# Reactivity of the M-(η²-alkyne) bond [M = Cr, W]: A kinetic and DFT study

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A B S T R A C T

The displacement of $\eta^2$-coordinated 1-hexyne and 3-hexyne by 2-picoline from the $Cr(CO)_5$, $BzCr(CO)_2$ and $W(CO)_5$ fragments was studied. For the Cr systems, the data is consistent with a dissociative mechanism of alkyne displacement from the metal center. For $W(CO)_5(\eta^2$-1-hexyne), the alkyne displacement follows a largely associative mechanism. The bond dissociation enthalpies obtained from the kinetic analysis are in good agreement with the values obtained by detailed DFT calculations. The calculations indicate that the energy required for the steric reorganization of the alkyne ligand prior to binding with the metal is an important factor in the determination of the overall metal–$(\eta^2$-alkyne) bond strength.

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## 1. Introduction

In several organic transformations mediated by transition metal organometallic complexes, the active species and intermediates are quite often coordinatively unsaturated [1]. Ultrafast studies have demonstrated that solvation of a vacant coordination site occurs within picoseconds of ligand loss from a metal center [2–4]. Therefore, it is reasonable to assume that in homogenous reactions, the unsaturated metal complexes are weakly solvated and that this metal–solvent interaction has to be disrupted before substrate binding and the subsequent chemical transformations can occur. It is therefore important to study the substitution mechanisms and energetics of such weakly bound ligands from metal centers to achieve a fundamental understanding of the role of the metal in promoting catalytic and non-catalytic reactions.

With the advent of fast time resolved spectroscopic techniques, the reaction dynamics of several solvated organometallic complexes have been investigated. The lifetimes of complexes such as $Cr(CO)_5$(solvent) depend on the solvent characteristics and can vary from nanoseconds (solvent = fluorocarbons) to seconds (solvent = THF) at room temperature [5,6]. While the displacement of a number of weakly coordinated ligands (<85 kJ/mol) such as noble gases, saturated hydrocarbons, arenes, and alkenes have been studied [7–9], fewer studies have focused on the substitution chemistry of the metal–alkyne bond. The $\eta^2$ coordination of alkynes to metal centers and the subsequent rearrangement to metal–vinylidene species has received much attention [10–13]. However, there is relatively little information available about the strength of the metal–alkyne interaction and the mechanisms of alkyne displacement

from metal centers. This lack of information is surprising, especially since alkyne carbonyl complexes have been shown to catalyze the polymerization and cyclization of alkynes [11–14].

Recently, Harris and coworkers investigated the interaction of 1-hexyne with $M(CO)_5$ [M = Cr, Mo, W] fragments generated by photolysis of the parent hexacarbonyls using picosecond infrared spectroscopy [15]. The results were consistent with initial formation of both a $\sigma$ (C–H) and $\pi$ (C≡C) bonded metal complex. The $\sigma$ complex converted to the thermodynamically stable $\pi$ bonded complex within 100 ps. Importantly, no evidence was observed for the rearrangement of the $\pi$ complex to the vinylidene species, M=C=CHR, that was previously postulated in low temperature matrix and room temperature NMR studies [11,14,16,17].

Based upon this study, and the importance of obtaining information about the energetics and reactivity of the metal–$(\eta^2$-alkyne) bond, we report in this paper a kinetic investigation centered on the substitution kinetics of 1-hexyne and 3-hexyne from Cr and W centers. The mechanisms of the substitution reactions and kinetic estimates for the strength of the metal–$(\eta^2$-alkyne) bond supported by DFT calculations are presented.

## 2. Experimental

### 2.1. Materials and measurements

All kinetic investigations were performed with a Bruker Vertex 80 FTIR using the rapid-scan option. Unless noted otherwise, all spectra were obtained at 8 cm⁻¹ resolution. Sample photolysis was conducted using a single shot of 355 nm light (40–50 mJ) from a Nd:YAG laser (Continuum Surelite I-10). A temperature controlled IR cell (Harrick Scientific) with CaF₂ windows and a 0.5 mm pathlength was used for all experiments. The temperature

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was monitored with a thermocouple located close to the photolysis solution and maintained by a water circulator to within ±0.5 °C.

The photolysis solution was ∼2 mM in either $Cr(CO)_6$, $W(CO)_6$, or $BzCr(CO)_3$ ($Bz = \eta^6$-$C_6H_6$) in heptane solvent and 0.44 M in 1-hexyne or 3-hexyne. To this solution, varying amounts of 2-methylpyridine (picoline) was added as the displacing ligand. All kinetic runs were carried out under pseudo first order conditions with the concentration of the incoming ligand at least 10 times greater than that of the reactant complexes. The observed rate constants ($k_{obs}$) were obtained from single exponential fits to the absorbance vs. time dependence of the reactant metal–($\eta^2$-hexyne) complexes. The $k_{obs}$ values reported in this paper were obtained after subtraction of the background decay rate constants measured in the absence of added picoline from those obtained in the presence of ligand. The errors in the reported rate constants were obtained from least squares fits to the $k_{obs}$ vs. [picoline] data. The heptane solvent was anhydrous grade and the hexynes and picoline of >97% purity. The purity of the hexynes was checked with NMR spectroscopy and 3-hexyne was distilled prior to its use in the experiments.

## 2.2. Theoretical details

All calculations were performed in the development version of the GAUSSIAN suite of programs [18], using the functional of Tao, Perdew, Staroverov, and Scuseria (TPSS) [19] and the LANL2DZ basis set [20–23]. Calculations listed as enthalpies include vibrational corrections to the energy, whereas those labeled as energies do not. Distortion or preparative energies are calculated as the difference in SCF energies between low energy gas phase geometry and the geometry adopted in the metal complex under consideration.

