$$\underset{\mathbf{1}}{H_4Re(PMe_2Ph)_4^+} + B \overset{K_{eq}}{\rightleftharpoons} \underset{\mathbf{4}}{H_3Re(PMe_2Ph)_4} + BH^+ \quad (2)$$

$$[BH^+]^2 + \left\{[B]_{tot} - 2[\mathbf{4}] + \frac{1}{K_f}\right\}[BH^+] - \frac{[\mathbf{4}]}{K_f} = 0 \quad (3)$$

$$pK_a^{MH} = pK_{eq} + pK_a^{BH^+} \quad (4)$$

hydride peaks in the $^1H$ NMR spectra. As both of these bases are known to associate with their conjugate acid $BH^+$, eq 3[1b] was used to calculate $[BH^+]$ from [**4**], the total amount of B added $[B]_{tot}$, and the $B/BH^+$ association equilibrium constant $K_f$ (1.3 $M^{-1}$ for TMG[10b,e] and 32 $M^{-1}$ for DBU[12]). Charge balance was then used to calculate $[BHB^+]$ ([**4**] − $[BH^+]$), and mass balance used to calculate [B] ($[B]_{tot} - 2[BHB^+] - [BH^+]$). The resulting values of $K_{eq}$ (given in Table I) were substituted into eq 4[1a,b] to give the acetonitrile $pK_a$ of **1** as 25.5 (1).

It is instructive to compare **1** with **2**, which, because it is deprotonated by $Et_3N$, must have a $pK_a < 18.5$; the neutral conjugate base of **1**, $H_3Re(PMe_2Ph)_4$ (**4**), must be at least 7 orders of magnitude more basic than the neutral conjugate base of **2**, $H_3Re(CO)(PMe_2Ph)_3$ (**5**). This increase with the substitution of $PMe_2Ph$ for CO is about what we would expect from the effect of phosphine substitution on the $pK_a$ of neutral carbonyl hydrides: $PPh_3$ substitution increases the $pK_a$ of $HMn(CO)_5$ and $HCo(CO)_4$ by 6–7 units, and substitution by the stronger σ-donor phosphine $PMe_3$ increases the $pK_a$ of $HW(CO)_3Cp$ by 10 units.[1b,13,14]

**Kinetic Acidity.** When **1** was allowed to react with a 300-fold excess of aniline-$d_2$ (0.78 M), no deuterium exchange was observed after 72 h at 40 °C or 12 h at 82 °C. We therefore used the stronger base $DNBu_2$ (the $CH_3CN$ $pK_a$ of $Bu_2NH_2^+$ is 18.3[10c]) to measure the kinetic acidity of **1**. In the presence of 0.1 M $DNBu_2$ in acetonitrile at 82 °C (conditions under which the $pK_a$ values of **1** and $Bu_2NH_2^+$ indicate that no net deprotonation occurs), the hydride signal of **1** disappeared with a pseudo-first-order rate constant $k_{obsd}$ of $1.5 \times 10^{-5}$ $s^{-1}$. Application of the McKay equation for a species with four equivalent protons (eq 5)[6,15] gives $k_{HD}$ (defined by eq 6) at 82 °C as $6.0 \times 10^{-4}$ $M^{-1}$ $s^{-1}$. (We assume that $k_{HD}$ is the rate constant for the removal of *any* $H^+$ by *any* molecule of dibutylamine and is independent of the isotopic nature of the remaining protons on rhenium (i.e., of the value of $x$) or on nitrogen and that H/D exchange among nitrogens is sufficiently fast that any H removed is replaced by D.[16])

$$k_{obsd} = k_{HD}\frac{[DNBu_2]}{4} \quad (5)$$

$$[H_{4-x}D_xReL_4]^+ + DNBu_2 \xrightarrow{k_{HD}} H_{3-x}D_xReL_4 + [HDNBu_2]^+ \quad (6)$$

