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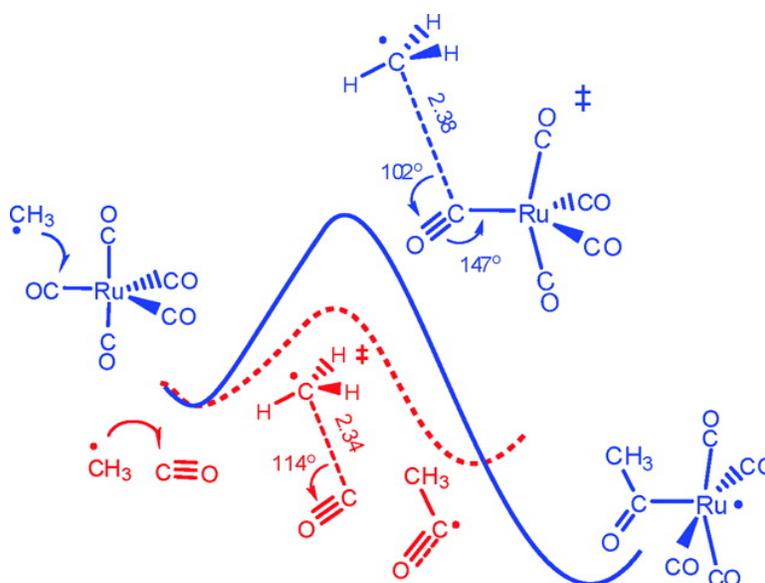
Addition of Alkyl Radicals to Transition-Metal-Coordinated CO: Calculation of the Reaction of [Ru(CO)] and Related Complexes and Relevance to Alkane Carbonylation

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Addition of Alkyl Radicals to Transition-Metal-Coordinated CO: Calculation of the Reaction of [Ru(CO)₅] and Related Complexes and Relevance to Alkane Carbonylation

Faraj Hasanayn,*,[†] Nadeen H. Nsouli,[†] Adnan Al-Ayoubi,[†] and Alan S. Goldman[‡]

Department of Chemistry, The American University of Beirut, Beirut, Lebanon, and Department of Chemistry, Rutgers University, Piscataway, New Jersey 08855

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Abstract: Electronic structure methods have been used to study the transition state and products of the reaction between alkyl radicals and CO coordinated in transition-metal complexes. At the B3LYP DFT level, methyl addition to a carbonyl of [Ru(CO)₅] or [Ru(CO)₃(dmpe)] is calculated to be about 6 kcal/mol more exothermic than addition to free CO. In contrast, methyl addition to [Mo(CO)₆] is 12 kcal/mol less exothermic than addition to CO, while the reaction enthalpy of methyl addition to [Pd(CO)₄] is comparable to that of free CO. Related results are obtained at the CCSD-T level and for the reactions of the cyclohexyl radical. The transition state for these reactions is characterized by significant distortion of the geometry of the reactant complex, which include lengthening and bending of the M−CO bond, but with negligible C−C bond formation. Accordingly, the activation energy for addition to coordinated carbonyls is 2−10 kcal/mol greater than that of addition to free CO. Additional calculations were also carried out on representative unsaturated metal carbonyls. The calculated results afford an understanding of the mechanism of previously reported photochemical alkane carbonylation systems utilizing d⁸-ML₅ metal carbonyls as cocatalysts. In particular, it is strongly indicated that such systems operate via direct attack by an alkyl radical at a CO ligand, a reaction that has not previously been proposed.

Introduction

The formation of a C−C bond by reaction of a carbon-centered radical with unsaturated molecules such as alkenes and nitriles affords an important methodology in synthetic and polymer chemistry.[1,2] Understanding the factors that control the kinetics and thermodynamics of such reactions is important from both fundamental and practical perspectives and has been a goal of current experimental[3,4] and theoretical research.[5,6] A recent review by Fischer and Radom of radical addition to alkenes highlights the nature and complexity of the reactivity

problems encountered in free-radical addition reactions.[7] The coordination of an unsaturated substrate to a transition metal is expected to modify the energetics of its reaction with organic radicals, and can thereby provide a channel to manipulating reactivity and selectivity in radical chemistry. Accordingly, there have been several recent studies in which a free radical adds to an arene,[8,9] allyl,[10,11] or carbene[12] ligand of an organometallic compound, and the topic has been reviewed.[13] But in spite of the growing interest in this area, there have been no systematic studies that provide an electronic-structural view of how coordination to a metal may influence the free-radical addition reactions.

[†] The American University of Beirut.

[‡] Rutgers University.

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Scheme 1. Possible Products from Alkyl Radical Addition to an 18-e Metal Carbonyl
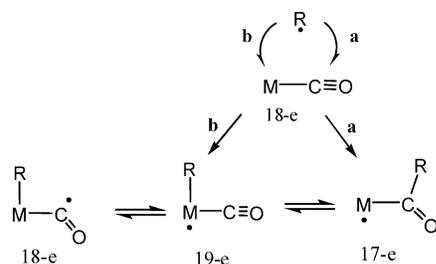
Carbon monoxide is among the simplest of unsaturated substrates that react with alkyl radicals (eq 1), but the reversibility of the reaction limits its utility and also complicates the use of independently generated free acyl radicals in synthesis.[14,15]

$$R\cdot\ +\ CO \ \rightleftharpoons\ R-C\overset{O}{\underset{\cdot}{\Vert}} \tag{1}$$

Several years ago Boese and Goldman reported that in the presence of aryl ketones, d^8 metal carbonyls such as [Ru(CO)$_3$-(dmpe)] mediate photocatalytic carbonylation of alkanes via a free-radical mechanism.[16] The observed activity was proposed to be initiated by alkyl radical addition to the metal–carbonyl and the formation of a metal–acyl radical intermediate (eq 2), which, to our knowledge, has no reported precedent.