## 3. Results and discussion

### 3.1. $Cr(CO)_5(\eta^2$-hexyne)

As shown in Fig. 1, photolysis of a heptane solution of $Cr(CO)_6$ in the presence of 1-hexyne results in the formation of a complex with CO stretching absorbances at 2076, 1958, and 1941 $cm^{-1}$.
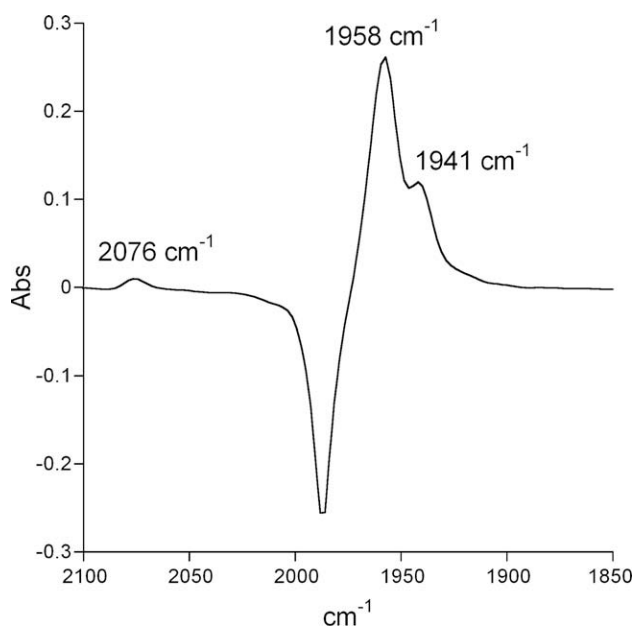
The number of the peaks and their relative intensities suggests that this complex may be characterized as a $Cr(CO)_5L$ species which is expected to have three IR active bands ($2a_1 + e$). Since formation of $Cr(CO)_5L$ complexes is well established upon photolysis of $Cr(CO)_6$ in the presence of a variety of ligands, L, this species by analogy with known $\eta^2$-coordinated alkene species [24], is assigned to the $Cr(CO)_5(\eta^2$-1-hexyne) complex. The peak positions of the CO stretching bands are also consistent with those observed previously for the $Cr(CO)_5(\eta^2$-1-hexyne) complex [15]. Similar spectral features were also observed in the case of 3-hexyne and the peak locations are presented in Table 1.

As shown in Fig. 2, in the presence of picoline, the peaks associated with $Cr(CO)_5(\eta^2$-3-hexyne) observed at 2071, 1951, and 1939 $cm^{-1}$ decrease in intensity and the growth of the $Cr(CO)_5$(picoline) complex is observed at the same rate. The identity of the product was confirmed by comparing the position of its CO stretching bands to those observed upon photolysis of a heptane solution of $Cr(CO)_6$ in the presence of picoline which is expected to only yield $Cr(CO)_5$(picoline). The variation of $k_{obs}$ was monitored as a function of [picoline] and the results shown in Fig. 3 demonstrate that $k_{obs}$ approaches a limiting value at high [picoline] for both 1-hexyne and 3-hexyne.

**Table 1**
Position of the CO stretching bands for the complexes observed in this study. All spectra were taken in heptane solvent at 298 K.

| Complex | $\nu_{CO}$ ($cm^{-1}$) |
|---|---|
| $Cr(CO)_5(\eta^2$-1-hexyne) | 2076, 1958, 1941 |
| $Cr(CO)_5(\eta^2$-3-hexyne) | 2071, 1951, 1939 |
| $Cr(CO)_5$(picoline) | 2067, 1937, 1917 |
| $BzCr(CO)_2(\eta^2$-3-hexyne) | 1867, 1923 |
| $BzCr(CO)_2$(picoline) | 1897, 1845 |
| $W(CO)_5(\eta^2$-1-hexyne) | 2085, 1960, 1942 |
| $W(CO)_5(\eta^2$-3-hexyne) | 2072, 1954, 1933 |
| $W(CO)_5$(picoline) | 2071, 1932, 1918 |



**Fig. 1.** Spectrum obtained upon photolysis of a ∼2 mM heptane solution of $Cr(CO)_6$ in the presence of 0.44 M 1-hexyne. The positive peaks are assigned to the $Cr(CO)_5(\eta^2$-1-hexyne) complex, while the negative absorbance is due to depletion of the parent $Cr(CO)_6$ complex upon photolysis.



