Organometallics **1989,** *8,* 2471–2474

Enthalpy of CO Dissociation from $M(CO)_6$ (M = Cr, Mo, W) in Alkane Solvent: Determination of Intermolecular Agostic Bond Strengths

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Received February 7, 1989

The enthalpy of CO dissociation from $M(CO)_6$ (M = Cr, Mo, W) in alkane solvent has been determined by photoacoustic calorimetry (PAC). The reaction involves the substitution of an M–CO bond by an intermolecular agostic bond (M–alkane bond). The enthalpies for CO dissociation from $Cr(CO)_6$ in pentane, heptane, isooctane, and cyclohexane are endothermic by 28, 27, 26, and 24 kcal/mol, respectively. The difference in enthalpies for heptane and cyclohexane is significant and is attributed to a stronger agostic bond to cyclohexane. It is concluded that agostic bond formation is preferred with secondary CH bonds relative to primary. The enthalpies for CO dissociation from $Mo(CO)_6$ and $W(CO)_6$ in heptane are endothermic by 32 and 33 kcal/mol, respectively. From literature M–CO bond energies and the above enthalpies the corresponding agostic bond strengths with heptane can be calculated yielding 10, 9, and 13 kcal/mol (Cr, Mo, and W, respectively). The significance of these results and the role of agostic bonding in the reactions of metal carbonyls are discussed.

Introduction

Coordinatively unsaturated metal complexes have been postulated to be intermediates in many important reactions.[1] Recent pico- and femtosecond flash photolysis studies have been directed at observing such species in solution at ambient temperatures.[2] Some coordinatively unsaturated metal complexes are so reactive that they have been found to form complexes with alkanes. These complexes have a stereospecific interaction between the metal and alkane that can be formally described as an intermolecular agostic bond.[3] The occurrence of such an interaction leaves doubt as to whether ground-state "naked" $M(CO)_5$ species (M = Cr, Mo, W) occur as intermediates in solution. A recent femtosecond flash photolysis study indicates that naked $M(CO)_5$ have lifetimes of only a few picoseconds in alkane solutions, but even these $M(CO)_5$ species are probably electronically excited.[2a]

The existence of intermolecular agostic bonds had been established by earlier studies using matrix isolation and flash photolysis techniques,[4] but the enthalpies of these interactions have been measured in only two cases.[5] Agostic bonding may play a role in C–H insertion, β-elimination, ligand-exchange, and hence catalytic reactions.[5a,6] An important step in evaluating whether agostic bonding can play a significant role in these reactions is to determine the enthalpy of these bonds. If an agostic bond is weak, about 1 kcal/mol, then a coordinatively unsaturated metal complex ought to be in equilibrium with the agostic bonded complex in alkane solvents. For much stronger agostic bonds, the coordinatively unsaturated metal complex is not going to form to a significant extent if entropy changes are small.

In this study we have examined the enthalpy of eq 1 in alkane solvents using photoacoustic calorimetry (PAC) (S = alkane).[7]

$$M(CO)_6 \overset{S}{\rightleftharpoons} M(CO)_5(S) + CO \qquad (1)$$

In this method, the amplitude of an acoustic wave after photolysis is dependent on the amount of heat liberated from chemical and physical processes. If the concentrations of products and reactant are kept low, the reverse of reaction 1 and the reaction of products with reactant are slow. As a result, only the heat of the forward reaction is measured. Since ΔH_1, the enthalpy of reaction 1, is the difference between the M–CO and M–S (agostic) bond energies, the M–S bond energy can be calculated from ΔH_1 if the M–CO bond energy is known. This makes the reasonable assumption that nonstereospecific solvation of reactants and products in alkane solvents are nearly the same and has a small effect on the enthalpy of reaction.[8]

Experimental Section

Materials. All chemicals were obtained from Aldrich unless otherwise noted. Some chromium hexacarbonyl was also obtained from Pressure Chemical as well. Alkanes and tetrahydrofuran (THF) were HPLC or spectrophotometric grade and refluxed under N_2 with Na, K, Na–K amalgam, or Na/benzophenone overnight. All glassware was dried overnight at 140 °C and assembled hot while purged with inert gas. Distilled solvent was collected in a storage bottle fitted with a septum via a cannula and purged with helium. The metal carbonyls and ferrocene were sublimed three or more times until transparent crystals about 0.5 mm in length were obtained. Amines were refluxed over Na or K until their absorbance at 337.1 nm was less than 0.005 (neat

