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Observation of a Tungsten Alkane σ-Complex Showing Selective Binding of Methyl Groups Using FTIR and NMR Spectroscopies

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Supporting Information

ABSTRACT: The alkane σ-complex (HEB)W(CO)$_2$(pentane) (HEB = η^6-hexaethylbenzene) is produced from the UV photolysis of (HEB)W(CO)$_3$ in alkane solvents at low temperature. IR and ^{1}H and ^{13}C NMR spectroscopic data are reported, representing the first NMR data for a group 6 alkane complex. Only binding of the methyl functionality of the pentane ligand was observed in (HEB)W(CO)$_2$(pentane). This contrasts with the previously reported binding of pentane to rhenium fragments, wherein both methylene and methyl groups were observed to bind, with a slight preference for binding of the former. The reason for the preference for binding through the methyl group is investigated, and the steric requirement for the pentane to adopt an unfavorable gauche conformation when bound via a methylene is identified as a contributing factor.

On account of their significance in terms of both fundamental coordination chemistry[1,2] and their role in C−H activation processes,[3,4] transition metal alkane σ-complexes are of substantial current interest. Though dihydrogen, silane, germane, and stannane σ-complexes have been isolated and comprehensively characterized to elucidate their structures and chemistry,[5−8] no report of a C−H σ-complex that is both stable in the solid state[9,10] and solution has been reported. Here we report the first NMR spectroscopic observation of a group 6 alkane σ-complex (HEB)W(CO)$_2$(pentane) (HEB = η^6-hexaethylbenzene) and present preliminary evidence for the formation of the analogous 2,2-dimethylbutane, isobutane, and cycloheptane complexes.

To date, the only alkane complexes observed using NMR spectroscopy are those of the type LpM(CO)$_2$(alkane) (M = Re, Lp = η^5-C$_5$H$_5$ (Cp), η^5-C$_5$H$_4{}^i$Pr, κ^3-HB(pz)$_3$ (Tp), cyclopentadienyltris(diethylphosphito)cobaltate (Kp); M = Mn, Lp = Cp)[11−15] and the cationic methane complex [(PONOP)Rh(CH$_4$)]$^+$.[16] Many more alkane complexes have been observed by means of UV−vis and, most frequently, TRIR spectroscopies, techniques that have the advantage of speed and sensitivity. NMR spectroscopy has the advantage of directly interrogating the alkane ligand and so is an information-rich method of observing alkane adducts.[17]

Short-lived products of flash photolysis of group 6 metal complexes in the presence of alkanes were postulated as the first alkane complexes.[18] Group 6 complexes of the type LM(CO)$_n$(alkane) are among the most well studied alkane complexes using IR and UV methods[1] but have not been observed using NMR spectroscopy. Arene tricarbonyl tungsten species, (arene)W(CO)$_3$, isoelectronic to the previously investigated (η^5-C$_5$H$_5$)Re(CO)$_3$ precursor, are highly soluble in alkane solvents. Previous attempts in our laboratory to photolyze (mesitylene)W(CO)$_3$ in alkanes with low temperature NMR monitoring resulted in the formation of significant amounts of free mesitylene, and no alkane complexes were observed. Following reports of an increase in arene-metal bond strength of more highly substituted arenetricarbonyl chromium complexes,[19] tricarbonyl(η^6-hexaethylbenzene)tungsten, (HEB)W(CO)$_3$ (**1**), Figure 1, was selected as a precursor for the formation of an alkane adduct.

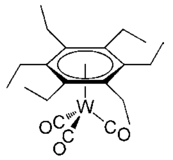

Figure 1. Tricarbonyl(η^6-hexaethylbenzene)tungsten (**1**).