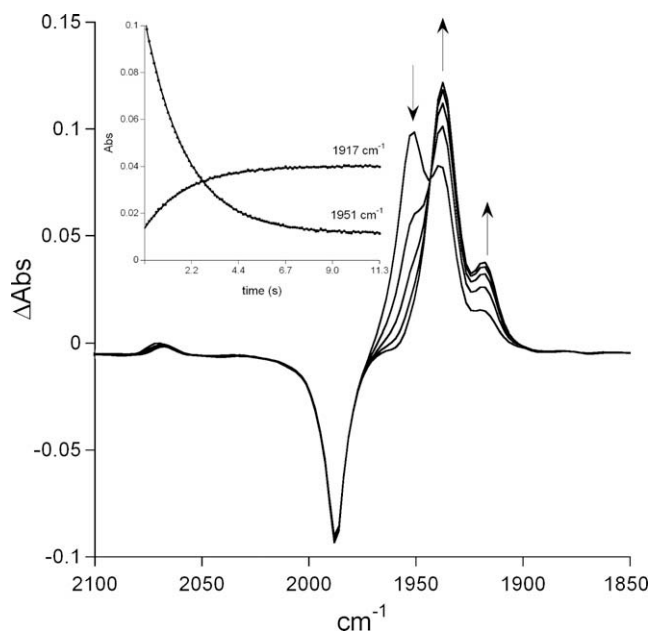**Fig. 2.** Spectral changes observed upon photolysis of a heptane solution of $Cr(CO)_6$ in the presence of 0.44 M 3-hexyne and 0.02 M picoline at 303 K. The inset shows the decay and growth of the $Cr(CO)_5(\eta^2$-3-hexyne) and $Cr(CO)_5$(picoline) complexes, respectively.
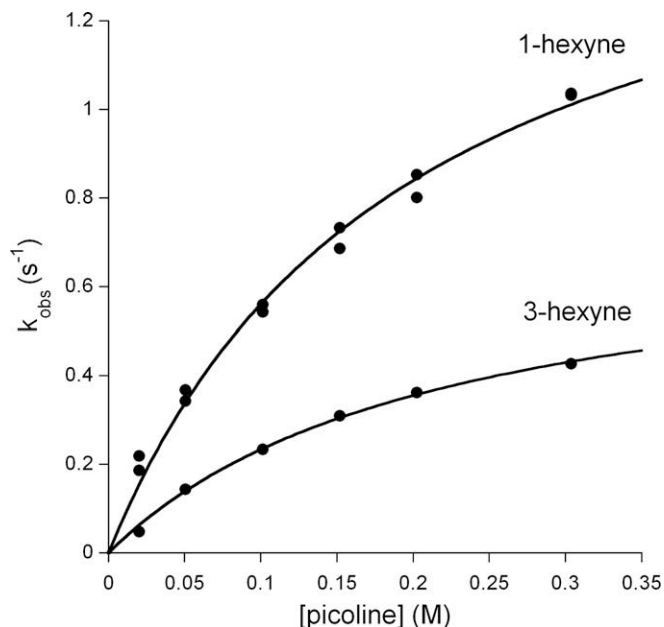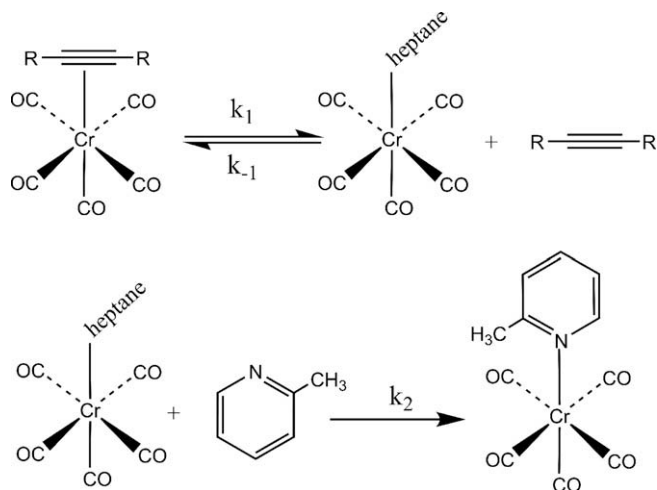
**Fig. 3.** A plot of $k_{obs}$ vs. [picoline] at 288 K for the displacement of alkyne from $Cr(CO)_5(\eta^2$-alkyne) by picoline. The limiting behavior of $k_{obs}$ at high [picoline] is consistent with a dissociative mechanism of alkyne displacement from the Cr center.

**Table 2**
Rate constants for the Cr systems measured at 303 K. A complete listing of rate constants at all temperatures studied is provided in the supplementary information.

| Complex | $k_1 \times 10^2$ (s$^{-1}$) | $k_2/k_{-1}$ |
|---|---|---|
| $Cr(CO)_5(\eta^2$-1-hexyne) | 621 ± 34 | 3.0 ± 0.3 |
| $Cr(CO)_5(\eta^2$-3-hexyne) | 346 ± 31 | 2.1 ± 0.4 |
| $BzCr(CO)_2(\eta^2$-3-hexyne) | 8.9 ± 0.4 | 2.4 ± 0.2 |

complex for either alkyne or picoline. The relevant rate constants are shown in Table 2.

$$k_{obs} = \frac{k_1 k_2 [\text{picoline}]}{k_{-1}[\text{hexyne}] + k_2[\text{picoline}]} \tag{1}$$

The limiting form of the $k_{obs}$ vs. [picoline] dependence suggests that the reaction is dissociative in nature with the disruption of the metal–alkyne bond as the rate determining step ($k_1$) at high picoline concentration. The activation enthalpy associated with $k_1$ is therefore expected to yield an estimate for the strength of the Cr-($\eta^2$-alkyne) interaction. As shown in Table 3, an Eyring analysis yields values of $\Delta H_1^{\ddagger}$ = 64.0 ± 2.9 kJ/mol and 76.6 ± 2.9 kJ/mol for the Cr-($\eta^2$-1-hexyne) and Cr-($\eta^2$-3-hexyne) systems, respectively. These values, particularly for 3-hexyne, are in good agreement with calculated estimates of ~80–84 kJ/mol for the strength of the $Cr(CO)_5(\eta^2$-alkyne) bond (Table 4).

The $k_2/k_{-1}$ ratio of 2–3 suggests that the $Cr(CO)_5$(heptane) complex reacts faster with picoline than with the alkynes. The temperature independence of this ratio points to a small difference in the activation enthalpies for these reactions, i.e., $\Delta H_2^{\ddagger} - \Delta H_{-1}^{\ddagger} \sim 0$. This observation is consistent with the results of previous studies aimed at investigating the reactivity of the $Cr(CO)_5$heptane species. For example, Dobson and coworkers report that the $Cr(CO)_5$(heptane) complex reacts approximately 5–6 times faster with picoline than with 1-hexene [26]. Furthermore, the reactions were thought to proceed through an interchange mechanism which is consistent with the overall displacement pathway for the hexyne ligand shown in Scheme 1.