The rate constant for proton transfer to *aniline* from **1** can be estimated from this measured $k_{HD}$ for transfer to $DNBu_2$. Extrapolation from 82 to 25 °C with typical proton-transfer activation parameters ($\Delta H^‡ = 17.6$ kcal/mol and $\Delta S^‡ = -26.7$ eu)[6] gives $5 \times 10^{-6}$ $M^{-1}$ $s^{-1}$; the assumption that at least half of the decrease in thermodynamic driving force from $DNBu_2$ to $PhNH_2$ ($\Delta pK_a$ between $PhNH_3^+$ and $Bu_2NH_2^+$ is 7.75) will be reflected in the rate constant[17] allows estimation of the aniline second-order rate constant $k_{H^+}$ (defined in eq 1) as $<10^{-9}$ $M^{-1}$ $s^{-1}$. This estimate is *more than 5 orders of magnitude slower* than the rate constant ($3 \times 10^{-4}$ $M^{-1}$ $s^{-1}$ at 25 °C) predicted by the linear relationship between rate constant and $pK_a^{MH}$ that we have found for aniline deprotonations of *uncrowded* mononuclear hydrides.[1b,6]

Little structural rearrangement is needed to deprotonate **1**: for steric reasons the structures of the $Re(PMe_2Ph)_4$ core must be very similar in **1** ($[H_4Re(PMe_2Ph)_4]^+$) and in its conjugate base **4**. The slow rate measured for proton transfer from **1** must therefore be due to steric factors—the ability of this $Re(PMe_2Ph)_4$ core to prevent close approach by aniline to Re from any direction.[18] A similar screening function must be performed by the $Mo(dppe)_2$ core in $[HMo(CO)_2(dppe)_2]^+$ (known to undergo very slow proton transfer to nitrogen bases)[19] and the $Cr(tripod)_2$ core in $HCr(tripod)_2^+$ (tripod = $MeC(CH_2PMe_2)_3$) (known to undergo slow proton transfer to its conjugate base)[20] but not by the $Ir(PMe_2Ph)_3$ core in **3** (for which fast transfer to $Et_3N$ has been observed qualitatively at −80 °C).[9a]

**Acknowledgment.** This research was supported by NSF Grant CHE-8819760.

**Registry No.** **1**, 123674-40-8; TMG, 80-70-6; DBU, 6674-22-2; dibutylamine, 111-92-2; aniline, 62-53-3.

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(17) We are assuming that the change in $\Delta G^‡$ with $\Delta G^\circ$ as we change nitrogen bases (the Brønsted coefficient α) is at least 0.5—the value found for thermoneutral transfers from M–H to substituted anilines in ref 6. If α is larger (as it could well be for a thermodynamically unfavorable deprotonation such as that of **1**[6]), $k_{H^+}$ is even smaller.

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Contribution from the Department of Chemistry
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# Octahedral Metal Carbonyls. 78.[1] Mechanism of Alkane Displacement by 1-Hexene from (Alkane)W(CO)$_5$ Complexes (Alkane = Cyclohexane, *n*-Heptane). Estimates of the Alkane–W Bond Strengths in Condensed Media

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and Colin W. Cate

*Received April 18, 1991*

(Solvent)$M(CO)_5$ intermediates are produced in predominant concentration in solution after flash photolysis of $M(CO)_6$ complexes (M = Cr, Mo, W; eq 1); the solvation process has been

$$M(CO)_6 \xrightarrow{h\nu} [M(CO)_5] \xrightarrow{k[\text{solv}]} (\text{solv})M(CO)_5 \quad (1)$$

studied intensively.[2-7] Where the solvent (=solv) is an alkane,

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(1) Part 77: Zhang, S.; Wang, I-H.; Wermer, P. H.; Dobson, C. B.; Dobson, G. R. *Inorg. Chem.*, manuscript submitted.