IR monitoring of the flash photolysis (266 nm, 100 flashes) of (HEB)W(CO)$_3$ (**1**) in *n*-pentane at 158 K gave the alkane adduct (HEB)W(CO)$_2$(*n*-pentane). Bands at 1890 and 1836 cm^{-1}, Figure 2, correspond to the carbonyl stretching modes for the formation of the alkane adduct, while the bleaching of bands at 1953 and 1880 cm^{-1} correspond to depletion of the precursor, **1**.

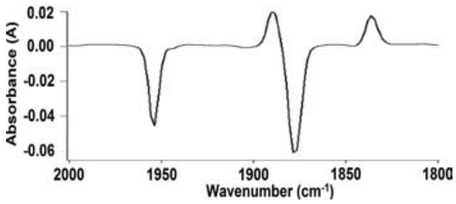

Figure 2. FTIR difference spectrum of a 5 mM solution of (HEB)W(CO)$_3$ in pentane after 100 pulses of 266 nm radiation at 158 K. Reference spectrum taken prior to irradiation.

Decay of the products (in the absence of added CO) did not fit any simple kinetic models well. More than one significant decay pathway is likely to be operating.

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When monitoring the photolysis with NMR spectroscopy, the light source in most cases was a 248 nm KrF excimer laser (GAM EX5-500, GAM Laser Inc. Orlando, FLA). The light from the laser is directed horizontally via two prisms in an optics box to a point above the center of the bore of the magnet of the 600 MHz NMR instrument. At this point a long focal length (*ca* 1 m) lens focuses the beam via a third prism that directs the light vertically down the bore of the magnet onto the top of a 9 cm long, 4 mm OD quartz pipe. This pipe directs the light into the top of the NMR solution contained in a short screw-cap NMR tube fitted with an O-ring around the quartz pipe.[20] The alkane complexes could also be generated using light from a 100 W Hg arc lamp directed into the NMR sample via a silica fiber optic as described previously.[11]

When a solution of (HEB)W(CO)$_3$ (**1**) (0.2−0.5 mg) in *n*-pentane/*n*-pentane-d_{12} (9−12:1; *ca.* 600 μL) is photolyzed at 153−163 K, a decline in the resonances due to the two types of CH$_2$ groups in **1** at δ 2.20 and 2.51 is observed. New peaks at δ 1.91, 1.92, 2.31, 2.39, and 2.53 (overlapped) are observed to grow in along with a shielded resonance at δ −1.59, which we assign to the alkane complex (HEB)W(CO)$_2$(pentane-η^2-C^1,H^1) (**2**) (Figure 3). The resonance at δ −1.59 is a triplet with $^3J_{HH}$ = 6.5 Hz (Figure 3, inset), indicating that this resonance is due to a pentane ligand bound through the methyl group (C1). The data for **2** suggest that the HEB ligand, with alternating "up and down" ethyl groups, is not freely rotating around the W-HEB centroid axis,[21] but the alkane is sufficiently free to move to generate a *pseudo* mirror plane. In this case, six types of ethyl protons should be observed in the ^{1}H NMR spectra, each with an intensity of two protons. A combination of 2D TOCSY (50 ms) and ROESY (200 ms) experiments (Supporting Information (SI)), performed on the photoproducts, permits the identification of five different chemical shifts of HEB benzylic protons. One of the resonances has an intensity of four protons, presumably due to an accidental equivalence of two of these types of hydrogens. Resonances due to the methyl protons present on the arene moiety are hidden by a suppression window required to mask the solvent signal. Four types of CH$_3$ protons in 2 can be identified in the 2D NMR spectra in the range 0.8−1.4 ppm.