As shown in Fig. 3 and Table 2, the limiting rate constant, $k_1$, is almost a factor of two lower in the case of 3-hexyne compared to 1-hexyne. The activation parameters point to a lower activation enthalpy for 1-hexyne which is partly responsible for this difference in $k_1$. If the activation parameters reasonably reflect the bond dissociation enthalpies (BDE's), then the data may be interpreted

This type of saturation behavior suggests a displacement mechanism that involves the reversible generation of an intermediate complex which then reacts with picoline to form the final $Cr(CO)_5$(picoline) product. Since the photolysis is performed in heptane solution and $Cr(CO)_5$(heptane) is a known complex [25], it is likely that it is formed as an intermediate in this reaction. The observed dependence of $k_{obs}$ on [picoline] is therefore consistent with the mechanism shown in Scheme 1. Application of the steady state assumption to the $Cr(CO)_5$(heptane) complex yields the dependence of $k_{obs}$ on [picoline] shown in Eq. (1). To further confirm this mechanistic assignment, experiments were conducted in which [1-hexyne] was varied as [picoline] was held constant. For example, at [picoline] = 0.05 M, $k_{obs}$ displayed an inverse dependence on [1-hexyne], consistent with Eq. (1). A fit of the $k_{obs}$ vs. [picoline] data to Eq. (1) yields values for $k_1$ and the $k_2/k_{-1}$ ratio which reflects the selectivity of the intermediate $Cr(CO)_5$(heptane)

**Table 3**
Activation parameters obtained from the kinetic data for the metal–($\eta^2$-alkyne) complexes.

| Complex | $\Delta H_1^{\ddagger}$ (kJ/mol) | $\Delta S_1^{\ddagger}$ (J/mol K) |
|---|---|---|
| $Cr(CO)_5(\eta^2$-1-hexyne) | 64.0 ± 2.9 | −18 ± 9 |
| $Cr(CO)_5(\eta^2$-3-hexyne) | 76.6 ± 2.9 | +19 ± 8 |
| $BzCr(CO)_2(\eta^2$-3-hexyne) | 95.3 ± 1.7 | +50 ± 5 |
| $W(CO)_5(\eta^2$-1-hexyne) | 42.3 ± 0.8 | −105 ± 5 |

**Table 4**
Calculated bond enthalpies for some metal–($\eta^2$-alkyne) complexes. Values in parenthesis are experimental estimates obtained from the kinetic analysis.

| Complex | Bond enthalpy (kJ/mol) |
|---|---|
| $Cr(CO)_5$-($\eta^2$-acetylene) | 84.9, 82.0[a] |
| $Cr(CO)_5$-($\eta^2$-1-hexyne) | 84.1 (64.0) |
| $Cr(CO)_5$-($\eta^2$-3-hexyne) | 79.9 (76.6) |
| $BzCr(CO)_2$-($\eta^2$-3-hexyne) | 101 (95.3) |
| $W(CO)_5$-($\eta^2$-acetylene) | 115, 106[a] |
| $W(CO)_5$-($\eta^2$-1-hexyne) | 113 |

[a] Ref. [32].



**Scheme 1.**

as suggesting that 1-hexyne is bound weaker to the Cr center than 3-hexyne. However, the results of the DFT study detailed below, predict similar values for the Cr-($\eta^2$-1-hexyne) and Cr-($\eta^2$-3-hexyne) bond strengths. Therefore, a lower $\Delta H_1^\ddagger$ in the case of 1-hexyne may be the result of slight differences in the nature of the dissociative transition state due to a change in the steric properties of the hexyne ligand. Thus, with the less sterically encumbered 1-hexyne, the transition state may have some residual bonding with the departing alkyne and some binding with the incoming heptane solvent. This would result in a slightly negative $\Delta S_1^\ddagger$ and a $\Delta H_1^\ddagger$ that would underestimate the true binding strength as observed. For the larger 3-hexyne ligand, the transition state is likely more dissociative leading to both a positive $\Delta S_1^\ddagger$ and better agreement between $\Delta H_1^\ddagger$ and the calculated BDE, as observed.

Given the electron releasing character of alkyl groups, it is reasonable to expect differing $\pi$ donor and acceptor properties for acetylene, 1-hexyne, and 3-hexyne. Indeed, as shown in Table 1, the CO stretching bands of the 3-hexyne complex are about 3–7 cm$^{-1}$ lower than that of the 1-hexyne complex suggestive of a stronger donor and/or weaker $\pi$ acceptor ability of the former ligand. Despite this difference, the theoretical results indicate that the strength of the (CO)$_5$Cr-($\eta^2$-alkyne) interaction does not depend strongly upon the steric and electronic properties of the alkyne ligand. This observation is discussed later in the context of the DFT calculations performed on these systems.

## 3.2. BzCr(CO)$_2$($\eta^2$-3-hexyne)

Photolysis of a heptane solution of BzCr(CO)$_3$ in the presence of 3-hexyne results in the generation of two CO bands consistent with the formation of a dicarbonyl species. By analogy with previous studies that show the generation of $\eta^2$-alkene species when BzCr(CO)$_3$ is photolyzed in the presence of alkenes [27], and the fact that alkynes $\eta^2$ bonded to the ($\eta^6$-C$_6$Me$_6$)Cr(CO)$_2$ fragment have been observed [28,29], the species absorbing at 1867 cm$^{-1}$ and 1923 cm$^{-1}$ is assigned to the BzCr(CO)$_2$($\eta^2$-3-hexyne) complex. As shown in Fig. 4, this complex reacts with picoline to form



