

Transition Metal–Alkane σ -Complexes with Oxygen Donor Co-ligands

Rowan D. Young,[†] Anthony F. Hill,^{*,†} Warwick Hillier,[†] and Graham E. Ball^{*,†}

[†]Institute of Advanced Studies, Australian National University, Canberra, ACT 0200, Australia

^{*}School of Chemistry, University of New South Wales, Sydney, NSW 2052, Australia

S Supporting Information

ABSTRACT: A new family of long-lived alkane σ -complexes of the type $(L_{OEt})Re(CO)_2(\text{alkane})$ [alkane = cyclopentane, cyclohexane, pentane; L_{OEt} = cyclopentadienyltris(diethylphosphito)cobaltate(III)] has been observed using both IR and NMR spectroscopies and computationally interrogated with DFT methods. The oxygen-rich coordination spheres makes these complexes perhaps more relevant as models for intermediates in metal oxide mediated hydrocarbon transformations than other known alkane σ -complexes.

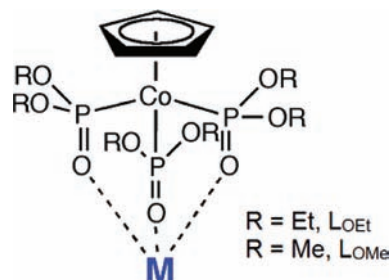


Figure 1. Cyclopentadienyltris(diethylphosphito)cobaltate(III) ligand.

The promise of homogeneous catalysts capable of functionalizing alkanes^{1–3} has led to a great deal of research into transient molecular metal–alkane σ -complexes. These σ -complexes are considered to be short-lived intermediates rather than transition states in the key step of C–H bond activation. Such activation processes may proceed to the formation of (frequently more stable) alkyl hydride complexes, produced through oxidative cleavage of the bound alkane. Alternatively, σ -complex-assisted metathesis (σ -CAM) processes may operate.^{4,5} These σ -complexes are formed by the unorthodox interaction of a metal-centered fragment with the σ electrons shared by a C–H bond. From the perspective of microscopic reversibility, σ -complexes also represent intermediates in the reductive elimination of alkanes from *cis*-hydrido-alkyl complexes. In this respect, the recent spectroscopic identification of a methane complex formed by protonation of a rhodium methyl complex is especially noteworthy.⁶ Model studies of molecular σ -alkane complexes have typically involved classical organometallic co-ligands (CO, cyclopentadienyls, phosphines). In contrast, industrial processes involving the modification of alkanes commonly employ silica, alumina, or metal oxide bound metal sites such that the metal is in an oxygen-rich coordination environment; e.g., so-called “rheniforming” of petroleum to provide high-octane hydrocarbons is mediated by rhenium deposited on the surface of alumina or silica.⁷ To provide a bridge between molecular σ -alkane complexes and the behavior of alkanes on a metal oxide surface, we report herein the spectroscopic characterization and computational interrogation of σ -alkane complexes in which the metal center has an oxygen-rich coordination sphere.

Previously, metal–alkane adduct species of the type $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Re}(\text{CO})(\text{L})(\text{alkane})$ (L = CO, PF₃; R = H, ⁱPr) have been observed and characterized using IR and NMR spectroscopy.^{8–12} These metal–alkane species exhibit a higher stability and longer lifetime than others previously reported using time-resolved IR (TRIR) methods. The shorter lived manganese analogue

$\text{CpMn}(\text{CO})_2(\text{C}_3\text{H}_8)$ has also been observed using NMR spectroscopy very recently.¹³ Computational studies on the hypothetical complex $[\{\text{HB}(\text{N}=\text{NH})_3\}\text{Re}(\text{CO})_2(\text{CH}_4)]$ had suggested that oxidative addition of the coordinated methane molecule would be endothermic,¹⁴ and recently this was substantiated by the spectroscopic observation (FTIR, NMR) of $\text{TpRe}(\text{CO})_2(c\text{-C}_5\text{H}_{10})$ [Tp = hydrotris(pyrazol-1-yl)borate].¹⁵