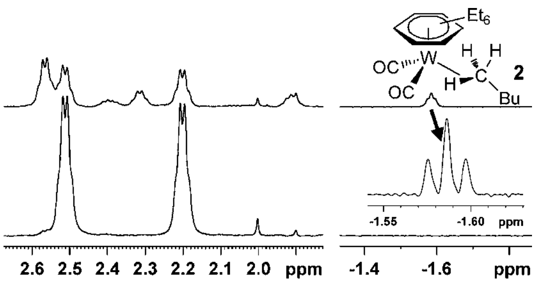

Figure 3. ^{1}H NMR spectra of (HEB)W(CO)$_3$ in *n*-pentane/*n*-pentane-d_{12} (9:1) at 153 K (128 scans) before (bottom) and after (top) photolysis (Hg arc lamp). Inset: resolution enhanced bound methyl resonance of (HEB)W(CO)$_2$(pentane-η^2-C^1,H^1) (**2**) showing coupling to a CH$_2$ group ($^3J_{HH}$ = 6.6 Hz) (2928 scans).

A peak at δ 2.56 was also seen to grow during irradiation and continued to grow even as the bound alkane peak at δ −1.59 decreased in intensity ($t_{1/2}$ >5 h at 153 K). This peak remained after warming to rt, and the addition of a small amount of hexaethylbenzene to the sample confirmed that this peak was due to the formation of the free arene. Repeating the photolysis of a solution of the precursor **1** at 163 K in pentane-1-^{13}C gave (HEB)W(CO)$_2$(^{13}CH$_3$C$_3$H$_6$CH$_3$) (**2-^{13}C$_1$**) and (HEB)W(CO)$_2$(CH$_3$C$_3$H$_6$^{13}CH$_3$). The bound methyl resonance displayed a large C−H coupling constant ($^1J_{CH}$) of 118.4 ± 1 Hz, marginally greater than that of 116.5 Hz in the analogous (η^5-C$_5$H$_4$^{i}Pr)Re(CO)$_2$(pentane).[9] An HSQC experiment (SI) of the sample was conducted, revealing a highly shielded bound carbon atom (δ_C = −39.6). These data confirm **2** to be an alkane complex. We note that interaction of the related (1,3,5-triisopropylbenzene)W(CO)$_2$ fragment with hydrogen leads to dihydride rather than dihydrogen complexes.[22]

The most striking feature of the ^{1}H NMR spectrum of (HEB)W(CO)$_2$(pentane) is that no shielded resonances due to pentane bound via the methylenic hydrogens on C2 or C3 of the pentane could be found. In contrast to previous reports of (η^5-C$_5$H$_4$^{i}Pr)Re(CO)$_2$(pentane) favoring the methylene bound alkane adduct,[12] only the methyl bound proton resonance was observed. Likewise, binding to both the methyl and methylene sites was observed in TpRe(CO)$_2$(alkane), CpMn(CO)$_2$(butane) and KpRe(CO)$_2$(alkane). These other species show little selectivity between binding of CH$_2$ and CH$_3$ sites, but in CpMn(CO)$_2$(butane) a slight preference for binding of the methyl groups is suggested.[13] Accurate integration of the relative intensities of peaks due to different isomers is obfuscated by variations in excitation across the NMR spectra caused by suppression schemes that are mandated by the use of protio alkane solvents.[12]

When (HEB)W(CO)$_3$ (**1**) is irradiated in a variety of other alkane solvents/alkane solvent mixtures at 143−168 K, NMR spectroscopic evidence may be obtained for the formation of the corresponding (HEB)W(CO)$_2$(alkane) species.

More specifically, when **1** is irradiated in 2,2-dimethylbutane/pentane-d_{12} 9:1 at 158 K, two new resonances are observed at δ −1.69 (s) and δ −1.35 (t, $^3J_{HH}$ ~6.6 Hz) assigned to the alkane complexes (HEB)W(CO)$_2$(2,2-dimethylbutane-η^2-C^1,H^1) and (HEB)W(CO)$_2$(2,2-dimethylbutane-η^2-C^4,H^4) respectively. A $^1J_{CH}$ value of 119 ± 2 Hz was measured in the case of (HEB)W(CO)$_2$(2,2-dimethylbutane-η^2-C^1,H^1), confirming this to be an alkane complex. A ^{183}W edited 1D ^{1}H NMR spectrum suggested, with minimal signal-to-noise, that the protons of the bound methyl group of (HEB)W(CO)$_2$(2,2-dimethylbutane-η^2-C^1,H^1) are coupled to tungsten with $^1J_{WH}$ < 20 Hz, confirming the interaction of the alkane with tungsten. The small size of the $^1J_{WH}$ coupling and low abundance of ^{183}W hampered the acquisition of ^{1}H−^{183}W correlation data, and several attempts at acquiring ^{183}W edited 1D and ^{1}H−^{183}W 2D experiments on solutions of **2** were unsuccessful to date.