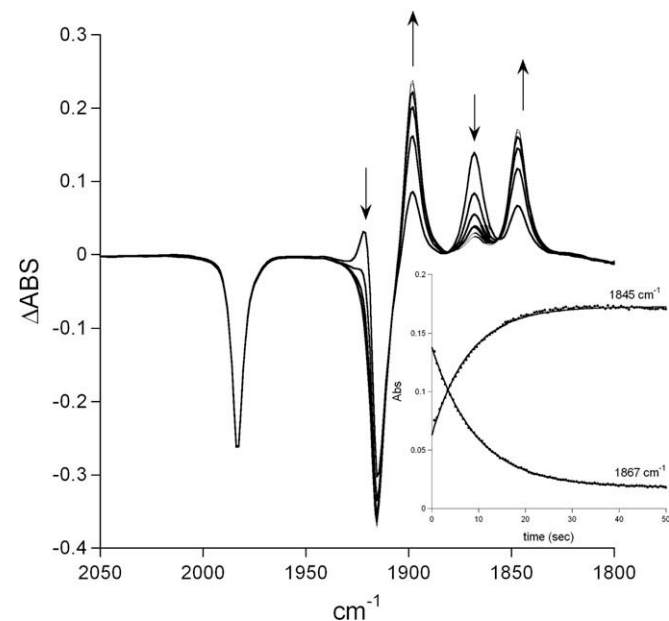**Fig. 4.** Spectral changes observed upon photolysis of a heptane solution of BzCr(CO)$_3$ in the presence of 0.44 M 3-hexyne and 0.1 M picoline at 313 K. The negative absorptions are due to depletion of parent complex upon photolysis. The inset shows the decay of the reactant BzCr(CO)$_2$($\eta^2$-3-hexyne) complex at 1867 cm$^{-1}$ and growth of the BzCr(CO)$_2$(picoline) product at 1845 cm$^{-1}$.
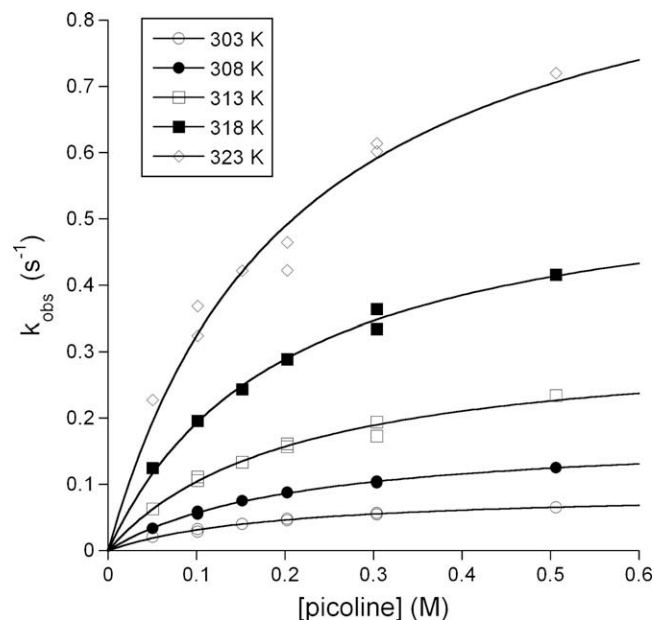


**Fig. 5.** A plot of $k_{obs}$ vs. [picoline] at several temperatures for the displacement of 3-hexyne from BzCr(CO)$_2$($\eta^2$-3-hexyne) by picoline. A dissociative mechanism of substitution is suggested by the limiting behavior of $k_{obs}$.

the BzCr(CO)$_2$(picoline) species absorbing at 1897 cm$^{-1}$ and 1845 cm$^{-1}$. The identity of the product complex was confirmed by photolysis of BzCr(CO)$_3$ in the presence of only picoline. Furthermore, the CO band positions are similar to those of the previously observed and closely related BzCr(CO)$_2$(pyridine) complex [30].

Similar to the kinetic behavior observed in the case of the Cr(CO)$_5$($\eta^2$-hexyne) system, a plot of $k_{obs}$ vs. [picoline] exhibits saturation behavior consistent with a dissociative mechanism for 3-hexyne substitution (Fig. 5). However, the rate constants shown in Table 2, demonstrate that $k_1$ is almost 40 times less for the BzCr(CO)$_2$($\eta^2$-3-hexyne) system. Consistent with a dissociative transition state, the activation entropy is positive ($\Delta S_1^\ddagger = +50 \pm 5$ J/mol K) and the $\Delta H_1^\ddagger$ value of 95.3 $\pm$ 1.7 kJ/mol is expected to provide an estimate for the BzCr(CO)$_2$-($\eta^2$-3-hexyne) bond dissociation energy. As shown in Table 4, the experimental value for $\Delta H_1^\ddagger$ is in good agreement with a calculated value of 101 kJ/mol for the binding strength of 3-hexyne to the BzCr(CO)$_2$ fragment.

## 3.3. W(CO)$_5$($\eta^2$-1-hexyne)

Photolysis of a heptane solution of W(CO)$_6$ in the presence of 1-hexyne results in the generation of a complex with CO stretching absorbances at 2085, 1960 and 1942 cm$^{-1}$. These bands are assigned to the W(CO)$_5$($\eta^2$-1-hexyne) species since their positions are consistent with those previously observed for the W(CO)$_5$(RC≡CH) [R = H, CH$_3$, t-butyl] complexes [16,17,31]. This species reacts with picoline to form the W(CO)$_5$(picoline) complex with CO bands at 2071, 1932, and 1918 cm$^{-1}$. However, as shown in Fig. 6, a weak and broad band centered at 1907 cm$^{-1}$ also grows in and it remains unassigned.