$$R\cdot\ +\ L_nM\text{-}CO \ \underset{?}{\rightleftharpoons}\ L_n\overset{\cdot}{M}-C\overset{O}{\underset{R}{\Vert}} \tag{2}$$
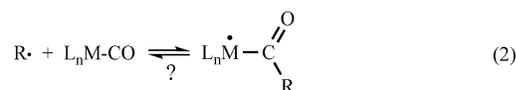
The addition of an alkyl radical to a metal carbonyl as in eq 2 raises unusual considerations about the nature of the product and transition state (TS) of the reaction. To start with, depending upon the site of addition, alkyl addition to an 18-e metal carbonyl can yield either a 19-e metal–alkyl or a 17-e metal–acyl product (Scheme 1). The metal–alkyl product could retain an 18-e count by shifting the unpaired electron to a carbonyl ligand to give a metalloacyl radical of the type known for the [Fe(CO)$_5$]$^-$ anion radical.[17] Currently, however, there is little experimental or theoretical data that can be used to estimate the relative energies of these very different species.

CO coordination also raises unusual questions regarding the kinetics of its reaction with free radicals. Specifically, direct attack of the radical on the carbonyl requires shifting the unpaired electron from the C–C reaction center to the metal center. The impact of this condition on the electronic structure, geometry, and energy of the transition state of the C–C bond-making step is not obvious. Such fundamental issues raised in an analysis of this reaction presumably also have relevance to the radical chemistry of coordinated ligands in general.

In the present work, we use density functional and correlated ab initio calculations to elucidate how CO coordination in [Ru-(CO)$_5$] affects the activation and reaction enthalpies of its reaction with alkyl radicals. The results reveal that coordination in this system increases the exothermicity of C–C bond formation by 6 kcal/mol (relative to addition to free CO) but at the same time it increases the activation enthalpy by 6 kcal/mol. Formation of a metal-alkyl species appears to be unlikely in this system. To elucidate the effect of variable properties among different metal complexes, we also studied the reaction of [Mo(CO)$_6$], [Pd(CO)$_4$], and representative unsaturated [M(CO)$_n$] fragments. Finally, the relevance of the results with respect to understanding the carbonylation system of Boese and Goldman is discussed on the basis of new calculations involving cyclohexyl radical addition to [Ru(dmpe)(CO)$_3$].

Computational Details

All calculations were carried out using Gaussian 98.[18] Previous method-validation studies by the Radom group[19] had demonstrated that to obtain accurate energies in free-radical chemistry it is crucial to use ab initio methods that include a refined treatment of electron correlation, such as the coupled cluster theory which includes single, double, and triple (perturbatively calculated) excitations (CCSD-T).[20] The Radom group also evaluated some density functional methods (DFT),[21,22] and found the popular B3LYP hybrid Hartree Fock/DFT method based on the implementation by Becke, Lee, Yang, and Parr[23] to provide a cost-effective means to obtain geometries and satisfactory activation and reaction energies. Significantly, the B3LYP method was found to be "very respectable" in reproducing the experimental trends in the activation and reaction energies of free-radical addition to substituted alkenes.[7] Although the B3LYP method does not reach chemical accuracy in the description of every aspect of radical addition reactions,[24] this method seemed adequate for our purposes of elucidating the effects of CO coordination on its reaction with an alkyl radical. We have used this method to minimize the geometries and to conduct normal mode vibrational analysis. For the reaction of methyl addition to the [M(CO)$_n$] series of complexes we have also conducted single-point calculations on the B3LYP-minimized geometries using the CCSD-T method. In general, our B3LYP and CCSD-T activation and reaction energies are in good agreement, and this lends support to our conclusions.

In our study, H, C, and O carried the 6-31G** basis set.[25] The transition metals and phosphorus carried the Hay–Wadt effective core potential (ECP's) and the double-ζ basis set supplied with them,[26] along with a set of 10f or 6d polarization functions with exponents equal to 0.4 (Ru, Mo, Tc and Pd) or 0.55 (P).[27] As recommended by Radom

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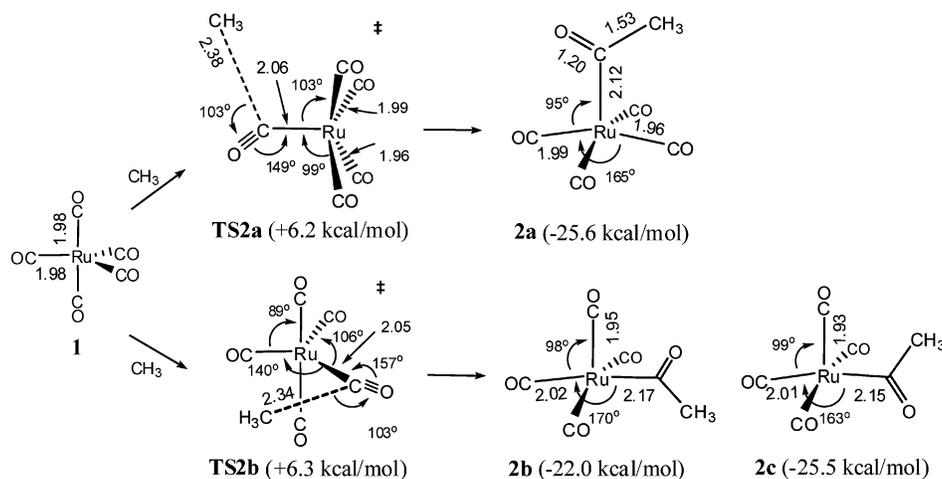
Figure 1. Selected structural parameters, in degrees and Å, of the transition states and products of methyl addition to **1**, and their electronic energy (E_{B3LYP}) relative to the separate reactants.

and others,[28] the doublet states were of the unrestricted type (UB3LYP), and these afforded spin expectation values close to 0.75 even before annihilation of the first spin contaminant. Vibrational enthalpy and entropy terms were obtained using unscaled harmonic frequencies.[29] The reported spin densities were obtained by the Mulliken scheme[30] using restricted open shell wavefunctions (ROB3LYP), which though comparable to the Mulliken UB3LYP densities, were more convenient to analyze. Finally, the molecular orbital (MO) displays were made by GaussView using an isosurface of 0.05.