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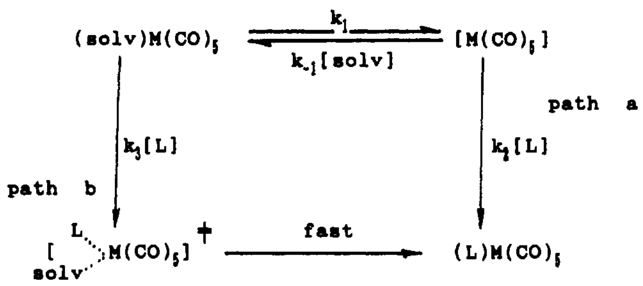
0020-1669/91/1330-4471$02.50/0

**Scheme I**



it is coordinated to the metal via a C–H–M "agostic" interaction.[8,9] Most studies of the rates of alkane desolvation in the presence of a "trap", L(=Lewis base, eq 2) have been mechanistically

$$(\mathrm{solv})\mathrm{M(CO)_5} \xrightarrow{+\mathrm{L}} (\mathrm{L})\mathrm{M(CO)_5} + \mathrm{solv} \qquad (2)$$

ambiguous because, at low [L], mechanisms involving either solvent displacement or initial fission of an M–solv bond (Scheme I, paths a and b, respectively), obey the same limiting (second-order) rate laws.[10-13] In a preliminary study of solvent displacement from photogenerated (*n*-heptane)Cr(CO)$_5$ by the nucleophile piperidine (=pip), the data suggested both pathways to be accessible;[14] volumes of activation for solvent displacement reactions (eq 2) also suggest both pathways to be accessible, especially for strong nucleophiles.[12]

A recent study of solvent displacement from ($\eta^2$-benzene)Cr(CO)$_5$ (solv = benzene), which employed very wide ranges of concentration of the solvent and traps (pip and 1-hexene) so that the influences of solvent on rate could be evaluated, provided conclusive evidence that solv displacement takes place by initial Cr–benzene bond fission.[15] This study afforded the enthalpy of activation for Cr–benzene bond fission, which, in view of the very rapid interaction between solv and [Cr(CO)$_5$] (picosecond time scale),[2-6] should approach the Cr–benzene bond dissociation energy. However, the data also suggested that residual C–H–Cr agostic bonding persisted in the transition state leading to Cr–benzene bond dissociation. In view of the interest in the mechanism and energetics of desolvation in such species, the kinetics methods employed for the ($\eta^2$-benzene)Cr(CO)$_5$ system have been applied to W(CO)$_6$/alkane solutions;[16] this note reports studies of the displacement by 1-hexene of alkanes from (alkane)W(CO)$_5$ intermediates generated through pulsed laser flash photolysis.

## Experimental Section

**Materials.** Tungsten hexacarbonyl (Pressure Chemical Co.), 1-hexene (99+%, Aldrich), *n*-heptane (anhydrous, 99+%, Aldrich), and cyclohexane (99+%, Aldrich) were used as obtained. In view of the high concentrations of 1-hexene, *n*-heptane, and cyclohexane employed in these studies (>0.5 M in all cases), contributions of possible contaminants in the reagents to the observed rate constants were well within the experimental uncertainties of the kinetics measurements.

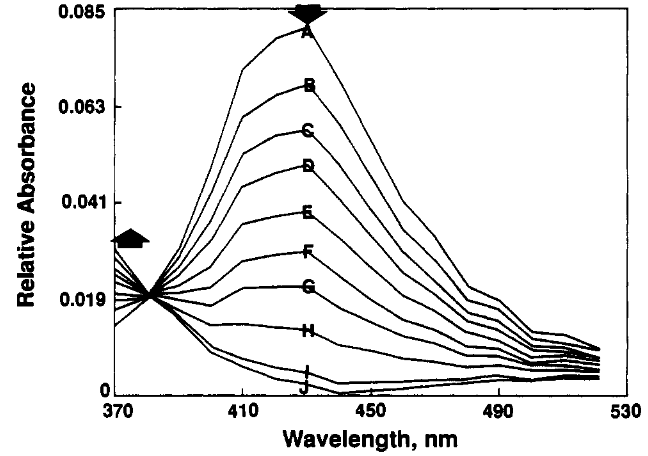


**Figure 1.** Time-resolved spectra for the reaction taking place after flash photolysis of W(CO)$_6$ in a cyclohexane/1-hexene solution (0.5212 M) at 25.0 °C. Times after the flash (μs): A, 0.8; B, 1.4; C, 2.0; D, 2.6; E, 3.4; F, 4.4; G, 5.4; H, 7.4; I, 12.9; J, 22.2.