In search of an oxygen-based scaffold that might emulate the behavior of cyclopentadienyl and tris(pyrazolyl)borate ligands, we chose the cyclopentadienyltris(diethylphosphito)cobaltate ligand (Figure 1), L_{OEt} first described by Kläui.¹⁶ The complex $(L_{OEt})\text{Re}(\text{CO})_3$ (**1**)¹⁷ displays a slightly more octahedral geometry even than $\text{TpRe}(\text{CO})_3$, and the carbonyl stretching frequencies in the IR spectra for **1** suggest that L_{OEt} is a better net electron donor than Tp. Herein we report that IR and NMR spectroscopic monitoring of the photolysis of **1** in the presence of the alkanes cyclopentane (*c*-C₅H₁₀), cyclohexane (*c*-C₆H₁₂), and pentane (*n*-C₅H₁₂) indicates the formation of $(L_{OEt})\text{Re}(\text{CO})_2(\text{alkane})$ (alkane = *c*-C₅H₁₀, **2**; *c*-C₆H₁₂, **3**; *n*-C₅H₁₂, **4**). This provides the first NMR data for an oxygen-ligated alkane complex.¹⁸

Flash photolysis (266 nm, Nd:YAG laser fourth harmonic, 100 flashes) of **1** in neat *c*-C₅H₁₀ at 195–210 K gave the alkane adduct $(L_{OEt})\text{Re}(\text{CO})_2(c\text{-C}_5\text{H}_{10})$ (**2**). Bands at 1916 and 1825 cm⁻¹ (Figure 2) correspond to the carbonyl stretching modes for the formation of the alkane adduct **2**, while the bleaching of bands at 2020 and 1892 cm⁻¹ correspond to depletion of the parent tricarbonyl species **1**.

After irradiation, the bands attributed to **2** diminished with time, obeying an apparent first-order decay constant ($t_{1/2(200\text{K})} = 470$ s; see Supporting Information). Subsequent experiments

Received: April 15, 2011

Published: July 15, 2011



Figure 2. FTIR difference spectrum of $\sim 10^{-3}$ M $(L_{OEt})Re(CO)_3$ (**1**) in $c\text{-C}_5\text{H}_{10}$ at 200 K after exposure to 266 nm radiation.

between 195 and 210 K also followed a first-order decay and allowed the determination of the activation energy, $E_a = 29.7 \pm 5.8$ kJ mol $^{-1}$, for the disappearance of **2** and $\Delta H^\ddagger = 28.0 \pm 5.8$ kJ mol $^{-1}$, $\Delta S^\ddagger = -156 \pm 29$ J mol $^{-1}$ K $^{-1}$. The ΔH^\ddagger value gives a lower limit on the binding energy of the $c\text{-C}_5\text{H}_{10}$ and would provide a correct value in the case of a purely dissociative process. However, the large negative ΔS^\ddagger value suggests an associative mechanism for the decay process, and so the binding energy is likely much larger. By comparison, $CpRe(CO)_2(c\text{-C}_5\text{H}_{10})$ reacts with CO with $\Delta H^\ddagger = 34.8$ kJ mol $^{-1}$, $\Delta S^\ddagger = -78.3$ J mol $^{-1}$ K $^{-1}$.¹⁹

The most common decay product observed was the parent tricarbonyl **1**, indicated by a regrowth of bands at 2020 and 1892 cm $^{-1}$, presumably via recombination of **2** with previously photo-ejected carbon monoxide. However, a portion of the product **2** decayed to other species, corresponding to the growth of new bands at 1958 and 1847 cm $^{-1}$, the latter perhaps being indicative of $\nu(\mu\text{-CO})$ in a binuclear species. We note that the mechanism of re-formation of **1** may be complex since direct recombination of **2** with CO should be a second-order process, which is not observed.

The high solubility of **1** in alkane solvents allowed low-temperature NMR spectroscopy to be employed in characterizing the alkane adducts formed when **1** was irradiated in $c\text{-C}_5\text{H}_{10}$, $n\text{-C}_5\text{H}_{12}$, and $n\text{-C}_5\text{H}_{12}/c\text{-C}_6\text{H}_{12}$ solutions.

