supporting Information. Spectra showing formation of CpRe(CO)₂(propane) and CpRe(CO)₂(butane). This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

mike.george@nottingham.ac.uk; robin.perutz@york.ac.uk

■ ACKNOWLEDGMENT

We thank the EPSRC (EP/D058031 and EP/D055768) and the Universities of Nottingham and York for funding. O.T. would like to thank the Ministerio de Ciencia e Innovación and the Fundación Española para la Ciencia y la Tecnología for funding. M.W.G. gratefully acknowledges receipt of a Royal Society Wolfson Merit Award. We would also like to thank P. Fields, R. Wilson, M. Guyler, C. Mortimer, and D. C. Williamson for technical assistance. We thank Prof A. F. Lee for a sample of Pt on charcoal.

■ REFERENCES

- (1) Perutz, R. N.; Turner, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4791.
- (2) Poliakov, M.; Turner, J. J. *Dalton Trans.* **1974**, 2276.
- (3) Perutz, R. N.; Hall, C. *Chem. Rev.* **1996**, *96*, 3125.
- (4) Crabtree, R. H. *Angew. Chem., Int. Ed.* **1993**, *32*, 789.
- (5) Kelly, J. M.; Hermann, H.; von Gustorf, E. K. *J. Chem. Soc., Chem. Commun.* **1973**, 105.
- (6) Hermann, H.; Grevels, F. W.; Henne, A.; Schaffner, K. *J. Phys. Chem.* **1982**, *86*, 5151.
- (7) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507.
- (8) Crabtree, R. H. *J. Chem. Soc., Dalton Trans.* **2001**, 2437.
- (9) Kubas, G. J. *Metal Dihydrogen and σ -Bond Complexes*; Kluwer Academic Publishers: New York, 2001.
- (10) Brookhart, M.; Green, M. L. H.; Parkin, G. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 6908.
- (11) Lersch, M.; Tilset, M. *Chem. Rev.* **2005**, *105*, 2471.
- (12) Bercaw, J. E.; Chen, G. S.; Labinger, J. A.; Lin, B. L. *Organometallics* **2010**, *29*, 4354.
- (13) Jones, W. D. *Inorg. Chem.* **2005**, *44*, 4475.
- (14) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154.
- (15) Perutz, R. N.; Sabo-Etienne, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 2578.
- (16) Hartwig, J. F.; Cook, K. S.; Hapke, M.; Incavito, C. D.; Fun, Y.; Webster, C. E.; Hall, M. B. *J. Am. Chem. Soc.* **2005**, *127*, 2538.
- (17) Wei, C. S.; Jimenez-Hoyos, C. A.; Videa, M. F.; Hartwig, J. F.; Hall, M. B. *J. Am. Chem. Soc.* **2010**, *132*, 3078.
- (18) Bernskoetter, W. H.; Schauer, C. K.; Goldberg, K. I.; Brookhart, M. *Science* **2009**, *326*, 553.
- (19) Lo, H. C.; Iron, M. A.; Martin, J. M. L.; Keinan, E. *Chem.-Eur. J.* **2007**, *13*, 2812.
- (20) Bengali, A. A.; Hall, M. B.; Wu, H. *Organometallics* **2008**, *27*, 5826.
- (21) Bengali, A. A.; Fan, W. Y. *Organometallics* **2008**, *27*, 5488.
- (22) Weaver, J. F.; Hakanoglu, C.; Hawkins, J. M.; Asthagiri, A. *J. Chem. Phys.* **2010**, *132*, 024709.
- (23) Janak, K. E.; Parkin, G. *J. Am. Chem. Soc.* **2003**, *125*, 6889.
- (24) Jones, W. D. *Inorg. Chem.* **2005**, *44*, 4475.
- (25) Balcells, D.; Clot, E.; Eisenstein, O. *Chem. Rev.* **2010**, *112*, 749.
- (26) Vastine, B. A.; Hall, M. B. *Coord. Chem. Rev.* **2009**, *253*, 1202.
- (27) Mkhali, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2010**, *110*, 890.