For reasons that are not clear, similar chemistry is not observed in the case of 3-hexyne. The W(CO)$_5$($\eta^2$-3-hexyne) complex is formed upon photolysis of W(CO)$_6$ with CO bands observed at 2072, 1954, and 1933 cm$^{-1}$, however, it does not appear to react with picoline to form W(CO)$_5$(picoline). Instead, the reactant bands decrease in intensity without any evidence for the growth of a

product complex. This lack of reaction appears to be unrelated to the possibility of tautomerization of the initially formed $\eta^2$ complex to the vinylidene species since no product peaks are observed. Furthermore, theoretical calculations indicate that the tautomerization process in the case of $W(CO)_5(\eta^2$-propyne) is endothermic by 2.4 kcal/mol [15]. The anomalous behavior of the $W(CO)_5(\eta^2$-3-hexyne) complex remains unexplained.

In marked contrast to the Cr system, $k_{obs}$ obtained from a first order exponential fit to the temporal profile of the $W(CO)_5(\eta^2$-1-hexyne) complex exhibits a linear dependence on picoline concentration (Fig. 7). This difference in the behavior of $k_{obs}$ with [picoline] indicates that the mechanism of 1-hexyne substitution from Cr and W centers is different. However, while substitution of 1-hexyne by picoline does occur, as mentioned above, there is also spectroscopic evidence for the formation of another product absorbing at 1907 cm$^{-1}$. The results of the kinetic study therefore become difficult to interpret. It is to be noted that $\Delta H_1^{\ddagger} \sim 40$ kJ/mol, is less than half of the calculated value of 113 kcal/mol for the $W(CO)_5$-$(\eta^2$-1-hexyne) binding strength and the large negative value of $-105$ J/mol K for $\Delta S_1^{\ddagger}$ also indicates a transition state with significant interaction of the W center with the incoming picoline ligand. The activation parameters are consistent with a largely associative mechanism of 1-hexyne displacement.

This change in displacement mechanism from more dissociative to associative has been observed before in the case of other weakly solvated $Cr(CO)_5L$ and $W(CO)_5L$ complexes. For example, measurement of the activation entropies and volumes of activation for the substitution of THF by several amine and phosphine ligands from the $M(CO)_5$ fragments [M = Cr, Mo, W] provides evidence for a gradual change in mechanism from more dissociative to more associative along the series, Cr, Mo, and W [6]. Displacement of THF from $W(CO)_5$THF by a variety of incoming ligands yielded $\Delta S_1^{\ddagger}$ values ranging from $-122$ to $-89$ J/mol K, similar to the activation entropy obtained for the present system. It must be emphasized once again however, that the results of the $W(CO)_5(\eta^2$-1-



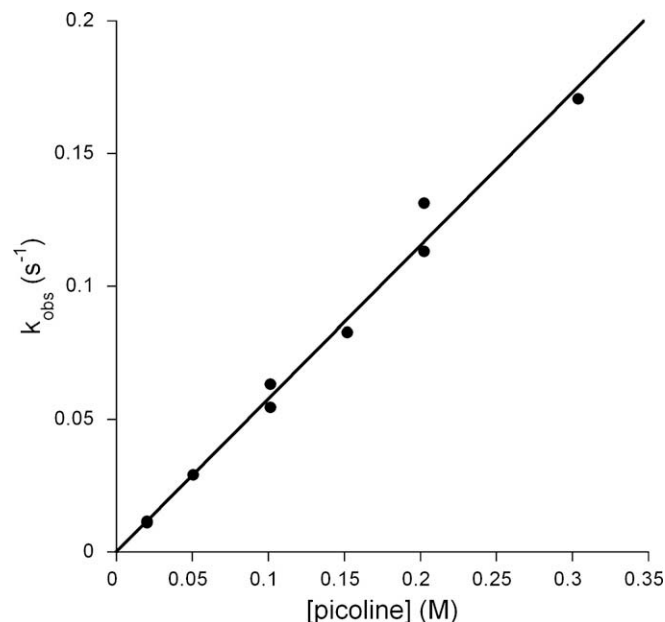**Fig. 7.** A plot of $k_{obs}$ vs. [picoline] for the displacement of alkyne from $W(CO)_5(\eta^2$-1-hexyne) by picoline at 298 K. The linear dependence of $k_{obs}$ on [picoline] is different from the limiting behavior observed in the case of the analogous Cr system and suggests a different mechanism of alkyne substitution.

hexyne) system should be viewed with caution given the formation of an unassigned product in addition to the expected $W(CO)_5$(picoline) complex.

### 3.4. Theoretical modeling

The calculated structure for the $Cr(CO)_5(\eta^2$-3-hexyne) complex is shown in Fig. 8. The results indicate a distortion of both the metal fragment and the alkyne upon binding. The calculated geometric parameters are shown in Table 5 and are defined by the structure shown in Fig. 9.

For the $M(CO)_5(\eta^2$-alkyne) complexes, the C≡C bond distance in the coordinated alkyne is 2–3% greater than in the free ligand. This lengthening of the strong C≡C bond is consistent with previous theoretical studies which predict that the $(CO)_5M$-$(\eta^2$-C$_2$H$_2$) [M = Cr, W] bond has equal contributions from both M ← L $\sigma$ and M → L $\pi*$ donation [32], both of which are expected to weaken the C≡C bond. Interestingly, in the case of the $BzCr(CO)_2(\eta^2$-3-hexyne) species, the difference between the coordinated and uncoordinated C≡C bond lengths is larger than for the $M(CO)_5$ systems. This difference may be due to increased backdonation from the more electron rich $BzCr(CO)_2$ fragment to the $\pi*$ orbitals of the alkyne ligand which would also result in a stronger overall bond as is observed (Table 4).