Illumination of **1** in 90:10 $c\text{-C}_5\text{H}_{10}$:pentane- d_{12} in the NMR spectrometer (fiber-optics/Hg arc lamp) again gave alkane adduct **2**. Diagnostic for the appearance of **2** was a new signal at $\delta_H -4.12$, shown in Figure 3, which has a width at half-height of 19 Hz (17 Hz when ^{31}P decoupled) which is attributed to the averaged resonances of the bound CH_2 unit of a $c\text{-C}_5\text{H}_{10}$ ligand. This resonance is sufficiently broad to obscure any anticipated multiplicity, cf. the quintet observed for the $\text{CH}_2\text{-Re}$ resonance of $CpRe(CO)_2(c\text{-C}_5\text{H}_{10})$ ($^3J_{\text{HH}} = 6.6$ Hz).¹¹ The signals for the Cp and ethyl protons in complex **2** are obscured by relatively intense signals of the parent complex **1** as a result of the poor photochemical yield of complex **2**, $\sim 4.5\%$ in this case.

Further evidence supporting the presence of alkane σ -complex formation was obtained by monitoring the photolysis of **1** in 2:1 pentane- d_{12} : $c\text{-C}_6\text{H}_{12}$ at 178 K. Two new resonances at $\delta_H -1.06$ and -8.30 were observed which we assign to the equatorial and axial protons, respectively, of the complexed methylene unit in $(L_{OEt})Re(CO)_2(c\text{-C}_6\text{H}_{12})$ (**3**). At 178 K, the $c\text{-C}_6\text{H}_{12}$ moiety is effectively frozen in a chair conformation with chemically different $c\text{-C}_6\text{H}_{12}$ protons. Repeating the photolysis of **1** in 2:1 $n\text{-pentane-}d_{12}$:cyclohexane- $^{13}\text{C}_6$ at 178 K led to $(L_{OEt})Re(CO)_2(c\text{-C}_6\text{H}_{12-^{13}\text{C}_6})$ ($3\text{-}^{13}\text{C}_6$) being formed. The product continued to form after irradiation had ceased due to net conversion of unseen $(L_{OEt})Re(CO)_2(n\text{-pentane-}d_{12})$ to the $c\text{-C}_6\text{H}_{12}$ adduct. A ^{13}C -coupled HSQC spectrum (see SI)

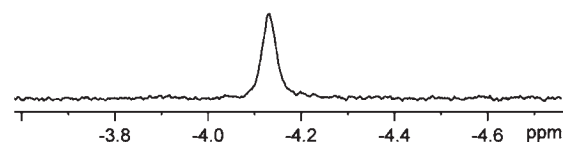


Figure 3. Expansion of the ^1H NMR spectrum of a solution of $(L_{OEt})Re(CO)_3$ in 90:10 cyclopentane:pentane- d_{12} after 40 min of illumination at 190 K. Spectrum at 200 K, LB = 2 Hz, NS = 768.

showed that the resonances at $\delta_H -1.06$ and -8.30 are geminal, both bonded to the same carbon ($\delta_C 1.4$, referenced to free $c\text{-C}_6\text{H}_{12}$ at $\delta_C 26.8$). The resonance at $\delta_H -8.30$ has $^1J_{\text{CH}} = 95.6 \pm 2.5$ Hz, consistent with an *agostic* interaction ($\sim 60\text{--}90$ Hz), whereas the resonance at $\delta_H -1.06$ has $^1J_{\text{CH}} = 124.4 \pm 1.5$ Hz, only slightly reduced from the value found in free $c\text{-C}_6\text{H}_{12}$ (~ 128 Hz). It has been shown that there is a direct correlation between a more shielded chemical shift and lower $^1J_{\text{CH}}$ value of a proton and its time spent coordinated to a metal center.^{9,20} Thus we conclude that the hydrogen with a resonance at $\delta_H -8.30$ spends a higher fraction of time bound to the rhenium center than the proton at $\delta_H -1.06$.