**Kinetics Studies.** Flash photolysis studies were carried out at the Center for Fast Kinetics Research (CFKR) at The University of Texas at Austin employing a Quantel YG581 ND:YAG Q-switched laser (third harmonic, 355 nm, 11-ns fwhi, 40-mJ maximum energy). Analyzing light was supplied by a 150-W xenon lamp (Oriel), detected by a Hammamatsu R928 photomultiplier tube (PMT). The PMT output was digitized by employing a Biomation 8100 oscilloscope (10 ns/point). Temperature was maintained to within 0.05 °C by employing a jacketed cell and a VWR Scientific 1140 external circulator. Solutions ca. 1 × 10$^{-3}$ in W(CO)$_6$ containing at least 0.5 M solvent (cyclohexane, *n*-heptane) and "trap" (1-hexene) were employed to ensure that pseudo-first-order conditions obtained; both solvent and trap were weighed so that the concentrations of each were known. 1-Hexene was selected as the trap because (a) it is a weak nucleophile whose use should suppress a possible competitive interchange pathway (Scheme I, path b), which would greatly complicate the observed kinetics; (b) upon photolysis, the (hex)W(CO)$_5$ product largely regenerates the [W(CO)$_5$] intermediate, allowing the use of data-averaging for successive flashes of the same reaction solution; and (c) rates of solvent displacement employing 1-hexene have been observed to be slow relative to those for other traps,[11,17] an important consideration, since the observed rates approached the digitization rate limits of the available equipment.

Values for the pseudo-first-order rate constants, $k_{\mathrm{obsd}}$, were obtained from three to ten successive flashes of the same reaction solution; three values of $k_{\mathrm{obsd}}$ were obtained for each concentration of L and at each temperature. The $k_{\mathrm{obsd}}$ data were analyzed on a PDP 11/70 minicomputer employing programs developed at the CFKR. Other data (rate constants, activation parameters) were evaluated at the University of North Texas by employing an IBM-compatible microcomputer and programs developed in-house.

Values of $k_{\mathrm{obsd}}$ are presented in Appendix I (supplementary material). The error limits for all data, presented in parentheses as the uncertainties of the last digit(s) of the cited values, are one standard deviation.

## Results

Figure 1 shows time-resolved spectra taken after flash photolysis of a W(CO)$_6$/CH/hex solution (CH = cyclohexane (0.5212 M); hex = 1-hexene) at 25.0 °C. The absorption centered at 430 nm is attributable to (CH)W(CO)$_5$, which then decays through reaction of this species with hex to afford ($\eta^2$-hex)W(CO)$_5$. The observation of an isosbestic point at 380 nm indicates that the intermediate is converted into a single product. These observations and the interpretation thereof are analogous to those for many closely related systems,[10-14,18] including W(CO)$_6$/hep/hex (hep = *n*-heptane),[12] and indicate that the chemical reaction taking place after flash photolysis is that shown in eq 2.

Since in the presence of photogenerated [M(CO)$_5$] intermediates the alkanes (=alk) CH and hep are reactive rather than dispersive solvents and since maximum mechanistic information can be obtained by varying the concentrations of alk and the trap,

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(16) W(CO)$_6$ was chosen for study rather than Cr(CO)$_6$ because of equipment limitations (digitization rate); alk displacement by 1-hexene is about 1 order of magnitude slower from (alk)W(CO)$_5$ than from (alk)Cr(CO)$_5$.[11]