The bond dissociation enthalpies (BDE's) of several metal–($\eta^2$-alkyne) complexes were calculated and the results are shown in Table 4. Surprisingly, for a given metal fragment, the metal–($\eta^2$-alkyne) BDE's are similar despite the differences in the steric and electronic characteristics of acetylene, 1-hexyne and 3-hexyne. Previous studies have suggested that the energetic cost of deforming the geometry of the free ligand to one that is suitable for bonding can be important in determining the overall trend in metal–ligand binding energies [24,32]. Thus, following the example of Frenking and coworkers [32], the overall metal–($\eta^2$-alkyne) bond dissociation energy was separated into two terms, $\Delta E_{prep}$ and $\Delta E_{int}$.

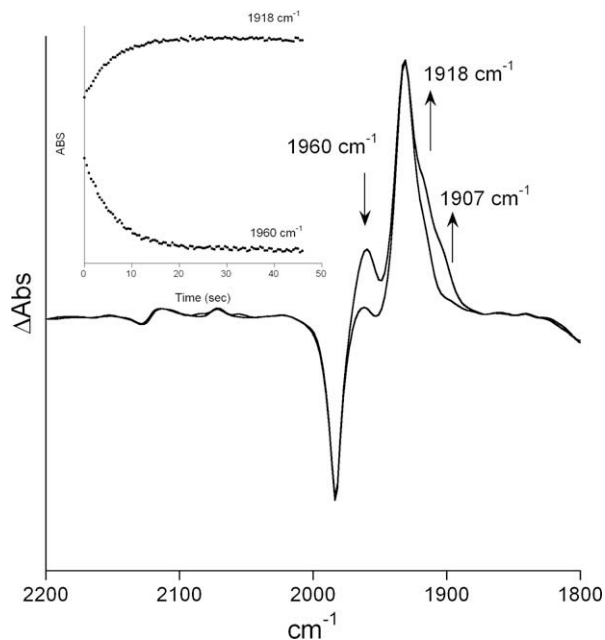$$-D_e = \Delta E_{prep} + \Delta E_{int} \qquad (2)$$



**Fig. 6.** Spectral changes observed upon photolysis of a heptane solution of $W(CO)_6$ in the presence of 0.44 M 1-hexyne and 0.20 M picoline at 293 K. The inset shows the growth of the $W(CO)_5$(picoline) complex observed at 1918 cm$^{-1}$ and the decay of the reactant $W(CO)_5(\eta^2$-1-hexyne) species at 1960 cm$^{-1}$. The peak at 1907 cm$^{-1}$ is unassigned and complicates the interpretation of the kinetic results.
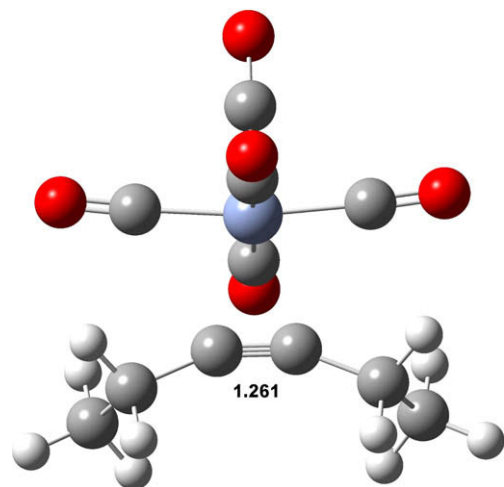
**Fig. 8.** Calculated structure of the $Cr(CO)_5(\eta^2$-3-hexyne) complex. The coordinated alkyne ligand is distorted relative to the free alkyne with a $\angle$ R–C–C = 121° in the complex. The coordinated C≡C bond length of 1.261 Å is 0.03 Å greater than that in the free alkyne.

The first term reflects the energy required to distort the alkyne and metal fragments from their equilibrium geometries to those suitable for binding [33]. The second term is the interaction energy between the prepared fragments. The results are shown in Table 6.

The $\Delta E_{prep}$ term for all metal fragments are small, ranging from 3 to 10 kJ/mol. However, the energetic cost of distorting the alkyne ligands to a geometry suitable for binding is relatively large and for the $Cr(CO)_5$ system increases in the order acetylene < 1-hexyne < 3-hexyne. This trend is not surprising since the larger bound alkyne is expected to be more distorted from its equilibrium geometry than the smaller ones for steric reasons. More significantly, the $\Delta E_{prep}$ term (to include both metal and alkyne fragment) is almost 40–60% of the overall binding energy ($D_e$) of the metal–($\eta^2$-alkyne) complexes. For the $Cr(CO)_5$ system, the $\Delta E_{int}$ term indicates an increase in stability in the order 3-hexyne > 1-hexyne > acetylene which is consistent when correlated with the better $\sigma$ donor ability of the more substituted alkyne. The opposite trend is observed in the case of the more electron rich $BzCr(CO)_2$ fragment where

**Table 6**
Decomposition of the overall binding energy ($D_e$) into $\Delta E_{prep}$ and $\Delta E_{int}$ for $Cr(CO)_5(\eta^2$-alkyne) and $BzCr(CO)_2(\eta^2$-alkyne) complexes (in kJ/mol).

| | $Cr(CO)_5$ | | | $BzCr(CO)_2$ | |
|---|---|---|---|---|---|
| | Acetylene | 1-Hexyne | 3-Hexyne | Acetylene | 3-Hexyne |
| $\Delta E_{prep}^a$ | (2.9 + 29.7) | (3.3 + 32.2) | (5.0 + 45.6) | (10.0 + 58.2) | (8.4 + 52.3) |
| $\Delta E_{int}$ | −122.6 | −125.5 | −136.4 | −185.8 | −166.5 |
| $D_e$ | 90.0 | 90.0 | 85.8 | 117.6 | 105.8 |

[a] Values in parenthesis are $\Delta E_{prep}$ for the metal fragment and alkyne, respectively.