These NMR data are indicative of a binding pattern similar to that observed in $CpRe(CO)_2(\text{alkane})$ species;^{8,9,20} when a methylene unit containing two identical protons, such as $c\text{-C}_5\text{H}_{10}$, interacts with the metal center, the two protons are rendered equivalent in the NMR spectra, due to an exchange process that is fast on the NMR time scale that interchanges which proton is instantaneously bound to the rhenium center; when a methylene unit containing two chemically different protons, such as $c\text{-C}_6\text{H}_{12}$, interacts with the metal center, the two protons cannot be rendered equivalent in the NMR spectra. While the exchange process that swaps which proton is instantaneously bound to the metal center is still fast, there is a thermodynamic preference for the binding of one of the protons, resulting in significantly different ^1H chemical shifts and $^1J_{\text{CH}}$ couplings within the bound methylene of the $c\text{-C}_6\text{H}_{12}$ unit, even for a relatively small preference. In the case of $CpRe(CO)_2(c\text{-C}_6\text{H}_{12})$, the NMR data indicated that binding of the axial proton was preferred.²⁰ In the case of **3**, we were unable to confirm the assignment of the resonances at $\delta_H -1.06$ and -8.30 between the axial and equatorial sites due to the broadness of the resonances masking the H–H couplings.

Illumination of **1** in $\sim 95:5$ $n\text{-C}_5\text{H}_{12}$:pentane- d_{12} at 180 K gave resonances at $\delta_H -2.98$, -4.82 , and -5.05 (Figure 4). We assign the three resonances in Figure 4 to the formation of three isomers of $(L_{OEt})Re(CO)_2(n\text{-C}_5\text{H}_{12})$ (**4**) in which the $n\text{-C}_5\text{H}_{12}$ is bound through C1, C2, or C3, specifically $\delta_H -2.98$ [$(L_{OEt})Re(CO)_2(n\text{-C}_5\text{H}_{12}\text{-}\eta^2\text{-C}^1\text{,H}^1)$, **4a**], $\delta_H -4.82$ [$(L_{OEt})Re(CO)_2(n\text{-C}_5\text{H}_{12}\text{-}\eta^2\text{-C}^2\text{,H}^2)$, **4b**], and $\delta_H -5.05$ [$(L_{OEt})Re(CO)_2(n\text{-C}_5\text{H}_{12}\text{-}\eta^2\text{-C}^3\text{,H}^3)$, **4c**], respectively.

The relative intensities of the three peaks were 3.0:1.5:0.6, close to the statistical ratio 3:2:1 that would be observed in the absence of any preference for binding to specific sites. There was insufficient signal-to-noise to generate accurate integrals that compensate for the integral distorting effects of solvent signal suppression as used previously.⁹ Hence, it remains uncertain if there is a slight preference for the binding of the methyl group vs the methylene groups of pentane in this system. Low signal-to-noise also precluded measurement of $^1J_{\text{CH}}$ coupling constants for any of these three complexes to confirm alkane complex character. The ^1H NMR spectrum of **4a–c** resembles much more closely that of

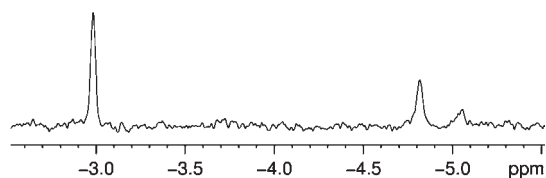


Figure 4. Expansion of the ^1H NMR spectrum of a solution of $\text{L}_{\text{OEt}}\text{-Re}(\text{CO})_3$ after photolysis in 95:5 $n\text{-C}_5\text{H}_{12}$:pentane- d_{12} at 180 K. LB = 7 Hz, NS = 1792.