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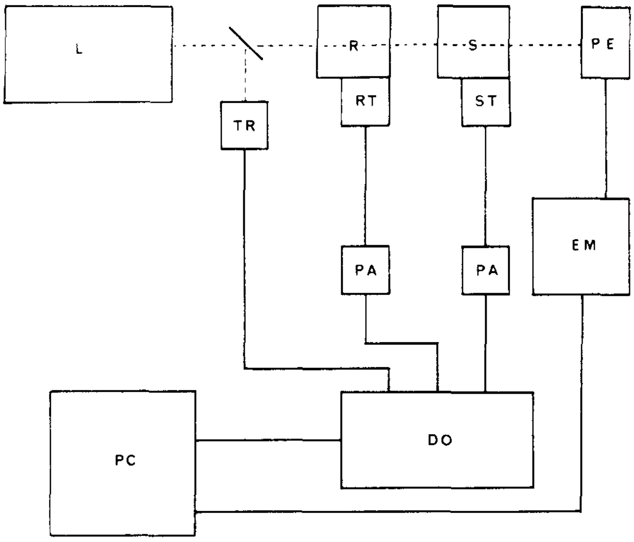

Figure 1. Components of photoacoustic calorimeter: L = PRA LN 1000 N_2 laser, TR = PRA optical trigger, R = reference cell, S = sample cell, PE = Laser Precision RJP-735 pyroelectric probe, EM = Laser Precision RJ-7620 energy meter, RT = Panametrics 2.25 MHz transducer, ST = Panametrics 1.0-MHz transducer, PA = Panametrics ultrasonic preamplifier, DO = Tektronix 2430 digital oscilloscope, PC = Zenith computer with IEEE interface.

amine purged 15 min with He in a 1-cm cell). The *o*-hydroxybenzophenone (OHB) was recrystallized repeatedly from hot ethanol or sublimed. Benzene and cyclohexane (2–3 mL) were passed through a 0.5 × 5 cm alumina column prior to use. All septa (Aldrich) were white rubber and washed repeatedly in alkane solvent until fresh solvent no longer became yellow when shaken overnight. Helium and argon were zero grade (Air Products).

Sample Preparation. All solvents and metal carbonyl solutions were transferred via cannula between septum-capped He- or Ar-purged glassware. About 3 mg of metal carbonyl were weighed in an oven-dried 25-mL flask fitted with a septum. The flask was evacuated to <100 μm and filled with argon and then alkane. A portion of this solution was transferred to a graduated reservoir. Freshly distilled amine was added by microsyringe to the reservoir to scavenge photoproducts (see Results). Ferrocene and metal carbonyl solutions were diluted to obtain absorbances of about 0.1 (337.1 nm, 1-cm cell) and within 5% of each other to ensure a linear PAC response. Reservoir solutions were purged with alkane-saturated helium for >15 min. Experiments were run in subdued light, and the flask and reservoir containing metal carbonyl were protected from light by foil. Solutions were usually used the same day they were prepared.

Measurements. Two methods were used to determine fractional transmission of solutions, and they normally yielded enthalpies that agreed to within 1 kcal/mol. The first method used absorbance measurements from UV spectrometry. The second method used PAC components, the energy meter and reference cell, to determine the transmission in situ (see Figure 1 and Equipment section). By this method, the fractional transmission, T, is determined from the energy of light passing through a metal complex solution (E_m) and a "blank" alkane solution (E_b). The T was calculated from eq 2 where R_m and R_b are normalization

$$T = E_m R_b/(E_b R_m) \qquad (2)$$

factors for variations in pulse energies and were determined from the reference cell signal amplitudes when the sample cell contains a metal complex solution and pure alkane, respectively.

The signals from the transducers were monitored by determining the voltage difference between two conveniently measured extrema. The transducer signals and energy meter readings were the average of 100 shots; four to six averages were obtained and then averaged with each other. Reference solutions in the sample cell were run before and after each metal carbonyl solution to correct for instrument drift. A metal carbonyl solution was run at least twice. Before the measurement of a new solution, the sample cell was rinsed with the new solution until the acoustic signal from the sample cell was constant.