Results and Discussion

Methyl Addition to [Ru(CO)₅] (1). In attempting to identify the lowest energy transition state (TS) for methyl addition to a carbonyl of **1**, we considered several initial reaction pathways that allowed location of two transition states, **TS2a** and **TS2b**, described schematically in Figure 1.[31]

Both TSs involve significant modification of the trigonal bipyramidal geometry of **1** toward the square pyramidal motif. On the basis of the angles between the Ru–C bonds of the ancillary carbonyl ligands and the carbonyl undergoing attack, 99° and 103° (Figure 1), **TS2a** appears to lead to an acyl product having a square pyramidal geometry in which the acyl ligand takes the apical position (**2a**). **TS2b** on the other hand connects the reactants to **2b**, a square pyramidal product with the acyl group at the basal site. **TS2a** and **TS2b** are calculated to have essentially the same energy, but **2a** is 3.6 kcal/mol lower than **2b**. However, the conformer of **2b** obtained by rotation of the acyl group by 180° (**2c** in Figure 1) is found also to be a minimum and is calculated to have energy similar to that of **2a**.

In studying the given reaction, we have also considered the six-coordinate metal–alkyl complex, [Ru(CO)₅(CH₃)], which could potentially result from methyl addition to the metal center of **1**. However, all attempts to locate a minimum for this species were unsuccessful; the calculations always converged to dissociate CO and to give the square pyramidal [Ru(CO)₄CH₃] metal–alkyl radical. For the net transformation from **1** and free

Table 1. Activation and Thermodynamic Parameters for Methyl Radical Addition to Free CO and **1**[a]

TS	$\Delta E^{\ddagger}_{B3LYP}$	$\Delta E^{\ddagger}_{CCSD-T}$	$\Delta H^{o\ddagger}_{B3LYP}$	$\Delta G^{o\ddagger}_{B3LYP}$
TS–CO (free CO)	0.8	5.3	1.8	8.5
TS2a	6.2	9.1	7.4	13.9
TS2b	6.3	9.3	7.5	14.1

product	ΔE_{B3LYP}	ΔE_{CCSD-T}	ΔH^{o}_{B3LYP}	ΔG^{o}_{B3LYP}
MeCO (free CO)	−19.9	−11.1	−16.2	−7.3
2a	−25.6	−19.8	−21.4	−11.8
2b	−22.0	−18.5	−18.2	−9.1
2c	−25.5	−20.8	−22.6	−12.3

[a] Units are in kcal/mol. ΔE is the electronic energy for the transformation from separate reactants to the specified TS or product and is given without ZPE correction. ΔH and ΔG are the standard state activation or reaction enthalpy and free energy, respectively, evaluated at 298 K and 1 atm.

CH₃ to [Ru(CO)₄CH₃] plus free CO, ΔG^{o}_{B3LYP} is −2.8 kcal/mol (i.e., much less favorable than formation of the acyl product **2a**).

The activation and thermodynamic parameters calculated for the transformation from separate reactants to each of the TSs and products described in Figure 1 are collected in Table 1. The table also includes data on the reaction of free CO.

Experimentally, the activation energy, E_a, for CH₃ addition to free CO in the gas phase is 4.4 kcal/mol, and is not changed significantly in benzene.[14] Table 1 shows that the B3LYP level underestimates this barrier, giving $\Delta E^{\ddagger} = 0.8$ kcal/mol, or $\Delta H^{o\ddagger} = 1.8$ kcal/mol. The CCSD-T level on the other hand gives a barrier slightly greater than the experiment, with $\Delta E^{\ddagger} = 5.3$ kcal/mol, or $\Delta H^{o\ddagger} = 6.3$ kcal/mol (using the B3LYP vibrational energies). For methyl addition to **1**, $\Delta E^{\ddagger}$ for C–C bond formation is 6.2 and 9.1 kcal/mol at the B3LYP and CCSD-T levels, respectively (**TS2a**, Table 1). The two methods converge therefore in predicting that the activation energy for CH₃ addition to CO is substantially greater (by 4 to 6 kcal/mol) when CO is coordinated in **1**.

At the B3LYP level, the reaction energy (ΔE) for CH₃ addition to free CO is −19.9 kcal/mol, which is a reproduction of a recent calculation by Yoshida.[32] Adding the thermal and

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(31) Each transition state has one normal mode of vibration having an imaginary frequency, $\nu^{\ddagger} = 337i$ (**TS2a**) or 323i cm⁻¹ (**TS2b**), with vector components corresponding to C–C bond formation/breakage.