$\text{CpRe}(\text{CO})_2(n\text{-C}_5\text{H}_{12})$, which is a mixture of three analogous alkane complexes,⁹ rather than that of “ $\text{CpRe}(\text{CO})(\text{PF}_3)(n\text{-C}_5\text{H}_{12})$ ”, which contains a mixture of 1-pentyl hydride and alkane complex components.⁸ Hence, we contend that **4a–c** are likely to be alkane complexes rather than alkyl hydrides.

Complexes of the type $(\text{L}_{\text{OMe}})\text{Re}(\text{CO})_2(\text{alkane})$ (alkane = $c\text{-C}_5\text{H}_{10}$, **2'**; $c\text{-C}_6\text{H}_{12}$, **3'-ax** axial and **3'-eq** equatorial; pentane- $\eta^2\text{-C}^1\text{H}^1$, **4a'**; pentane- $\eta^2\text{-C}^2\text{H}^2$, **4b'**; propane- $\eta^2\text{-C}^1\text{H}^1$, **6a'**; and propane- $\eta^2\text{-C}^2\text{H}^2$, **6b'**) were investigated computationally initially using B3PW91 and M06-L DFT methods (see Supporting Information). The smaller L_{OMe} ligand (indicated by the ' after the compound number) was used in computations. Several starting geometries for each compound studied that were likely to lead to low-energy conformations were explored. Values quoted are for the lowest energy conformation found. The large number of conformational permutations available for the binding of the alkanes to the $(\text{L}_{\text{OMe}})\text{Re}(\text{CO})_2$ fragment prevented an exhaustive exploration of all possible conformations to date.

The binding energy of $c\text{-C}_5\text{H}_{10}$ to the $\text{L}_{\text{OMe}}\text{Re}(\text{CO})_2$ fragment was calculated to be 47.7 (B3PW91) or 74.6 kJ mol^{-1} (M06-L).²¹ Given the significant difference in binding energies from the two DFT methods, a wider range of methods was applied to the $c\text{-C}_5\text{H}_{10}$ and $c\text{-C}_6\text{H}_{12}$ complexes (Table 1), including empirical D3 dispersion corrections.²²

Counterpoise corrections decrease all of the DFT binding energies in Table 1 by between 5.0 and 7.4 kJ mol^{-1} (see SI). This compares with binding energies of $c\text{-C}_5\text{H}_{10}$ to the $\text{CpRe}(\text{CO})_2$ fragment of 51.1/83.8 (B3PW91/B3PW91-D3) or 60.1/63.2 kJ mol^{-1} (M06-L/M06-L-D3) (which decrease by 3.1–3.7 kJ mol^{-1} with counterpoise correction). Dispersion-corrected functionals (-D3) employed the geometries from the noncorrected equivalent functional. In the case of B3LYP-D3, a full geometry optimization leads to a binding energy of 75.3 kJ mol^{-1} , almost identical to the single-point variant in Table 1. The LPNO-CCSD method provides a comparison with a relatively high level wave function method (an approximation to CCSD) that naturally includes dispersion effects and has been shown to be applicable to transition metal systems.²⁴

Traditional hybrid functionals e.g., B3LYP and B3PW91, do not account for dispersion interactions and give lower binding energies than newer functionals that take some account of dispersion interactions (M06, M06-L, $\omega\text{B97X-D}$). Applying the dispersion corrections to B3PW91 and B3LYP leads to a large increase in calculated binding energy, up to a factor of ~ 2 , and values that are closer to those obtained from newer functionals and the LPNO-CCSD method. D3 corrections can also be applied to the M06(-L) functionals with much less change, since these functionals are designed to account for dispersion already. While the accuracy of the empirical dispersion corrections in these systems requires further investigation, it is clear that dispersion interactions play a significant role in binding in these