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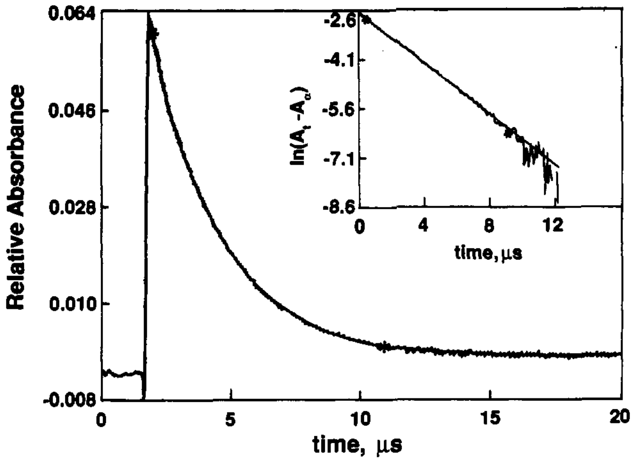

**Figure 2.** Plot of relative absorbance vs time, monitored at 430 nm, for the reaction taking place after flash photolysis of $W(CO)_6$ in a cyclohexane/1-hexene solution (0.5212 M) at 25.0 °C. Inset: Plot of ln ($A_t - A_\infty$) vs time ($A_t$ and $A_\infty$ are the relative absorbances at time $t$ and at infinite time, respectively) for this reaction.

hex, as widely as possible, rate data were taken over the following concentration ranges: 8.6 > [CH] > 2.8 M; 5.5 > [hex] > 0.5 M; 6.3 > [hep] > 3.3 M; 4.1 > [hex] > 0.5 M. Data were taken at five temperatures from 8.9 to 31.8 °C for each $W(CO)_6$/alk/hex solution. Figure 2 shows the plot of absorbance vs time for the solution for which the time-resolved spectra are given in Figure 1, fitted as an exponential decay. The inset is of a plot of ln ($A_t - A_\infty$) vs time for the solution ($A_t$ and $A_\infty$ are the relative absorptivities at time $t$ and at infinite time, respectively), which indicates that the disappearance of $(CH)W(CO)_5$ through reaction with hex obeys pseudo-first-order kinetics. Plots of the pseudo-first-order rate constants, $k_{obsd}$, vs both [hex]/[CH] and [hex]/[hep] for data taken each temperature are curved, suggestive of a mechanism involving consecutive steps, one or more of which are reversible. Thus, the most plausible mechanism for these reactions involves reversible dissociation of alk from photogenerated $(alk)W(CO)_5$ followed by nucleophilic attack of L at coordinatively unsaturated $[W(CO)_5]$ (Scheme I, path a). Assuming a steady-state concentration of $[W(CO)_5]$, the rate law corresponding to this mechanism is

$$-d[(alk)W(CO)_5]/dt = k_1k_2[(alk)W(CO)_5][hex]/(k_{-1}[alk] + k_2[L]) \quad (3)$$

In terms of the pseudo-first-order rate constants, $k_{obsd}$, this expression can be rearranged to

$$1/k_{obsd} = 1/k_1 + (k_{-1}/k_1k_2)[alk]/[hex] \quad (4)$$

Thus, plots of $1/k_{obsd}$ vs [alk]/[hex] are expected to be linear, with intercepts $1/k_1$ and slopes $k_{-1}/k_1k_2$. Values of intercept/slope will be $k_2/k_{-1}$, the ratios of the rate constants for attack at $[W(CO)_5]$ by hex and alk, respectively, the "competition ratios". Figure 3 presents plots of $1/k_{obsd}$ vs [alk]/[hex] for alk = CH (25.0 °C) and hep (24.9 °C), which are linear, consistent with eq 4 and the mechanism presented in path a, Scheme I. Table I gives values for $k_1k_2/k_{-1}$, $k_1$, and $k_2/k_{-1}$ obtained from the data taken over five temperatures, together with the corresponding activation parameters.