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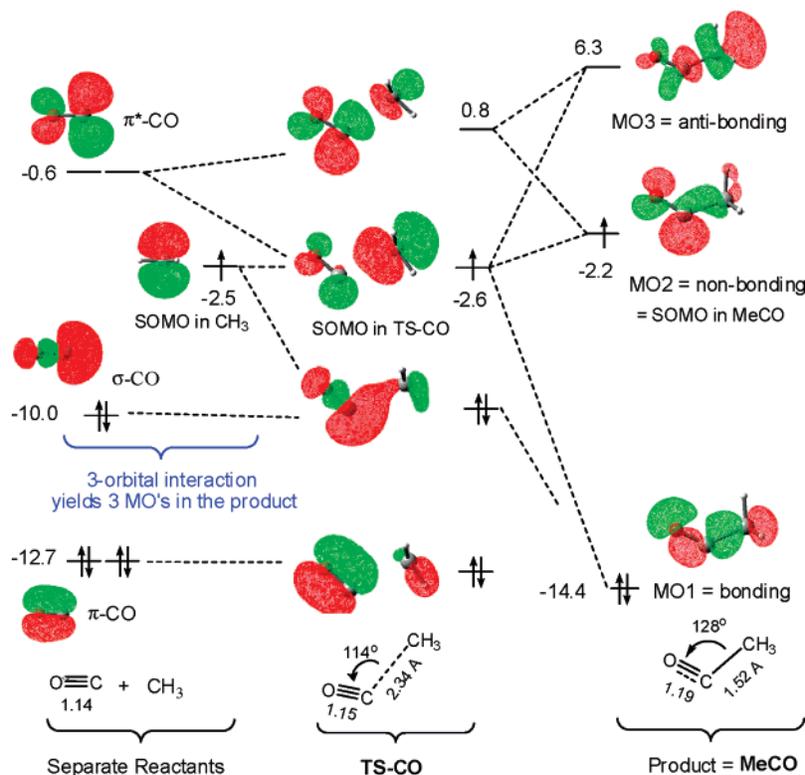
Figure 2. A simplified MO-diagram of the frontier orbital interactions in the TS of methyl addition to free CO, and how they evolve into delocalized MOs in the final product. Energy values for selected MOs are from B3LYP calculations and are given in eV without scaling. The relative energy levels of the MOs are not presented to scale.

entropy terms at 298 K gives $\Delta H^\circ_{B3LYP} = -16.7$ and $\Delta G^\circ_{B3LYP} = -7.3$ kcal/mol. The near 10 kcal/mol difference between these parameters is what would be expected from the loss of the translational entropy in bimolecular reactions. At the CCSD-T level, and using the B3LYP geometries, ΔE_{CCSD-T} is -11.1 kcal/mol, which affords $\Delta H^\circ_{CCSD-T} = -6.9$ kcal/mol when the B3LYP vibrations are used to evaluate the thermal terms. While the difference between the B3LYP and CCSD-T reaction energies is quite large, the values from the two methods satisfactorily bracket the experimental enthalpy of ca. -10 kcal/mol obtained by Ryu using heats of formation data or kinetic data available for CH_3 addition to CO and its reverse.[14] For methyl addition to $[Ru(CO)_5]$, ΔE for formation of **2a** is -25.6 kcal/mol (B3LYP) or -19.8 kcal/mol (CCSD-T). Thus, the two theoretical methods are in agreement that CH_3 addition to a carbonyl of **1** is substantially more exoergic than addition to free CO ($\Delta\Delta E_{B3LYP} = 5.7$, or $\Delta\Delta E_{CCSD-T} = 8.7$ kcal/mol).

Origin of the Effects of CO Coordination in 1. The data in Table 1 implies that CO coordination in **1** introduces opposite effects on the kinetics and thermodynamics of C−C bond formation by a free-radical mechanism. The agreement between the B3LYP and CCSD-T calculations gives confidence in these effects. This is a significant finding because, in general, related radical reactions tend to fulfill the Evans−Polanyi relationship,[33] which anticipates smaller barriers for the more exothermic reactions. For example,[7] the Evans−Polanyi relation holds for a large set of C−C and C−O free-radical bond formation reactions involving substituted alkenes. Thus our results dem-

onstrate one example on how coordination may modify the reactivity patterns of radical addition reactions. In this section we attempt to account for the origin of the calculated effects of coordination qualitatively on the basis of an analysis of the more obvious structural and electronic differences between the respective TSs for free and coordinated CO, and between the respective products.

Figure 2 provides an MO-energy level diagram that follows the frontier orbital interactions in the TS of methyl addition to free CO and how they evolve in the product. Note that the energy of the MOs are from the B3LYP calculations and are given without scaling, so the relative energies should be more meaningful than the absolute ones.[34]

In the TS of methyl addition to free CO, the C−C bond distance is 2.34 Å, which is indicative of minor degree of C−C bond formation. Long C−C bond distances are known for the TSs of radical addition to free alkenes.[7] Figure 2 shows that even at the C−C distance of 2.34 Å of **TS**−CO, some degree of orbital interaction has begun to take place between the methyl-based singly occupied molecular orbital (SOMO) and each of the π*-lowest unoccupied molecular orbital (LUMO) and the σ-highes occupied molecular orbital (HOMO) of CO. As the C−C bond becomes shorter, further mixing between these orbitals eventually affords three delocalized σ-type MOs in the product (MO1−MO3). MO1 is a delocalized bonding MO having an energy much lower than the HOMO of free CO. MO2 has its largest component from the carbonyl carbon in in-phase and out-of phase combination with the methyl and