The enthalpy of reaction is calculated from eq 3 where 84.8 is the energy of a mole of photos (kcal/mol for 337.1 nm), Φ is the quantum yield of reaction 1, and ϕ is the observed heat expressed as a fraction of the light energy absorbed. To determine ϕ the calorimeter was calibrated with a reference solution. The reference solution contained ferrocene, a compound that deposits all the light energy as heat.[9] The ϕ is calculated from eq 4 and

$$\Delta H = 84.8\ (1 - \phi)/\Phi \qquad (3)$$

$$\phi = (S_s/S_r)(R_r/R_s)(1 - T_r)/(1 - T_s) \qquad (4)$$

is the ratio of the signal amplitude for a metal carbonyl solution (S_s) to that for a reference solution (S_r). The other terms are simply normalization factors to correct for differences in the absorbtion of the two solutions (1 − T) and differences in laser energy during the measurement of the two signals (R). As before, R is the signal from the reference cell. The s and r subscripts refer to measurements with a sample (metal carbonyl) and a reference (ferrocene) solution in the sample cell, respectively. The signal amplitude for pure solvent was usually less than 0.2% of that for sample solutions. Any larger values were subtracted from the signal amplitudes of reference and sample solutions before eq 4 is used.

Equipment. The photoacoustic calorimeter was similar to that used previously (Figure 1).[7a] The sample cell transducer is 1 MHz and will respond to heat decays having rates of about 10^5 s^{-1} or greater.[10] A heptane solution of OHB (~2 × 10^{-5} M, $A_{337.1} \approx$ 0.1) was used in the reference cell. The sample cell was irradiated with ~25 μJ, 800-ps pulses at 2 Hz. The beam was 1 × 3 mm with the 3-mm axis parallel to the transducer face. The laser beam was focused to a point 2 cm beyond the center of the sample cell. The cell was a modified Hellma cell (137K) connected to a quartz 12/1 spherical joint. Graduated reservoirs fitted with gas dispersion tubes were used to helium purge solutions. The reservoirs were connected to the sample cell via a glass manifold where Teflon metering stopcocks and helium pressure controlled solution flow.

The following tests indicated the calorimeter functioned correctly. The ϕ values for OHB solutions in the sample cell were unity to within 1%. Both ferrocene and OHB should have a quantum yield of unity for nonradiative decay in less than a nanosecond.[9,11] The ϕ were unchanged by placing a 337-nm interference filter in the beam, by changing the OHB or ferrocene concentration in the sample cell (absorbances 0.01 to 0.12), or by increasing the solution flow rate from 0 to 4 mL/min in either cell (OHB or ferrocene). Finally, the enthalpy of exchange of $Cr(CO)_6$ with THF was found to be the same within 1 kcal/mol of the literature value.[5a]

The absorbances of solutions from the reservoirs were measured using a Gilford Response II spectrometer (337.1 ± 0.1 nm) with a thermostated 5-cm quartz cell. The cell was maintained to within 0.3 °C of the PAC experiment. Calibration of the spectrometer was performed with a holmium oxide standard (333.7-nm peak) before and after each measurement.

Results

To ensure that reaction 1 was the only one being measured, several tests and precautions were undertaken. The flow of $M(CO)_6$ solution was increased until ϕ was constant to ensure $M(CO)_6$ was not significantly depleted by photolysis (typical flow = 3 mL/min). The ϕ was found to be independent of *n*-butylamine concentration in the range of (1–10) × 10^{-3} M. This was also found to be the case for $Cr(CO)_6$ with piperidine. Near 0.1 M amine, ϕ increased indicating that the scavenging reaction at the lower amine concentrations (eq 5, A = amine) was too slow to be

$$M(CO)_5(S) + A \Rightarrow M(CO)_5(A) \qquad (5)$$

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Table I. Enthalpy of CO Dissociation from M(CO)$_6$ (ΔH_1) and the M(CO)$_2$–(S) Bond ($\Delta H_{\text{M-S}}$) in Alkane Solvent (S)[a]