## Discussion

Comparison of data taken at 25.0 °C indicates that the rate constants $k_1k_2/k_{-1}$, obtained from the slopes of the reciprocal plots (Figure 3), are 11.6 (1) × $10^6$ and 6.99 (5) × $10^6$ $s^{-1}$, for solv = hep and CH, respectively. The former is in excellent agreement with that for $W(CO)_6$/hep/hex obtained in dilute solution in another study, 11.0 (4) × $10^6$ $s^{-1}$,[12] and may be compared to those reported for dilute $W(CO)_6/hep/N_2$, $W(CO)_6$/hep/CO, and $W(CO)_6/hep/H_2$ solutions at 25 °C, 3.8 × $10^6$, 5.2 × $10^6$, and 1.3 × $10^7$ $s^{-1}$, respectively, determined by Poliakoff and coworkers.[13] The $W(CO)_6$/CH/hex rate constant, 6.99 (5) × $10^6$ $s^{-1}$, may be compared to that for the $W(CO)_6$/CH/4-acetylpyridine system, 3.37 (9) × $10^7$ $s^{-1}$, determined at 24.9 °C.[19] These values support some selectivity among L for the intermediate produced via alk–W bond fission, although the rate constant for the $W(CO)_6$/CH/4-acetylpyridine system, at least, probably includes a contribution from a solvent-displacement pathway (path b, Scheme I).[12,19]

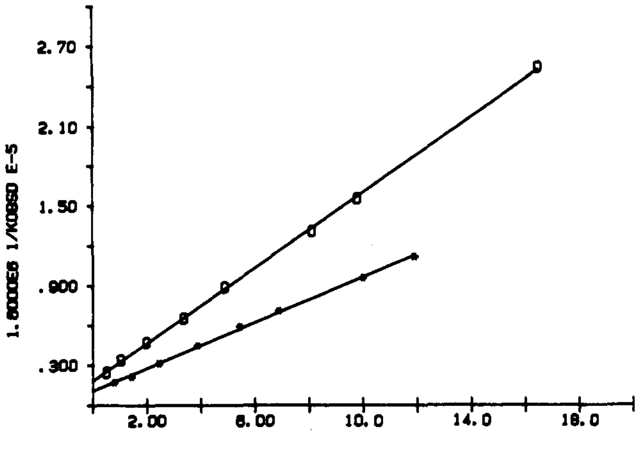

**Figure 3.** Plots of $1/k_{obsd}$ vs [alkane]/[1-hexene] for reactions taking place after flash photolysis of $W(CO)_6$ is alkane/1-hexene solutions at 25.0 °C: ✱, alkane = *n*-heptane; ○, alkane = cyclohexane.

**Table I.** Rate Constants and Activation Parameters for Displacement of Alkanes from $(Alkane)W(CO)_5$ by 1-Hexene

| $T$, °C | $10^{-6}k_1k_2/k_{-1}$, $s^{-1}$ | $10^{-6}k_1$, $s^{-1}$ | $k_2/k_{-1}$ |
|---|---|---|---|
| | Alkane = *n*-Heptane[a] | | |
| 8.85 | 5.97 (9) | 4.6 (3) | 1.32 (13) |
| 13.7 | 7.29 (9) | 6.0 (4) | 1.21 (11) |
| 18.9 | 9.18 (11) | 7.8 (5) | 1.18 (9) |
| 24.9 | 11.60 (11) | 9.8 (5) | 1.18 (7) |
| 31.8 | 15.0 (6) | 15.9 (3) | 0.94 (28) |
| | Alkane = Cyclohexane[b] | | |
| 8.85 | 3.46 (2) | 2.50 (7) | 1.36 (6) |
| 13.7 | 4.46 (9) | 3.0 (3) | 1.51 (17) |
| 18.9 | 5.35 (6) | 4.3 (3) | 1.25 (10) |
| 25.0 | 6.99 (5) | 5.6 (3) | 1.24 (7) |
| 31.8 | 9.20 (8) | 7.5 (4) | 1.22 (8) |

[a] $\Delta H_1^\ddagger$ = 8.4 (5) kcal/mol; $\Delta S_1^\ddagger$ = 1.8 (17) cal/(deg mol). [b] $\Delta H_1^\ddagger$ = 8.2 (4) kcal/mol; $\Delta S_1^\ddagger$ = −3.7 (13) cal/(deg mol).