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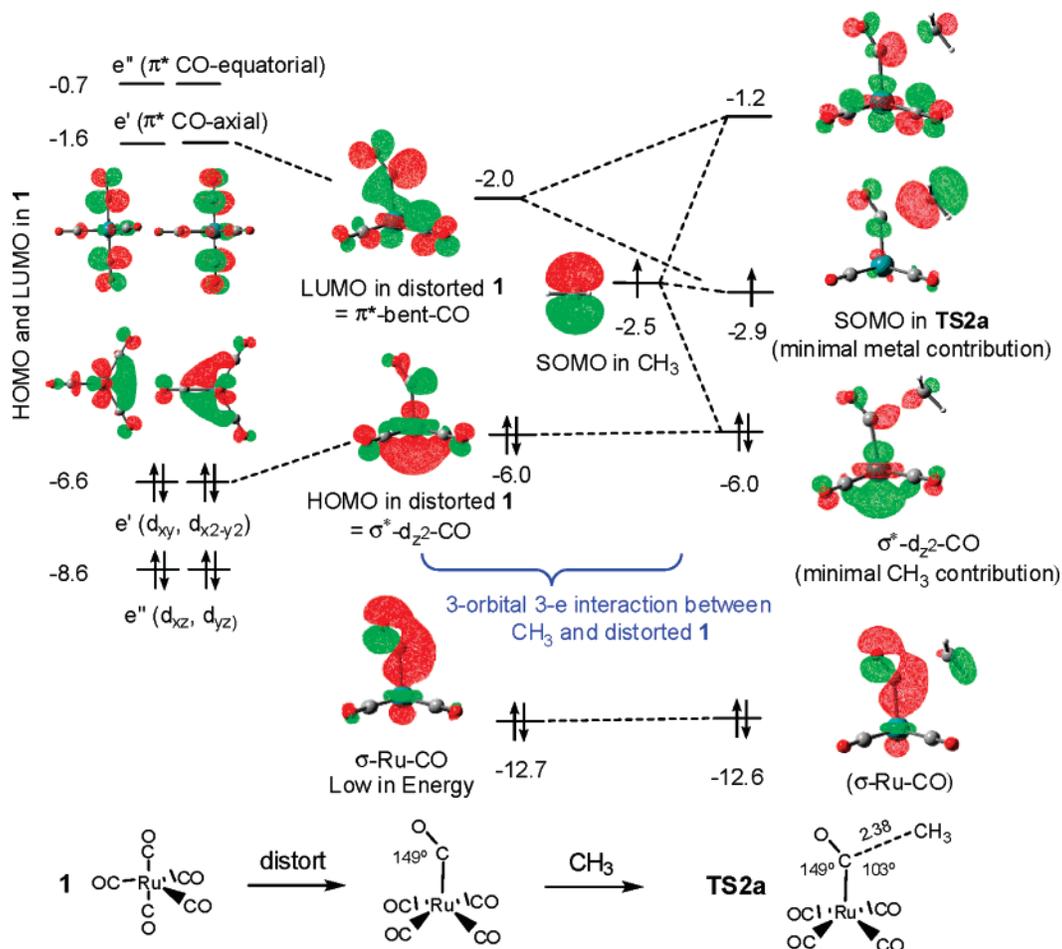
Figure 3. Qualitative MO-energy level diagram that follows the effect of distortion of **1** to the respective parameters in **TS2a** on its frontier orbitals and subsequent interactions between the frontier orbitals and the methyl radical. Energies of selected MOs are unscaled and given in eV. The relative energy levels are not given to scale.

oxygen orbitals, respectively. This formally nonbonding MO is singly occupied in the product and consistent with its display; Mulliken analysis allocates a spin density of 0.62 to the central C in the product, and a density of 0.12 and 0.26 to the methyl group and the oxygen atom, respectively. Finally, MO3 is antibonding in both the CC and CO bonds and remains unoccupied in MeCO. On the basis of this simplified interpretation of C−C bond formation as a three-orbital three-electron process, it is not unreasonable to think of the C−C−O angle of 111° characterizing the TS geometry as the angle that provides optimal alignment of the three orbitals to start C−C bond formation. Obviously, this angle can be achieved in free CO without the need for structural reorganization, and this helps to explain the near absence of an activation barrier to the reaction at the B3LYP level.

In contrast to the reaction of free CO, achieving the TS for methyl addition to a carbonyl coordinated in **1** requires substantial distortion toward the square pyramidal motif, along with bending of the Ru−CO bond of the incipient carbonyl from linear to 149° and stretching it from 1.98 to 2.05 Å (**TS2a**, Figure 1). However, the C−C bond distance in **TS2a** (2.38 Å) is also long, indicating that in **TS2a** too there is no significant degree of C−C bond formation. In this case the energy input required to reorganize the geometry of **1** provides a factor that selectively disfavors the kinetics of methyl addition to **1**. Consistent with such a view, the energy needed to distort the

geometrical parameters of **1** to obtain their respective values in **TS2a** or **TS2b** ($\Delta E_{distort}$) are close to the calculated difference between the activation energy of the reactions of **1** and free CO ($\Delta\Delta E^{\ddagger}$). Specifically, at the B3LYP level $\Delta\Delta E^{\ddagger}$ between **TS−CO** and **TS2a** is 5.6 kcal/mol, and $\Delta E_{distort}$ needed to distort **1** to give its geometry in **TS2a**, is 5.5 kcal/mol. The respective values at the CCSD-T level are 3.8 ($\Delta\Delta E^{\ddagger}$) and 6.1 kcal/mol ($\Delta E_{distort}$).

To elucidate the possible electronic advantages that may account for the requirement of the large degree of distortion to reach the TS in the reaction of **1**, we analyze in Figure 3 the effects of distortion on the character and energy of some of the orbitals involved in the TS of C−C bond formation.

In the trigonal-bipyramidal geometry of **1**, the higher energy occupied MOs are the formally nonbonding (d_{xy}, $d_{x^2-y^2}$) and (d_{xz}, d_{yz}) orbitals, and the lower energy unoccupied MOs are degenerate delocalized carbonyl π*-ligand group orbitals.[35] Distortion toward the square pyramidal motif alters the character and energy levels of these MOs. Most importantly, in the distorted geometry, the LUMO becomes more localized on the bent carbonyl, and the HOMO becomes a nondegenerate metal