Table 1. Calculated Binding Energies (kJ/mol) of Various Alkane Sites in Complexes **2'**, **3'**, **4'**, and **6'** Binding to the $(\text{L}_{\text{OMe}})\text{Re}(\text{CO})_2$ Fragment Using Different Methods and Optional D3 Dispersion Corrections

method	complex type						
	2'	3'-ax	3'-eq	4a'	4b'	6a'	6b'
B3PW91	47.7	47.8	46.7	46.6	42.1	45.4	45.1
M06-L	74.6	79.7	76.1	71.2	77.0	71.2	70.0
B3LYP	40.2	40.2	39.6				
M06	79.0	85.9	82.9				
B3PW91-D3	86.6	94.1	90.6	79.0	92.1	76.3	83.0
M06-L-D3	81.2	87.3	84.3	76.9	85.2	76.9	76.0
B3LYP-D3	74.2	79.9	77.6				
M06-D3	91.9	99.9	97.9				
$\omega\text{B97X-D}$	87.2	95.6	92.3				
LPNO-CCSD ²³	82.7						

systems and should be accounted for in studies of alkane binding, as noted recently.²⁵ The calculated geometries of the complexes indicate a typical asymmetric interaction of the bound CH_2 group, with one hydrogen closer to the metal, with a significantly stretched C–H bond, and the other hydrogen farther away, with an unstretched C–H bond (see SI).

Studies on the model 2-propane complex **4'** confirm that the process that interchanges which of the two hydrogens in a methylene unit is directly interacting with the metal is expected to be fast, the calculated barrier being 16.3/14.3 kJ mol^{-1} (B3PW91/-D3). In the case of binding of $c\text{-C}_6\text{H}_{12}$ to the $\text{L}_{\text{OMe}}\text{Re}(\text{CO})_2$ fragment, all DFT methods suggest that the binding of the axial $c\text{-C}_6\text{H}_{12}$ hydrogen is preferred relative to the binding of the equatorial hydrogen by 1.1–3.6 kJ mol^{-1} , and so the more highly shielded resonance at δ –8.30 is the axial hydrogen, as this spends a greater fraction of time directly interacting with the metal center.

Calculated relative binding energies for the C1- and C2-bound pentane complexes are method dependent. The B3PW91 method predicts that binding of the C1 methyl is preferred by 4.5 kJ mol^{-1} , whereas methods accounting for dispersion (M06-L (-D3) and B3PW91) predict the C2 isomer to be more stable by up to 13.1 kJ mol^{-1} . The relative free energies in solution appear to differ by less than ~ 2 kJ mol^{-1} based on our experimental data.

In the case of bound $c\text{-C}_5\text{H}_{10}$, the alkane complex, $[(\text{L}_{\text{OMe}})\text{Re}(\text{CO})_2(c\text{-C}_5\text{H}_{10})]$ (**2'**), was found to be significantly lower in energy in comparison with the potential products of oxidative cleavage of this compound, the cyclopentyl hydride complexes $[(\text{L}_{\text{OMe}})\text{Re}(\text{cyclopentyl})(\text{H})(\text{CO})_2]$ (**5'**), wherein the cyclopentyl and hydride ligands could be *cis* (**5c'**) or *trans* (**5t'**).²⁶ The relative energy of the *cis*-alkyl hydride **5c'** was calculated to be 27.9/16.3 (B3PW91/B3PW91-D3) or 30.4 kJ mol^{-1} (M06-L) higher and the *trans*-alkyl hydride **5t'** 38.3/25.7 (B3PW91/B3PW91-D3) or 35.1 kJ mol^{-1} (M06-L) higher in energy than the $c\text{-C}_5\text{H}_{10}$ complex. Likewise, The *n*-pentyl hydride complexes $[(\text{L}_{\text{OMe}})\text{Re}(n\text{-pentyl})(\text{H})(\text{CO})_2]$ (**7c'** *cis* and **7t'** *trans*), resulting from oxidative cleavage of the corresponding C1-bound pentane complex **4a'**, are calculated (B3PW91/B3PW91-D3) to be higher in energy than the alkane complex isomer **4a'** by 22.5/34.0 (**7c'**) and 31.2/41.0 kJ mol^{-1} (**7t'**). This leads to the conclusion that the observed NMR and IR data for the complexes **2**, **3**, and **5** should be due entirely to the

Table 2. IR Stretching Frequencies (cm^{-1}) of Complexes $\text{LRe}(\text{CO})_3$ and $\text{LRe}(\text{CO})_2(c\text{-C}_5\text{H}_{10})$ in Cyclopentane

ligand (temp)	$\text{LRe}(\text{CO})_3$	$\text{LRe}(\text{CO})_2(c\text{-C}_5\text{H}_{10})$
L_{OEt} (200 K)	2020, 1892	1916, 1825
Cp (180 K)	2029, 1937	1948, 1882
Tp (200 K)	2029, 1919	1940, 1862

alkane complex isomer, as the concentration of an equilibrium amount of alkyl hydride species is expected to negligible.