The rate constant $k_1$ for dissociation of hep from $(hep)W(CO)_5$, 9.8 (5) × $10^6$ $s^{-1}$, is somewhat less than twice that for CH dissociation from the pentacarbonyl, 5.6 (3) × $10^6$ $s^{-1}$. Since CH contains only methylene groups and thus an agostic interaction of H with W must involve one of them, it is unlikely that coordination of hep to W involves primary ($CH_3$) hydrogens. If this mode of interaction of hep with W was favored, the rate of alk dissociation from $(hep)W(CO)_5$ might be expected to be *slower* than that for dissociation of CH from its analogous solvate. The competition ratios, $k_2/k_{-1}$, observed in both hep and CH solution are close to 1 and, within experimental error, are temperature-independent. Activation parameters for alk dissociation from the two $(alk)W(CO)_5$ species (Table I) are quite similar; the enthalpies of activation, 8.4 (5) (hep) and 8.2 (4) kcal/mol (CH), are within experimental error.

The observed entropies of activation, 1.8 (17) and −3.7 (13) cal/(deg mol), respectively, are suggestive of some residual C–H–W bonding in the transition states leading to alk–W bond breaking. Xie and Simon have presented evidence which suggests that initial coordination of alcohols to photogenerated $[Cr(CO)_5]$ occurs randomly along the alkane chain and that this coordination is followed by unimolecular rearrangement of the species initially

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(19) Dobson, G. R.; Spradling, M. D. *Inorg. Chem.* **1990**, *29*, 880.

produced to afford the thermodynamically more stable O-bonded (alcohol)$Cr(CO)_5$ products.[4] Thus, it is possible that there might be statistical influences upon entropies of activation of the numbers of C-H functional groups in the alk molecules employed; these effects, however, are likely to be balanced by similar effects in the hex trap. The nondissociative nature of the rearrangements observed by Xie and Simon[4] does, however, suggest differing energetically accessible modes of agostic bonding of alk to the metal atom may exist along the reaction coordinate to bond dissociation.

Relationships between the enthalpies of activation for W-alkane bond breaking and W-alkane bond strengths are not yet clearly understood. The observations of Lee and Harris,[3] of Hopkins et al.,[5] and of Joly and Nelson[6] indicate that vibrational deexcitation accompanies solvent addition to photogenerated $[M(CO)_5]$. Thus, rates of addition of solvent to thermally equilibrated $[M(CO)_5]$ are not known, although it would seem reasonable to conclude that they are likely to be faster than are those observed for solvent addition to vibrationally excited $[M(CO)_5]$. This is particularly true, since Hackett, Rayner, and co-workers have shown that the reaction probability for interaction of CH with thermally equilibrated $[W(CO)_5]$ in the gas phase, that is, the ratio of the observed bimolecular rate constant for combination of CH with $[W(CO)_5]$ and the collision diameter, $Z_{collisn}$, is 0.07.[20] Thus, the rate of CH addition to $[W(CO)_5]$ is only slightly greater than 1 order of magnitude slower than the gas kinetics reaction cross section. Therefore, on the basis of Hammond's postulate, the activation enthalpy for W-alk bond dissociation to afford thermally equilibrated $[W(CO)_5]$ should closely approximate the bond dissociation energy.