(35) Qualitative description of bonding in the neutral metal carbonyl compounds considered in this study can be found in standard inorganic chemistry and group theory texts, see for example: (a) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry, Principles of Structure and Reactivity*, 4th ed.; Harper Collins: New York, 1993. (b) Cotton, A. F. *Chemical Applications of Group Theory*, 3rd ed.; Wiley-Interscience: New York, 1990.
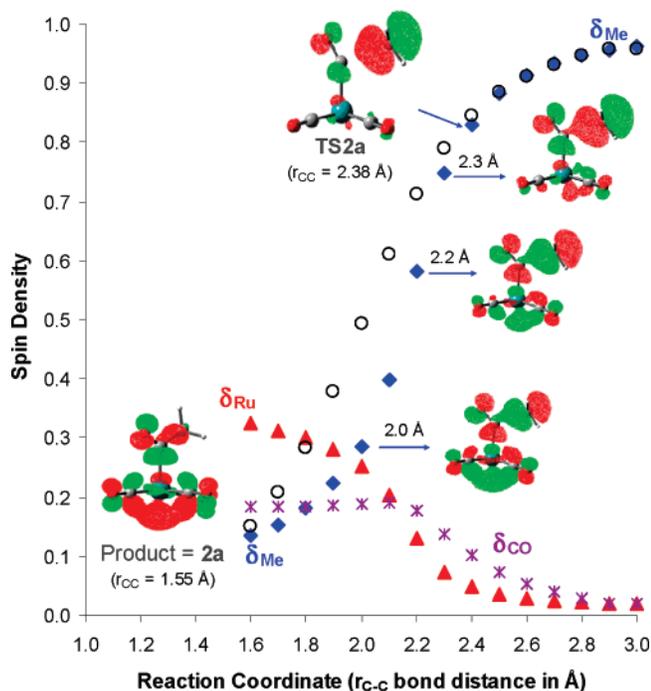
Figure 4. Mulliken spin-density distribution along the C−C reaction coordinate of methyl addition to **1** and to free CO. The open circles and filled diamonds are for the spin density on the methyl group (δ_{Me}) in the reaction of free CO and **1**, respectively. The red triangles are for the spin density on Ru (δ_{Ru}) and the asterisks are for the total spin on the incipient carbonyl (δ_{CO}) of **1**. The MO displays are for the SOMO in the reaction of **1** at the specified points.

based d_{z^2} AO having a significant out of phase component from the σ-orbital of the apical carbonyl (thus denoted as σ^*-d_{z^2}-CO in Figure 3). Distortion also increases the energy of the HOMO by 0.6 eV and decreases the energy of the LUMO by 0.4 eV.[36] This means that distortion increases the spatial availability of the HOMO and LUMO of **1** on the carbon reaction center and makes them energetically more prone to undergo reaction.

Despite the complications engendered by the large size and low symmetry of the system, the MO displays in Figure 3 reveal that in **TS2a** (C−C distance = 2.38 Å) the SOMO of the methyl group undergoes a significant degree of interaction with the carbonyl-based LUMO of the distorted **1**. Interaction between the methyl SOMO and the HOMO of the distorted **1** on the other hand is at best minimal. Note that the bonding MO from the in-phase combination between the σ-CO and the metal (σ-Ru-CO in Figure 3) is substantially lower in energy than the HOMO (−12.7 vs −6.6 eV, respectively), and there is no indication of any mixing between this MO and the methyl SOMO. However, as the TS is crossed, mixing between the HOMO of the distorted **1** and the methyl SOMO becomes pronounced. This is shown in Figure 4 which includes several displays of the SOMO at various points along the C−C reaction coordinate (r_{CC}).[37] The presence of a significant component from

the Ru-d_{z^2} in the SOMO is evident even at $r_{CC} = 2.30$ Å (vs $r_{CC} = 2.38$ Å in **TS2a**), and its weight increases steadily as the C−C distance decreases. At $r_{CC} = 2.0$ Å, the SOMO has nearly equal components from the methyl, π^* and s*-d_{z^2}-CO MOs. In the final product, the d_{z^2} AO dominates the SOMO, but the contributions from the initial methyl and π^*-CO orbitals continue to be important (Figure 4). This analysis demonstrates therefore that C−C bond making by radical addition to a coordinated carbonyl is a three-orbital three-electron problem that involves the SOMO of the methyl group and the HOMO and LUMO of the bent moiety of **1**. The requirement of geometry distortion to reach the TS can thus be profitably viewed as a mechanism that "prepares" a more favorable alignment and energy of the orbitals of **1** to begin C−C bond formation.

To obtain further insight into the electronic aspects of C−C bond formation in the reaction of **1** we have also analyzed in Figure 4 the spin-density distribution along the full reaction pathway.[37] For comparison, the figure includes results for the reaction of free CO. The open circles and filled diamonds are for the spin-density change on the methyl group (δ_{Me}) in the reaction of the free and coordinated CO, respectively. In the early stage of the reaction and until the TSs ($r_{CC} > 2.3$ Å) δ_{Me} decreases gradually and at a rate that is remarkably similar in the two systems. Significantly, at this early stage of the reaction of **1** the spin density removed from the methyl group is transferred primarily to the incipient carbonyl (δ_{CO}, asterisks in Figure 4) and not to the metal center (filled triangles, δ_{Ru}). Once the TSs are crossed ($r_{CC} = 2.3$ Å), the behavior of δ_{Me} in the two systems diverges, with δ_{Me} dropping off much more sharply in the reaction of **1** but then levels off to reach about the same value in the final product (**2a**) as δ_{Me} of **MeCO**. Similarly, the spin density on the metal (δ_{Ru}) undergoes a sharp rise right after the TS is crossed. This behavior supports the idea that before the metal-based orbitals can participate in the reaction, **1** needs to distort toward the square-pyramidal motif. The details of the spin-transfer process suggest that the TS-geometry provides a "threshold" degree of distortion that triggers the involvement of the metal-based MOs.