The lower experimental frequencies of the carbonyl bands of the parent complex **1** and the $c\text{-C}_5\text{H}_{10}$ complex **2**, compared with those of the corresponding Cp and Tp analogues (Table 2), suggest that the L_{OEt} facial ligand acts as a better net donor than the Cp or Tp ligands. Assuming this to be the case, the increased π -basicity of the d_{xy} , d_{xz} , and d_{yz} orbitals of the $\text{L}_{\text{OEt}}\text{Re}(\text{CO})_2$ fragment should lead to more effective population of the C–H σ^* antibonding orbital upon complexation, increasing the extent of travel along the reaction coordinate toward the product of oxidative cleavage. Despite this, the $^1J_{\text{CH}}$ values for the cyclohexane adduct **3** (average 110.0 Hz) and the DFT calculated bond lengths (<0.1 Å longer for the bound C–H bond in **2** vs the Cp analogue) are remarkably similar to those calculated for $\text{CpRe}(\text{CO})_2(c\text{-C}_6\text{H}_{12})$ (average $^1J_{\text{CH}}$ 110.8 Hz, within experimental error of that for **3**). This suggests a minimal difference in the extent of stretching of the bound CH_2 unit, consistent with the view that the backbonding component of alkane–metal interactions is relatively unimportant compared with other X–H σ -complexes.²⁷

The aim of this work was to observe alkanes binding to molecular species that more closely resemble the environment found in heterogeneous catalysts comprising alumina- or silica-supported metal centers, wherein the metal is supported by oxygen donor groups. With the successful observation of a new class of alkane σ -complexes, in which the metal center is likewise supported by multiple oxygen donors, the $\text{L}_{\text{OEt}}\text{Re}(\text{CO})_2(\text{alkane})$ species described here enable a more direct comparison of the binding of alkanes in a molecular setting with that found on a catalytically active surface.

■ ASSOCIATED CONTENT

S Supporting Information. Details of the FT-IR setup; kinetic plots with FT-IR and NMR monitoring; computational and synthetic details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

afhill@rsc.anu.edu.au; g.ball@unsw.edu.au

■ ACKNOWLEDGMENT

This work was supported by the ARC (DP0881692) and an award under the Merit Allocation Scheme through INTERSECT on the NCI National Facility at the ANU.

■ REFERENCES

(1) Mkhaliid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2010**, *110*, 890.