- (28) Alcaraz, G.; Grellier, M.; Sabo-Etienne, S. *Acc. Chem. Res.* **2009**, *42*, 1640.
- (29) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175.
- (30) Lin, Z. Y. *Struct. Bonding (Berlin)* **2008**, *130*, 123.
- (31) Nikonov, G. I. *Adv. Organomet. Chem.* **2005**, *53*, 217.
- (32) George, M. W.; Haward, M. T.; Hamley, P. A.; Hughes, C.; Johnson, F. P. A.; Popov, V. K.; Poliakov, M. *J. Am. Chem. Soc.* **1993**, *115*, 2286.
- (33) Cowan, A. J.; Portius, P.; Kawanami, H. K.; Jina, O. S.; Grills, D. C.; Sun, X.-Z.; McMaster, J.; George, M. W. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 6933.
- (34) Alamir, M. A. H.; Boyle, N. M.; Brookes, C. M.; George, M. W.; Long, C.; Portius, P.; Pryce, M. T.; Ronayne, K. L.; Sun, X.-Z.; Towrie, M.; Vuong, K. Q. *Organometallics* **2009**, *28*, 1461.
- (35) Besora, M.; Carreon-Macedo, J. L.; Cowan, A. J.; George, M. W.; Harvey, J. N.; Portius, P.; Ronayne, K. L.; Sun, X.-Z.; Towrie, M. *J. Am. Chem. Soc.* **2009**, *131*, 3583.
- (36) Calladine, J. A.; Vuong, K. Q.; Sun, X.-Z.; George, M. W. *Pure Appl. Chem.* **2009**, *81*, 1667.
- (37) Sun, X.-Z.; Grills, D. C.; Nikiforov, S. M.; Poliakov, M.; George, M. W. *J. Am. Chem. Soc.* **1997**, *119*, 7521.
- (38) Childs, G. I.; Colley, C. S.; Dyer, J.; Grills, D. C.; Sun, X. Z.; Yang, J. X.; George, M. W. *J. Chem. Soc., Dalton Trans.* **2000**, 1901.
- (39) Cowan, A. J.; George, M. W. *Coord. Chem. Rev.* **2008**, *252*, 2504.
- (40) Childs, G. I.; Grills, D. C.; Sun, X.-Z.; George, M. W. *Pure Appl. Chem.* **2001**, *73*, 443.
- (41) Kuimova, M. K.; Alsindi, W. Z.; Dyer, J.; Grills, D. C.; Jina, O. S.; Matousek, P.; Parker, A. W.; Portius, P.; Sun, X.-Z.; Towrie, M.; Wilson, C.; Yang, J. X.; George, M. W. *Dalton Trans.* **2003**, 3996.
- (42) Gefakis, S.; Ball, G. E. *J. Am. Chem. Soc.* **1998**, *120*, 9953.
- (43) Lawes, D. J.; Gefakis, S.; Ball, G. E. *J. Am. Chem. Soc.* **2005**, *127*, 4134.
- (44) Ball, G. E.; Brookes, C. M.; Cowan, A. J.; Darwish, T. A.; George, M. W.; Kawanami, H. K.; Portius, P.; Rourke, J. P. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 6927.
- (45) Lawes, D. J.; Darwish, T. A.; Clark, T.; Harper, J. B.; Ball, G. E. *Angew. Chem., Int. Ed.* **2006**, *45*, 4486.
- (46) Calladine, J. A.; Torres, O.; Anstey, M.; Ball, G. E.; Bergman, R. G.; Curley, J.; Duckett, S. B.; George, M. W.; Gilson, A. I.; Lawes, D. J.; Perutz, R. N.; Sun, X.-Z.; Vollhardt, P. C. *Chem. Sci.* **2010**, *1*, 622.
- (47) Duckett, S. B.; George, M. W.; Jina, O. S.; Matthews, S. L.; Perutz, R. N.; Sun, X.-Z.; Vuong, K. Q. *Chem. Commun.* **2009**, 1401.
- (48) Roithova, J.; Schroeder, D. *Chem. Rev.* **2010**, *110*, 1170.
- (49) Almelin, M.; Schlange, M.; Schwarz, H. *Chem.-Eur. J.* **2008**, *14*, 5229.
- (50) Schlange, M.; Schwarz, H. *Dalton Trans.* **2009**, *46*, 10155.
- (51) Da Silva, J. C. S.; De Almeida, W. B.; Rocha, W. R. *Chem. Phys.* **2009**, *365*, 85.
- (52) Clot, E.; Eisenstein, O.; Jones, W. D. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 6939.