Thus, addition of an alkyl radical to either free or coordinated CO can be viewed qualitatively as a three-electron three-orbital process. In the reaction of free CO the unpaired electron ultimately resides in a carbon-based MO, whereas in the reaction of **1** it is found on a delocalized metal-based MO. It is therefore not surprising that the two reactions have very different exothermicities. The transition states of the two systems, however, are similar in the sense that the spin density is still localized largely on the methyl group, and the C−C bond distance is relatively long. In the reaction of free CO the three orbitals involved in C−C bond making are all initially accessible to begin mixing. However, for the coordinated CO to begin to allow C−C bond formation it is necessary to significantly distort the geometry of **1**; this introduces a factor that significantly contributes to the activation barrier to the reaction. Viewed this way, we can rationalize why methyl addition to **1** encounters a much larger barrier than addition to free CO despite the fact that addition to **1** is thermodynamically much more favorable.

Methyl Addition to [Ru(CO)₃(dmpe)] (3). To evaluate the degree to which the ancillary ligands in **1** may modify the energetics of alkyl addition to d⁸ metal carbonyls, we considered

(36) While the absolute energy of the MOs calculated using DFT methods normally requires scaling to become meaningful, and different scaling factors may be needed when there are major changes in the system (such as when a transition metal is introduced or when the spin state is changed), the effects of distortion on the calculated HOMO−LUMO gap should be at least qualitatively valid.

(37) Each point in the figure corresponds to a geometry minimized in the C_s point group at the specified fixed r_{CC} value. In the reaction of **1**, the calculations were carried out by starting at **TS2a** and then elongating or shortening the r_{CC} bond while keeping the molecular plane of symmetry bisecting the two pairs of symmetry equivalent Ru−CO bonds.
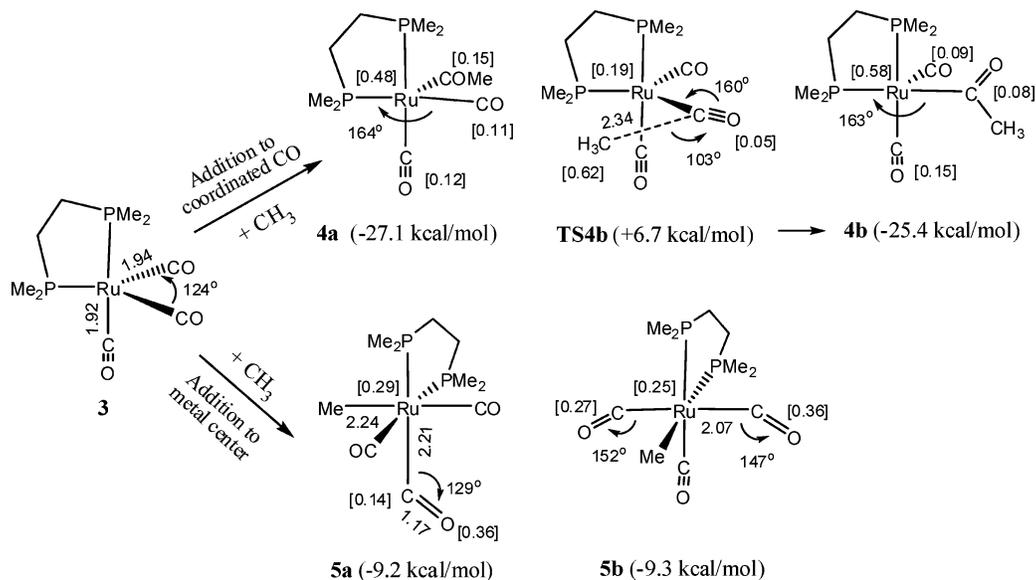
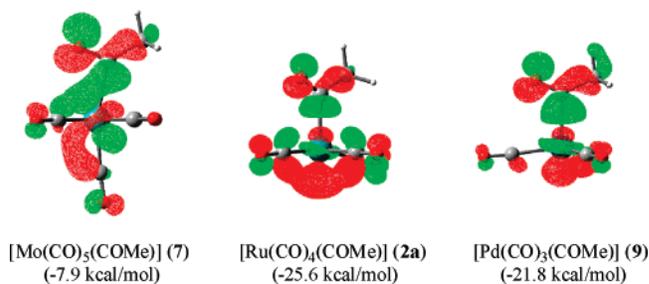**Figure 5.** Geometry and energy (E_{B3LYP}) relative to separate reactants of the TS and products from methyl addition to **3** (units in Å). Values in brackets are for selected spin densities.

the reaction of [Ru(CO)$_3$(dmpe)], **3**, which was among the more effective cocatalysts in the carbonylation experiments conducted by Boese and Goldman.[16] The results are presented in Figure 5. As in the reaction of [Ru(CO)$_5$], the geometry of the acyl product from methyl addition to **3** is square pyramidal. The four isomers that are possible in this geometry vary within 3 kcal/mol. Among these, the lowest energy isomer is **4a** (Figure 5) with the acyl group at the apical position. In studying the kinetics of methyl addition to **3**, we located two TSs, one leading to the acyl isomer having CO at the apical position of the square pyramid (**TS4b** leading to **4b**, Figure 5), and a slightly higher energy TS ($\Delta\Delta E^{\ddagger} = 1.5$ kcal/mol) leading to an isomer with apical phosphino group (not shown). Despite the large electronic differences between dmpe and two CO ligands, the activation energy of methyl addition to **3**, 7.3 kcal/mol (**TS4b**), is only slightly different from the activation energy of the reaction of **1** (6.2 kcal/mol). Perhaps more surprisingly, we also find that the reaction energies of methyl addition to **3** and **1** are similar: $\Delta E_{B3LYP} = -27.1$ and -25.6 kcal/mol, respectively.

In contrast to the reaction of **1**, for the reaction of **3** we could also locate three isomeric energy minima for the six-coordinate alkyl product (**5**, Figure 5) resulting from addition of CH$_3$ to the Ru center of **3** (as opposed to addition to a CO ligand). The three isomers are found to have comparable energies, but they are approximately 16 kcal/mol above the 17-e acyl species, and ΔG°_{B3LYP} for their formation by methyl addition to **3** is positive (3–4 kcal/mol). This indicates that such metal–alkyl species are unlikely to be involved in the reaction of d^8-ML$_5$ carbonyl complexes with alkyl radicals.