M	S	[amine][b]	Φ[c]	n[d]	ΔH_1[e]	$-\Delta H_{\text{M-S}}$[e]
Cr	pentane	2.5–5.0	0.67	3	27.9 ± 2.5	8.9 ± 3.2
	heptane	2.5–10		4	27.2 ± 1.2	9.6 ± 2.3
	isooctane	2.0–10		4	25.8 ± 0.7	11.0 ± 2.1
	cyclohexane	2.0–10		3	24.2 ± 0.7	12.6 ± 2.1
Mo	heptane	2.5–5	0.67	8	31.8 ± 1.3	8.7 ± 2.7
W	heptane	2.0–10	0.72	4	32.6 ± 0.4	13.4 ± 2.8

[a] See eq 1, ambient temperature (20–25 °C). [b] $\times 10^{-3}$. [c] See ref 14. [d] Number of determinations, each determination involved a new solution prepared on a different day. [e] kcal/mol, $\Delta H_{\text{M-S}} = \Delta H_1$ – M–CO bond energy, reported errors are 1σ.

measured by the transducer. This is consistent with rate constants for these reactions being about 10^7 M^{-1} s^{-1}.[12] The ϕ was independent of laser power for 6–25 μJ/pulse. For Cr(CO)$_6$ the ϕ was found to be independent up to 100 μJ and unchanged when a 337-nm interference filter was placed in the laser beam path. These results indicate the absence of multiphoton effects and absorption of laser emissions other than 337 nm.

Tests were also run to determine if the cyclohexane was contaminated by traces of benzene and/or cyclohexene. Benzene is easily detected spectrophotometrically down to 10^{-4} M in cyclohexane at 254 nm. The benzene spectrum has distintive fine structure that aids its identification. The cyclohexane clearly had no benzene at this concentration. Even at this concentration, the rate of reaction of benzene with Cr(CO)$_5$(alkane) would have to approach diffusion control to give an appreciable contribution to the PAC signal.[13] Cyclohexene has a broad shoulder in the UV, and 0.01 M added cyclohexene could be easily detected but not distinguished from the background shoulder of HPLC cyclohexane. Passing the cyclohexane through a 1 × 50 mm column of 10% AgNO$_3$/alumina did not decrease the absorbance at 250 nm. Furthermore, the ΔH_1 for 0.01 M cyclohexene in cyclohexane was the same, within experimental error, as that for low concentrations of amine in cyclohexane; therefore, we are confident that ΔH_1 is a measurement of only the reaction with cyclohexane.

The enthalpies for CO dissociation from different metal carbonyls in heptane and from Cr(CO)$_6$ in other alkane solvents are reported in Table I. It is assumed that the Φ for CO dissociation are the same as for ligand substitution under saturation conditions.[14] The Φ for Mo(CO)$_6$ is assumed to be the same as Cr(CO)$_6$ due to its similar electronic structure. The agostic bond energies ($-\Delta H_{\text{M-S}}$) are calculated from ΔH_1 and gas-phase activation energies for M–CO dissociation.[15] The M–CO bond energies are taken to be equal to the latter.[15]

Discussion

The enthalpy of CO dissociation from Cr(CO)$_6$ in heptane determined here agrees with that from a previous study.[5a] The ΔH_1 for Cr(CO)$_6$ in heptane and pentane are experimentally indistinguishable as might be expected considering the alkanes have both primary and secondary CH bonds. The ΔH_1 for Cr(CO)$_6$ in isooctane is slightly more exothermic but is still within experimental error of the ΔH_1 for heptane and pentane. Isooctane has a tertiary CH as well as primary and secondary, and we feel the molecule is too complex to suggest anything definitive about its agostic bonding. On the other hand, we are convinced that the difference in ΔH_1 for cyclohexane and heptane is real and that this is a manifestation of a stronger agostic bond with cyclohexane ($\Delta H_{\text{Cr-S}}$, Table I). This is consistent with the trend observed for displacement of heptane and cyclohexane from Cr(CO)$_5$(alkane) by strongly bonding ligands. Invariably heptane is displaced faster than cyclohexane.[2g,5a,16] Greater rates of displacement for heptane versus cyclohexane were also observed for (η^2-C$_5$H$_5$)Mn(CO)$_2$(alkane).[16b]

Cyclohexane has only secondary CH bonds which ought to be less sterically hindered than those of pentane and heptane. This suggests that agostic bonds prefer to form with secondary CH versus primary CH; otherwise, stronger agostic bonds would be formed with pentane and heptane. This behavior departs from that observed for metal insertion into alkane CH where insertion prefers primary CH over secondary.[6a,b] This reverse behavior relative to insertion may result from the fact that agostic bonds are less sterically demanding than the corresponding metal–carbon bonds. Such behavior requires that some other factor favors secondary CH agostic bonds. A possible electronic effect is that secondary CH are more electron rich than primary CH.