When a sample of (HEB)W(CO)$_3$ in a mixture of isobutane, cycloheptane, and *n*-pentane-d_{12} 80:10:10 was irradiated at 153 K, new resonances were seen at δ −1.59 (d, $^3J_{HH}$ *ca.* 6.0 Hz) assigned to (HEB)W(CO)$_2$(isobutane-η^2-C^1,H^1) and δ −2.04 (broad), (HEB)W(CO)$_2$(*c*-heptane). Measurement of $^1J_{CH}$ values to confirm that the isobutane and cycloheptane complexes are alkane complexes was not possible in this case. Significantly, the observation of the cycloheptane complex indicates that methylene bound alkane complexes of the (HEB)W(CO)$_2$ fragment can be observed with NMR. However, in contrast to the CpRe(CO)$_2$ fragment, where there is a large preference for binding cycloheptane over isobutane ($K \approx 65$),[23] the methylene bound cycloheptane complex did not appear to be strongly preferred over the methyl bound isobutane product ($K < 2$).

Having confirmed that **2** is clearly an alkane σ-complex, we next address the issue of preferential binding of the pentane via the methyl group. First, we note that the signal-to-noise ratio is relatively low in our spectra, so low concentrations of the C2 or C3 bound isomers may be present in our spectra but below the detection limit (*ca.* 5% of total alkane complex).

The possibility that the C1 isomer is the kinetic product was also considered. A 2D ROESY spectrum recorded at 153 K indicates that there is intramolecular exchange between the bound methyl at δ −1.59 and another resonance at δ 0.90, close to the methyl resonance of free pentane (δ 0.92). We propose that the resonance at δ 0.90 is due to the methyl group of the pentane ligand in **2** that is not interacting with the metal center (C5) (yet to be confirmed). The exchange is occurring at a rate of *ca.* 0.7 s^{-1}. Hence, there is an intramolecular exchange of bound and unbound methyl groups within the pentane ligand. This suggests that equilibration between binding sites within a pentane ligand is likely to occur rapidly after photolysis.

We considered the possibility that the C2 and C3 bound methylene complexes (HEB)W$(CO)_2$(pentane-η^2-C^2,H^2) (**3**) and (HEB)W$(CO)_2$(pentane-η^2-C^3,H^3) (**4**) are actually present but that they were not visible in the ^1H NMR spectra. The WET solvent suppression method employed to acquire the spectrum in Figure 3 (SI) should show any resonances below δ 0 even if relatively broad. We note also that a CH_2 bound complex, the cycloheptane complex, can be detected using NMR spectroscopy. Scenarios in which the bound methylene protons may not be observable due to exchange processes are possible. For example, a rapid exchange between C2 and C3 isomers **3** and **4** could lead to the C2 and C3 protons being undetectable in the spectrum; likewise, a slowing of the processes that renders the two protons in a bound methylene group equivalent may obscure these protons. To account for the possibility that there may be some methylene bound isomers present in the mixture that have undetectable bound alkane proton resonances, the ^1H NMR spectrum of (HEB)-W$(CO)_2$(*n*-pentane) was integrated in the HEB ligand region and compared with the resonance intensity of the bound methyl group. Assuming that the corresponding HEB ligand resonances from the equivalent methylene and methyl bound isomers are at approximately the same chemical shifts (2.26−2.44), if there were solely the C1 bound isomer present, the integral of the CH_3 resonance at δ −1.59 should be 2.7 to 2.8 units, given that 10% of the pentane is deuterated and there is expected to be a slight preference for binding to the protio *n*-pentane based on observations made with [CpRe$(CO)_2$-(c-C_5H_{10})].[11] The observed integrals (4 samples) suggest that 80−100% of the alkane complex is present as the C1 bound form. Hence the methyl bound complex appears to be the major alkane complex, favored by an equilibrium constant, $K > 4$, corresponding to a Gibbs free energy difference of at least 1.8 kJ mol^{-1}.