- (2) Conley, B. L.; Tenn, W. J.; Young, K. J. H.; Ganesh, S. K.; Meier, S. K.; Ziatdinov, V. R.; Mironov, O.; Oxgaard, J.; Gonzales, J.; Goddard, W. A.; Periana, R. A. *J. Mol. Catal. A: Chem.* **2006**, *251*, 8.
- (3) Crabtree, R. H. *J. Chem. Soc., Dalton Trans.* **2001**, 2437.
- (4) Labinger, J. A.; Bercaw, J. E. *Nature (London)* **2002**, *417*, 507.
- (5) Perutz, R. N.; Sabo-Etienne, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 2578.
- (6) Bernskoetter, W. H.; Schauer, C. K.; Goldberg, K. I.; Brookhart, M. *Science* **2009**, *326*, 553.
- (7) (a) ElGuindy, M. I. In *Rhenium and Rhenium Alloys*; Bryskin, B. D., Ed.; The Minerals, Metals & Materials Society: Warrendale, PA, 1997; p 89. (b) Gates, B. C.; Katzer, J. R.; Schut, G. C. A. *Chemistry of Catalytic Processes*; McGraw-Hill: New York, 1979. (c) Menon, P. G.; Z. Paal, Z. *Ind. Eng. Chem. Res.* **1997**, *36*, 3282.
- (8) Ball, G. E.; Brookes, C. M.; Cowan, A. J.; Darwish, T. A.; George, M. W.; Kawanami, H. J.; Portius, P.; Rourke, J. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 6927.
- (9) Lawes, D. J.; Geftakis, S.; Ball, G. E. *J. Am. Chem. Soc.* **2005**, *127*, 4134.
- (10) Sun, X.-Z.; Grills, D. C.; Nikiforov, S. M.; Poliakov, M.; George, M. W. *J. Am. Chem. Soc.* **1997**, *119*, 7521.
- (11) Geftakis, S.; Ball, G. E. *J. Am. Chem. Soc.* **1998**, *120*, 9953.
- (12) Cowan, A. J.; George, M. W. *Coord. Chem. Rev.* **2008**, *252*, 2504.
- (13) Calladine, J. A.; Duckett, S. B.; George, M. W.; Matthews, S. L.; Perutz, R. N.; Torres, O.; Vuong, K. Q. *J. Am. Chem. Soc.* **2011**, *133*, 2303.
- (14) Bergman, R. G.; Cundari, T. R.; Gillespie, A. M.; Gunnoe, T. B.; Harman, W. D.; Klinckman, T. R.; Temple, M. D.; White, D. P. *Organometallics* **2003**, *22*, 2331.
- (15) 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.
- (16) El Murr, N.; Chaloyard, A.; Kläui, W. *Inorg. Chem.* **1979**, *18*, 2629.
- (17) Kramer, D. J.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **2001**, *312*, 215.
- (18) A series of crystallographically characterized alkane adducts of uranium ligated by a trialkoxide chelate has been reported: Castro-Rodriguez, I.; Nakai, H.; Gantzel, P.; Zakharov, L. N.; Rheingold, A. L.; Meyer, K. *J. Am. Chem. Soc.* **2003**, *125*, 15734.
- (19) Childs, G. I.; Colley, C. S.; Dyer, J.; Grills, D. C.; Sun, X.-Z.; Yang, J.; George, M. W. *J. Chem. Soc., Dalton Trans.* **2000**, 1901.
- (20) Lawes, D. J.; Darwish, T. A.; Clark, T.; Harper, J. B.; Ball, G. E. *Angew. Chem., Int. Ed.* **2006**, *45*, 4486.
- (21) DFT methods contain optimized geometries and frequencies using a smaller basis (BS1). Quoted energies are from single-point calculations with the larger basis (BS2) and include the BS1 ZPVE, e.g., B3PW91/BS2//B3PW91/BS1. BS1 = SDD+f for Re and Co, 6-31G(d,p) for other atoms; BS2 = SDD+f for Re and Co, 6-311+G(2d,p) for other atoms.
- (22) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104. See Supporting Information for technical details.
- (23) LPNO-CCSD/def2-TZVPP using M06/BS1 geometries.
- (24) (a) Liakos, D. G.; Hansen, A.; Neese, F. *J. Chem. Theory Comput.* **2011**, *7*, 76. (b) Anoop, A.; Thiel, W.; Neese, F. *J. Chem. Theory Comput.* **2010**, *6*, 3137.
- (25) Flener-Lovitt, C.; Woon, D. E.; Dunning, T. H., Jr.; Girolami, G. S. *J. Phys. Chem. A* **2010**, *114*, 1843.
- (26) The cyclopentyl hydride complexes have geometry closer to a distorted pentagonal bipyramid, with the axial positions occupied by CO and O=P donors, more like PBPY-7-12-11243 (**5c'**) and PBPY-7-12-11324 (**5t'**) using the IUPAC nomenclature.
- (27) (a) Cobar, E. A.; Khaliullin, R. Z.; Bergman, R. G.; Head-Gordon, M. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 6963. (b) Kubas, G. J. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 6901.