Our $\Delta H_{\text{W-heptane}}$ value for W(CO)$_5$(heptane) is in agreement with the enthalpy of ethane dissociation recently obtained in the gas phase for W(CO)$_5$(ethane) (9.6 ± 3).[5b] While it is reasonable to argue that the difference between these values is within experimental error, it is important to note that the error in the Φ for photolysis of W(CO)$_6$ is 0.05.[14] Using the lower limit of 0.67 for Φ yields a $\Delta H_{\text{W-heptane}}$ of –10 kcal/mol (note that 0.67 is the same value used for the other metal carbonyls). Nevertheless, a weaker agostic bond for ethane relative to heptane is consistent with our interpretation of the dependence of $\Delta H_{\text{Cr-S}}$ on alkane structure.

It has been reported recently that the PAC signal can result from reaction volume changes as well as thermal expansion.[7b] The agreement of our results for $\Delta H_{\text{W-heptane}}$ with the value for W(CO)$_5$(ethane) in the gas phase suggests that the reaction volume changes are not large. Negligible volume changes are expected considering the similar structure of reactants and products. We conclude that $\Delta H_{\text{M-S}}$ should be a good measure of the enthalpy difference between M(CO)$_5$(S) and M(CO)$_5$ + S.

We believe these results help clarify the chemistry of M(CO)$_5$ species in solution. The gas-phase activation enthalpies for CO dissociation from Mo(CO)$_6$ or W(CO)$_6$ (40 and 46 kcal/mol, respectively) are considerably greater than the corresponding values in alkane solvent (32 and 40 kcal/mol, respectively), while the corresponding values for Cr(CO)$_6$ are within experimental error of each other.[15,17] The differences in gas-phase and solution activation enthalpies for Mo(CO)$_6$ and W(CO)$_6$ (8 and 6 kcal/mol, respectively) can be explained by the stabilization of the solution transition states by agostic bonding. This is reasonable since the agostic bond strengths of the intermediates formed via these transition states ($-\Delta H_{\text{M-S}}$) are

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as large or larger than the apparent transition-state stabilizations. The agostic bonding in the transition states for Mo and W may be greater than for Cr because the latter are more hindered sterically.[17b] If the transition state for CO substitution by alkane on $Mo(CO)_6$ and $W(CO)_6$ involves coordination of the alkane, it is unlikely that naked $M(CO)_5$ is formed to a significant extent in these reactions. We therefore conclude that these substitutions occur via an associative process; however, some of the substitution occurring by a dissociative process cannot be ruled out. In support of an associative process, it is known that $Mo(CO)_6$ and $W(CO)_6$ have a much greater tendency to undergo associative ligand exchange than $Cr(CO)_6$.[17b] Consistent with this conclusion is the interpretation of a recent femtosecond flash photolysis study of the photodissociation of CO from these complexes.[2a] Apparently naked $M(CO)_5$ is only observed in an excited state and reacts with a solvent molecule before returning to the ground state.

Our results and conclusion that naked $W(CO)_5$ is not formed upon CO dissociation in solution appear to be inconsistent with those of a flash photolysis study of $W(CO)_6$ in methylcyclohexane.[18] It was asserted that $W(CO)_5$(methylcyclohexane) was 0.9 kcal/mol more stable than $W(CO)_5$ (plus free methylcyclohexane) and that both species are important intermediates. Our measurement of $\Delta H_{\text{W-heptane}}$ (as well as the gas-phase $W(CO)_5$(ethane) value)[5b] does not agree with this result. Our results in Table I indicate the order of magnitude difference between $\Delta H_{\text{W-heptane}}$ and the above value is not likely to be due to the difference in agostic bonding to heptane and methylcyclohexane.