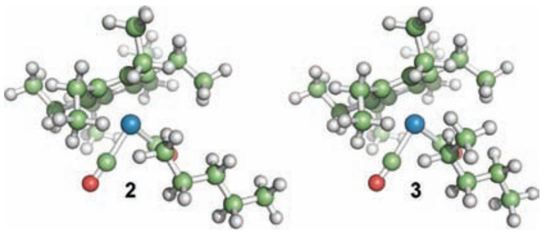

Figure 4. Lowest energy conformations of (HEB)W$(CO)_2$(pentane-η^2-C^1,H^1) **2** and (HEB)W$(CO)_2$(pentane-η^2-C^2,H^2) **3** (M06/BS1).

The source of this free energy difference between CH_3 and CH_2 bound pentane complexes was investigated computationally. Initially, preferred geometries for the C1, C2, and C3 bound complexes were calculated using DFT and the M06 functional (/BS1) from 22 initial isomers of (HEB)W$(CO)_2$(pentane).[24] The same lowest energy conformations of **2** and **3** (Figure 4) were likewise found to be the lowest in energy using the ωB97X-D functional. The most notable feature of the lowest energy conformation of (HEB)W$(CO)_2$(pentane-η^2-C^2,H^2) **3** is that the pentane ligand was found to be in a *trans*−*gauche* conformation rather than an all-*trans* conformation that is the lowest in energy for free pentane. Conformations in which the pentane is bound via the C2 methylene in an all-*trans* conformation are higher in energy due to steric clashes with the ethyl groups of the HEB ligand and/or the CO ligands, resulting in a significantly distorted pentane ligand. This occurs whether the pentane chain is running approximately perpendicular or parallel to the plane of the arene ligand (see SI). The lowest energy conformation of (HEB)W-$(CO)_2$(pentane-η^2-C^1,H^1) **2** contains an all-*trans* pentane conformation however.

The lowest energy conformations of **2** and **3** were then examined in detail using several methods (Table 1).

Table 1. Selected Binding Energies (BE), Relative Electronic Energy (ΔE = E2 − E3), and Relative Free Energy at 153 K (ΔG) of the Two Isomers 2 and 3 Calculated Using Various Methods with and without -D3 Dispersion Corrections[25] in kJ mol^{-1}

method[a]	BE 2	BE 3	ΔE	ΔG
M06/BS2[b]	60.9	64.3	3.3	0.7
M06/BS4[b]	–	–	2.2	−0.4
M06/BS4 SMD solvent[b]	–	–	0.4	−2.2
B3PW91/BS2[b]	28.7	19.7	−9.0	−10.4
ωB97X/BS2[b]	50.9	51.7	0.8	−0.3
B2GP-PLYP/BS3[c]	–	–	−1.8	−4.4
M06-D3/BS2[d]	73.7	80.0	6.3	3.7
B3PW91-D3/BS2[d]	73.1	76.5	3.4	2.0
ωB97X-D/BS2[b]	73.4	77.6	4.2	1.9
B2GP-PLYP-D3/BS3[c]	–	–	2.7	0.1
LPNO-CCSD/BS3[c]	61.9	63.5	1.5	−1.1
LPNO-CEPA-1/BS3[c]	61.0	63.3	2.2	−0.4

[a] All geometries, frequencies, and thermochemistry calculated using BS1. All values in the table include ZPVE correction calculated as outlined in b, c, or d. Binding energies do not include counterpoise correction; these are given in the SI. [b] Method/BSn//method/BS1; geometry optimized using same functional. [c] Method/BSn//M06/BS1; single-point calculation using M06 geometry. [d] Method-D3/BS2//method/BS1; single-point calculation using geometry from the equivalent functional without -D3 correction.