Morse, Parker, and Burkey[21] have attributed the observed difference between the enthalpy for W-CO bond dissociation in the gas phase, $\Delta H°$, 46.0 (28) kcal/mol,[22] and the enthalpy of activation for W-CO bond dissociation in alk solution (alk = decalin), 39.9 (16) kcal/mol,[23] to transition-state stabilization due to agostic bonding of alk to W in the latter; in view of the entropies of activation observed here, this would seem not to be an unreasonable conclusion. Taking this difference, 6.1 (44) kcal/mol, into consideration, alk-W bond strengths based on the results obtained here are 14.5 (49) (hep) and 14.3 (48) kcal/mol (CH), in good agreement with the W-hep bond dissociation energy obtained by Burkey et al.[21] from time-resolved photoacoustic calorimetric data, 13.4 (28) kcal/mol. However, the activation enthalpies reported here (8.4 (5) and 8.2 (4) kcal/mol for alk = hep and CH, respectively) also corresponded closely with W-alkane bond dissociation energies estimated from the equilibrium constants for reversible agostic binding of alkanes to W in $(\eta^1\text{-alkane})W(CO)_5$ complexes, which range from 7.2 (20) to 11.6 (30) kcal/mol;[20,22] that for $(CH)W(CO)_5$ is 11.6 (30) kcal/mol.[20] It thus will be important to obtain other comparisons of activation enthalpies for solvent dissociation and bond strengths obtained from photoacoustic calorimetric data, as well as more accurate values for bond strengths and activation parameters for CO dissociation from the hexacarbonyls both in the gas phase and in solution, to resolve the substantial uncertainties yet present in the available data.

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**Registry No.** $W(CO)_6$, 14040-11-0; hex, 592-41-6; *n*-heptane, 142-82-5; cyclohexane, 110-82-7.

**Supplementary Material Available:** Appendix I, listing rate constants for reactions taking place after flash photolysis of $W(CO)_6$ in *n*-heptane/1-hexene and cyclohexane/1-hexene solutions (10 pages). Ordering information is given on any current masthead page.

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# Structural and Redox Properties of the Tempo Adducts of Copper(II) Halides

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The coordination chemistry of nitroxide radicals has known in the recent past a surge of interest in relation to their use in the design of molecular magnetic materials.[1] Along these lines, most studies were aimed at developing ferro-[2] or ferrimagnetic[3] interactions between the organic radical and metal ions, so as to obtain molecules possessing the highest possible spin.[3-7]

Conversely, the potential use in coordination chemistry of the specific redox properties of nitroxides has been mostly overlooked. Nitroxide radicals can be either oxidized or reduced into, respectively, a nitrosonium or a hydroxylamino ion, and both processes are achievable at easily accessible redox potentials.[8,9] This justifies that, upon binding to a metal ion, charge transfers can take place, and since several mesomeric forms exist, the actual electronic structure of a complex may, in some cases, be difficult to assess. Electron transfers have been noted during complexation of nitroxides to some metal ions,[10-14] but this kind of chemistry has not been investigated in detail, since the resulting species are generally diamagnetic.

On the other hand, the oxidative properties of nitroxides have been investigated by several authors and an interesting versatility in the oxidation of alcohols has been reported.[13,15-19] Various methods have been used to generate the nitrosonium ion, which is the active oxidant. These include electrochemistry[17] as well as the use of copper(II) salts.[13] In the latter case, it is believed that the copper(I) complex that is formed is reoxidized by dioxygen, making the overall process catalytic. However, the exact nature of the species involved in the oxidative transformation is not known.

In the course of our investigations of the coordination chemistry of nitroxides, we have structurally characterized $CuBr_2$(Tempo) (**1**), the adduct of Tempo with $CuBr_2$.[20] In this article, in addition to the structural characterization of $CuCl_2$(Tempo) (**2**), the adduct of Tempo with $CuCl_2$, we report an investigation of the solution chemistry and oxidative ability of both compounds. From this study it follows that the active species in the oxidation of alcohols is not the free nitrosonium ion but the copper-tempo complex.

## Experimental Section

**X-ray Data Collection and Structure Determination.** Dark brown crystals of **2** were obtained by using the procedure described for $CuBr_2$(Tempo).[20] They melted at 136 °C, as reported previously.[21] Preliminary Weissenberg photographs revealed the monoclinic system. Systematic absences (*h0l*, $l = 2n$ and *0k0*, $k = 2n$) were only compatible with the $P2_1/c$ space group. A crystal of approximate dimensions 0.20 × 0.20 × 0.20 mm was mounted on an Enraf-Nonius CAD-4 four-circle

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