It is clear that agostic bonds are relatively large and agostic bonded complexes are important intermediates. It will be of great interest to determine the upper limit of agostic bond strengths. Presumably this limit is ultimately determined by the insertion into a C–H bond.

Acknowledgment. The donors of the Petroleum Research Fund, administered by the American Chemical Society, are acknowledged for the support of this research.

Registry No. $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; CO, 630-08-0; pentane, 109-66-0; heptane, 142-82-5; isooctane, 540-84-1; cyclohexane, 110-82-7.

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Deprotonation of the Adducts of β-Dicarbonyl Anions and [(η^4-Diene)Co(CO)$_3$]BF$_4$

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Received April 4, 1989

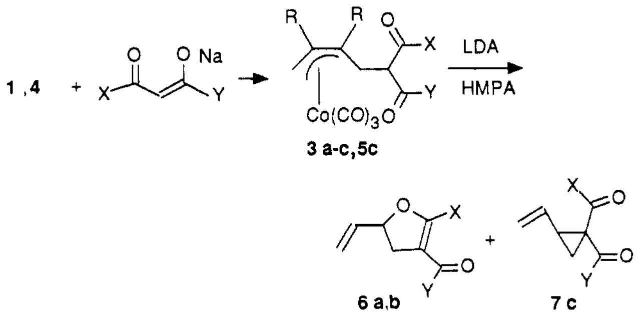
The adducts of stabilized enolates and [(η^4-1,3-butadiene)Co(CO)$_3$]BF$_4$ (**1**) and [(η^4-1,3-cyclohexadiene)Co(CO)$_3$]BF$_4$ (**2**) undergo deprotonation and subsequent reactions to form either hydrofurans, cyclopropanes, or α,β,γ,δ-diunsaturated dicarbonyl derivatives depending upon the reacting complex and the β-dicarbonyl component. All of the observed reactions are strongly promoted by HMPA.

Introduction

Recently we discovered the unexpected, yet synthetically versatile, conversion of [(η^4-diene)Co(CO)$_3$]BF$_4$ complexes to dihydrofurans and tetrahydrobenzofurans via their reactions with dianions of β-dicarbonyl compounds and the related 2,4-bis(trimethylsiloxy) dienes.[1] In order to explore the scope and to probe the mechanism of these transformations we have examined the stepwise addition/deprotonation of a set of β-dicarbonyl derivatives to [(η^4-1,3-butadiene)Co(CO)$_3$]BF$_4$ (**1**) and [(η^4-1,3-cyclohexadiene)Co(CO)$_3$]BF$_4$ (**2**). Herein we report the remarkably variable course of this reaction depending upon the nature of both the complex and the β-dicarbonyl derivative as well as a dramatic accelerating effect of added HMPA.

Results and Discussion

Scheme I



1: [(η^4-1,3-butadiene)Co(CO)$_3$]BF$_4$;

4: [(η^4-2,3-dimethyl-1,3-butadiene)Co(CO)$_3$]BF$_4$

a: X=CH_3, Y=C_6H_5; **b**: X=CH_3; Y=OCH_3; **c**: X=Y=OCH_3; R=H or CH_3

When [(η^4-1,3-butadiene)Co(CO)$_3$]BF$_4$ (**1**) is treated with 1 equiv of the sodium enolate of either benzoylacetone, methyl acetoacetate, or dimethyl malonate in THF at −78 °C, the corresponding C-alkylated adducts **3a–c** are produced (Scheme I) as determined by IR monitoring (typically $\nu(MC{\equiv}O)$ ca. 2060 and 1980 and $\nu(C{=}O)$ ca. 1720–1755 cm^{-1}) and acidic hydrolysis of the malonate adduct **3c** to a mixture of C-butenylated derivatives. Adducts **3a–c** were not completely characterized, however, due to their thermal instability. On the other hand, the product of malonate addition to [(η^4-2,3-dimethyl-1,3-butadiene)Co(CO)$_3$]BF$_4$ (**4**) was sufficiently stable to allow its complete spectroscopic characterization and identification as **5c**, the result of C-alkylation of the malonate nucleophile. Subsequent treatment at −78 °C of adducts **3a,b** with an equivalent of LDA or NaH in THF/HMPA

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