(53) (a) Evans, D. R.; Drovetskaya, T.; Bau, R.; Reed, C. A.; Boyd, P. D. W. *J. Am. Chem. Soc.* **1997**, *119*, 3633. (b) Castro-Rodriguez, L.; Nakai, H.; Gantzel, P.; Zakharov, L. N.; Rheingold, A. L.; Meyer, K. *J. Am. Chem. Soc.* **2003**, *125*, 15734.

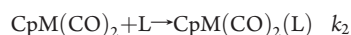
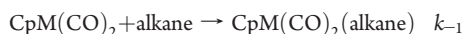
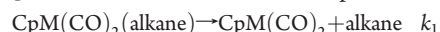
(54) (a) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726. (b) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

(55) Creaven, B. S.; Dixon, A. J.; Kelly, J. M.; Long, C.; Poliakov, M. *Organometallics* **1987**, *6*, 2600.

(56) (a) Foust, A. S.; Hoyano, J. K.; Graham, W. A. G. *J. Organomet. Chem.* **1971**, *32*, C65. (b) Hoyano, J. K.; Graham, W. A. G. *J. Chem. Soc., Chem. Commun.* **1982**, 27. (c) Casey, C. P.; Sakaba, H.; Paulette, N. H.; Powell, D. R. *J. Am. Chem. Soc.* **1991**, *113*, 8165. (d) Bitterwolf, J. E.; Lott, K. A.; Rest, A. J.; Mascetti, J. *J. Organomet. Chem.* **1991**, *419*, 113. (e) Zhang, X.; Li, Q.-S.; Xie, Y.; King, R. B.; Schaefer, H. F., III. *Organometallics* **2008**, *27*, 61.

(57) The observation of products is restricted by precipitation that occurs under the extremely low-temperature conditions, especially for the dinuclear products.

(58) The rate law for an associative reaction is $\text{rate} = k[\text{CpM}(\text{CO})_2(\text{alkane})][\text{L}]$. For a dissociative reaction, the steps are defined as:



The corresponding rate law is $-\text{d}[\text{CpM}(\text{CO})_2(\text{alkane})]/\text{d}t = k_1 k_2 [\text{CpM}(\text{CO})_2(\text{alkane})][\text{L}] / \{k_{-1}[\text{alkane}] + k_2[\text{L}]\}$. When $k_{-1}[\text{alkane}] \gg k_2[\text{L}]$, as is expected, this simplifies to: $k_1 k_2 [\text{CpM}(\text{CO})_2(\text{alkane})][\text{L}] / k_{-1}[\text{alkane}]$, and the rate is also first order in $[\text{L}]$.

(59) The isomers are formed in a 3:1 ratio of integrations. Because the resonances correspond to 3 and 2 protons, respectively, assuming no chain walking (see above), this works out as a 2:1 molar ratio. However, the use of solvent suppression makes these calculations error prone.

(60) The chemical shifts of the $\eta^2\text{-C-H}$ protons of $\text{CpMn}(\text{CO})_2(\text{alkane})$ and $\text{CpRe}(\text{CO})_2(\text{alkane})$ follow the same pattern as those for manganese and rhenium hydride complexes. Comparison of data for hydrides shows that the manganese complexes usually have chemical shifts 1.5–3 ppm to higher field than their Re analogues. Examples: (a) *fac*- $[\text{MH}(\text{CO})_3(\text{Pr}_2\text{POCH}_2\text{CH}_2\text{OPr}_2)]$ ($\delta(\text{Mn-H}) = -7.31$; $\delta(\text{Re-H}) = -5.69$) and *mer*- $[\text{MH}(\text{CO})_3(\text{Ph}_2\text{POCH}_2\text{CH}_2\text{CH}_2\text{OPPh}_2)]$ ($\delta(\text{Mn-H}) = -8.88$; $\delta(\text{Re-H}) = -6.09$). Bolaño, S.; Bravo, J.; Castro, J.; García-Fontan, S.; Lamas, E.; Rodríguez-Seoane, P. *Z. Anorg. Allg. Chem.* **2009**, *635*, 2503. Bolaño, S.; Bravo, J.; Castro, J.; García-Fontan, S.; Marín, M. C.; Rodríguez-Seoane, P. *J. Organomet. Chem.* **2005**, *690*, 4945. (b) $\text{HM}(\text{CO})_5$, $\delta(\text{Mn-H}) = -7.5$; $\delta(\text{Re-H}) = -5.7$. Davison, A.; McCleverty, J. A.; Wilkinson, G. *J. Chem. Soc.* **1963**, 1133. (c) $\text{CpM}(\text{H})_2(\text{CO})_2$ ($\delta(\text{Mn-H}) = -12.62$; $\delta(\text{Re-H}) = -9.62$) and $[\text{Et}_3\text{N}][\text{CpM}(\text{CO})_2\text{H}]$ ($\delta(\text{Mn-H}) = -12.15$; $\delta(\text{Re-H}) = -12.35$). Leong, V. S.; Cooper, N. J. *Organometallics* **1988**, *7*, 2080. (d) Bergman, R. G.; Yang, G. K. *J. Am. Chem. Soc.* **1983**, *105*, 6500. (e) Hoyano, J. K.; Graham, W. A. G. *Organometallics* **1982**, *1*, 783.

(61) George, M. W.; Poliakov, M.; Turner, J. J. *The Analyst* **1994**, *119*, 551.

(62) Poliakov, M.; Howdle, S. M.; Kazarian, S. G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1275.

(63) Cooper, A. I.; Poliakov, M. *Chem. Phys. Lett.* **1993**, *212*, 611.

(64) Hwang, T.-L.; Shaka, A. J. *J. Magn. Reson., Ser. A* **1995**, *112*, 275.

(65) McMurry, H. L.; Thornton, V.; Condon, F. E. *J. Chem. Phys.* **1949**, *17*, 918.