$\Delta E_{int}$ is less favorable for the more electron rich 3-hexyne compared to acetylene. The lower $\Delta E_{int}$ for acetylene indicates that relative to the $Cr(CO)_5$ system, Cr → ligand $\pi*$ backdonation plays a more important role in the binding of alkynes to the $BzCr(CO)_2$ fragment. This conclusion is also consistent with the observed ~20 kJ/mol stronger binding of 3-hexyne to $BzCr(CO)_2$ relative to the more electron deficient $Cr(CO)_5$ fragment. As the decomposition analysis shows, the primary reason for this difference is due to the more favorable $\Delta E_{int}$ term in the case of the $BzCr(CO)_2$ system.

The decomposition of the overall binding energy into $\Delta E_{prep}$ and $\Delta E_{int}$ terms explains to some extent, the invariance of the bond strength with the identity of the alkyne. For the $Cr(CO)_5$ system the interaction energy between the promoted metal and 1-hexyne and 3-hexyne ligands is more favorable than with acetylene due to the better $\sigma$ donor characteristics of the former alkynes. However, the overall binding energy is similar since a more favorable $\Delta E_{int}$ is offset by the larger $\Delta E_{prep}$ for the sterically encumbered alkynes.

In all the systems investigated in the present study, no evidence was obtained for the conversion of the initially formed metal–($\eta^2$-alkyne) species to the M=C=CR$_2$ vinylidene complex. While such an isomerization was thought to occur in some previous studies [11,17], our results are consistent with more recent work in which the isomerization reaction was also not observed [15]. Theoretical results indicate that for the $M(CO)_5(\eta^2$-alkyne) systems, the isomerization reactions are endothermic and that the activation barriers are >80 kJ/mol making it unlikely that such a reaction would be observed under the reaction conditions applied [15]. The present results are also consistent with a previous study which

**Table 5**
Calculated bond lengths (Å) and angles (°) in metal–($\eta^2$-alkyne) complexes.

| [M] | $Cr(CO)_5$ | | | $BzCr(CO)_2$ | | $W(CO)_5$ | |
|---|---|---|---|---|---|---|---|
| R | H | H | $C_2H_5$ | H | $C_2H_5$ | H | H |
| R* | H | $C_4H_9$ | $C_2H_5$ | H | $C_2H_5$ | H | $C_4H_9$ |
| C≡C | 1.257 | 1.257 | 1.261 | 1.277 | 1.274 | 1.266 | 1.265 |
| M–C[a] | 2.310 | 2.379 | 2.392 | 2.173 | 2.223 | 2.380 | 2.438 |
| $\alpha$[b] | 31.6 | 30.5 | 30.6 | 34.2 | 33.3 | 30.9 | 29.9 |
| $\beta$[b] | 160.2 | 157.4 | 156.6 | 153.2 | 154.8 | 157.0 | 155.1 |
| $\gamma$[b] | 160.2 | 161.9 | 156.6 | 152.0 | 155.6 | 156.9 | 159.7 |

[a] Average of both metal–alkyne bonds.
[b] The angles are defined as depicted in Fig. 9.
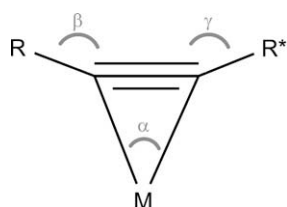


C≡C bond lengths (Å) in unbound alkynes

| | |
|---|---|
| R = R* = H | 1.227 |
| R = H, R* = $C_4H_9$ | 1.229 |
| R = R* = $C_2H_5$ | 1.231 |

**Fig. 9.** General calculated structure of the metal–($\eta^2$-alkyne) complexes.

reported that in solution phase the equilibrium between the $\eta^2$-alkyne complex and the vinylidene species favors the alkyne complex in the case of the $M(CO)_5(\eta^2\text{-}HC\equiv CPh)$ [M = Cr, Mo, W] system. Hence, spectroscopic evidence for the formation of the vinylidene complex was not obtained [34].

## 4. Conclusions

The displacement of $\eta^2$-coordinated alkynes from the $Cr(CO)_5$, $BzCr(CO)_2$ and $W(CO)_5$ fragments by picoline was studied. For all Cr systems studied, the data is consistent with a dissociative mechanism of alkyne substitution. The displacement rates for $BzCr(CO)_2(\eta^2\text{-}3\text{-hexyne})$ are almost 40 times lower than that of the analogous $Cr(CO)_5(\eta^2\text{-}3\text{-hexyne})$ system consistent with a stronger Cr-alkyne bond in the former complex. While substitution of 1-hexyne by picoline from the $W(CO)_5$ metal fragment does occur, there is also spectroscopic evidence for the formation of another product, complicating the interpretation of the data. In contrast to the Cr systems, the data suggest that for $W(CO)_5(\eta^2\text{-}1\text{-hexyne})$ the alkyne displacement follows a largely associative mechanism. Although $W(CO)_5(\eta^2\text{-}3\text{-hexyne})$ is formed after photolysis of $W(CO)_6$, it does not appear to react with picoline. For all systems studied, isomerization of the $\eta^2$-alkyne complexes to $M\equiv C\equiv CR_2$ vinylidene complexes was not observed. Theoretical modeling of the relevant $\eta^2$-alkyne complexes lends support for the experimental analysis and the bond dissociation enthalpies obtained by detailed DFT calculations are in good agreement with the experimentally determined values. Interestingly, for a given metal fragment, the metal–ligand BDE's are similar for the steric and electronically different acetylene, 1-hexyne and 3-hexyne ligands. This effect is largely due to the fact that the more favorable interaction between the metal and the better $\sigma$ donating 1-hexyne or 3-hexyne is offset by the larger energy required to distort these sterically encumbered alkynes from their equilibrium geometries to those suitable for binding.

## Acknowledgements

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.01.014.

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