Overall the calculations suggest the following:

1 The interaction of the metal with pentane is weaker than in the case of comparable rhenium pentane complexes.[26,14] The C−H bond coordinated to the metal is calculated to be stretched by a smaller amount to 1.13−1.14 Å in the case of tungsten (1.14−1.16 Å for Re) which results in the larger averaged $^1J_{CH}$ value that is observed for the tungsten pentane complex. Binding energies are lower in the case of **2** and **3** compared to pentane binding to CpRe$(CO)_2$ or KpRe$(CO)_2$ fragments when calculated with the same method.[14]

2. Electronic energies of C1 and C2 bound isomers are similar according to most of the methods used, and so it is computationally challenging to predict which isomer is preferred. Traditional hybrid functionals that neglect dispersion interactions (e.g., B3PW91) predict that the C1 isomer is lower in energy. However, as noted previously,[27,14] alkane binding energies calculated with such methods appear unreasonably low. Inclusion of dispersion interactions (M06, ωB97X-D and -D3 corrections) makes the binding energies significantly larger and more similar between methods and lowers the relative energy of the C2 bound isomer significantly, making it consistently the preferred isomer electronically.
3. Inclusion of enthalpy and entropy corrections tends to favor the C1 isomer. Alkanes "attached" at C1 are expected to have higher entropy than those attached at C2 due to the increased flexibility of the longer chain.[28] Larger basis sets and inclusion of solvent also stabilize the C1 isomer in the case of the M06 functional, single-point calculations at least.
4. Notably, the electronic energies from the wave function based approximate coupled cluster LPNO methods[29] (which should account for dispersion more accurately than the empirical corrections to the DFT methods) combined with thermodynamic parameters from the M06 method suggest that the free energy of **2** should be slightly lower than that of **3**.

Subtleties of the computations aside, the requirement that C2 (and C3) bound isomers require the pentane to adopt a gauche conformation introduces an energy penalty of around 2.6 kJ mol^{-1} when bound through C2.[30] This effect alone should cause a change in preference from CH_2 being preferred over CH_3 by 0.5 kJ mol^{-1} in the case of $CpRe(CO)_2$(pentane),[12] wherein pentane can bind through any carbon in an all-*trans* conformation, to CH_3 being preferred to CH_2 in the case of **2**.

Further experiments, including attempts to bind propane to the $(HEB)W(CO)_2$ fragment, are underway which will allow for the comparison of CH_3 and CH_2 binding without the possibility of *gauche* alkane conformations clouding the issue.

To date we have been unable to observe the equivalent alkane complexes, using either IR or NMR spectroscopy, when the hexamethylbenzene or mesitylene ligands have been employed in place of the HEB ligand. It may be that the reason that the use of the HEB ligand facilitates the observation of alkane complexes is simply because the HEB ligand is less prone to dissociate on photolysis compared to the analogous hexamethylbenzene ligand. Alternatively, steric shielding of the bound alkane by the bulkier ethyl groups may be a factor.

The observation that the nature of the combination of metal and coligand, in this case W and HEB, can lead to different site binding specificity in alkanes should inform the future design of organometallic fragments that permit the site directed functionalization of bound alkanes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, additional NMR spectra, and details of calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(24) Basis sets: BS1 = 6-31G(d,p), SDD+f for W; BS2 = 6-311+G(2d,p), SDD+f for W; BS3 = def2-TZVPP; BS4 = def2-QZVP.

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