Although they are probably too high in energy to form in competition with direct methyl addition to coordinated CO, the metal–alkyl addition products are quite interesting in the context of alkyl–radical/metal–carbonyl chemistry. For example, **5a** is distinguished by one strongly bent (129°) and greatly elongated (2.21 Å) Ru–CO bond (Figure 5). Mulliken analysis allocates a spin density of 0.49 to this bent carbonyl, of which 0.36 electrons are on the carbonyl carbon. **5a** can thus be described as a metalloacyl radical with an octahedral 18-e Ru-(I) center. Expressing this somewhat differently (but still

implicating an 18-e Ru(I) center), one may view the bent CO as an anionic radical ligand. Preston et al. have provided evidence for the presence of such metalloacyl bonding mode in the [Fe(CO)$_5$]$^-$ anion radical on the basis of its observed low-temperature EPR spectrum.[15] Interestingly, in the *trans*-CO–Ru–CO isomer (**5b**, Figure 5), two Ru–CO bonds are bent, though to a degree smaller than that found in **5a**: 150° (**5b**) vs 127° (**5a**). In this case the *trans*-CO–Ru–CO moiety is planar, and the spin density is delocalized nearly evenly over the Ru and the two bent carbonyls. Despite the pronounced degree of spin delocalization in **5b**, **5a** and **5b** are calculated to have essentially the same energy.

Thermodynamics of Methyl Addition to Other 18-e Metal Carbonyls. For both activation energies and reaction energies of radical addition, the differences between the two d^8-complexes considered above are calculated to be small. This observation raised the possibility that all metal carbonyl complexes might have similar properties. We therefore investigated methyl addition to [Mo(CO)$_6$] (**6**) and [Pd(CO)$_4$] (**8**) as representatives of metal carbonyls having d^6 and d^{10} electronic configurations, respectively. The geometry and the SOMO of the acyl products from addition to **6** and **8** are compared with those of **2a** in Figure 6. We note that as in the reaction of **1**, no bound metal–alkyl minima could be identified for the reaction of either **6** or **8**.

[Mo(CO)$_5$(COMe)] (**7**)   [Ru(CO)$_4$(COMe)] (**2a**)   [Pd(CO)$_3$(COMe)] (**9**)
(-7.9 kcal/mol)   (-25.6 kcal/mol)   (-21.8 kcal/mol)

Figure 6. Geometry and SOMO in the acyl products of methyl addition to [Mo(CO)$_6$] (**6**), [Ru(CO)$_5$] (**1**), and [Pd(CO)$_4$] (**8**), and their B3LYP energies relative to separate reactants (ΔE).

Table 2. Saturated Metal Carbonyl Complexes: Reaction Energy of Methyl Radical Addition, and Ionization and CO Bond Dissociation Energies[a]

reactant	ΔE_{B3LYP}[b]	ΔE_{CCSD-T}[b]	ΔH°_{B3LYP}[c]	IE[d]	BDE[e]
CO	−19.9	−11.1	−16.2		
[Mo(CO)$_6$]	−7.9	−3.0	−4.3	192	38.2
[Ru(CO)$_5$]	−25.6	−19.8	−21.4	172	26.4
[Pd(CO)$_4$]	−21.8	−14.3	−17.8	186	9.3
[Ru(dmp) (CO)$_3$]	−27.1		−22.8	139	34.2

[a] Units are in kcal/mol. [b] ΔE_{B3LYP} and ΔE_{CCSD-T} are the raw electronic energies for the transformation from separate reactants to the acyl product, and are given without ZPE corrections. [c] ΔH° values are reaction enthalpies evaluated at 298 K and 1 atm. [d] IE is ΔE_{B3LYP} for the ionization of the 18-electron metal carbonyls. The point group of the cations of the Mo, Ru, and Pd carbonyls is D_{3d}, C_{4v}, and D_{2d}, respectively. [c] BDE is the B3LYP energy for CO dissociation from the metal carbonyl that yields a product having a closed shell electronic state. The point group of the dissociation products is C_{4v} (Mo), C_{2v} (Ru), and D_{3h} (Pd).

Methyl addition to [Mo(CO)$_6$] yields a six-coordinate acyl product (**7**) having a structure exhibiting small angular deviations from the idealized octahedral frame. As known for [V(CO)$_6$],[38] distortion in **7** may be attributed to Jahn−Teller effects in the pseudo-O_h geometry of low spin d^5-ML$_6$ complexes. For methyl addition to tetrahedral [Pd(CO)$_4$], the product (**9**) is trigonal pyramidal with the acyl group at the apical position. In both of the given metal−radical complexes, the unpaired electron is in an MO having a metal-d$_{z^2}$ component in out of phase combination with an acyl based MO corresponding to the SOMO of the free MeCO radical described in Figure 2.
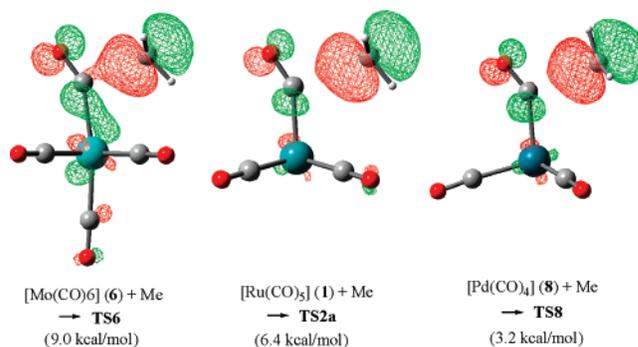
The energies of the reactions of the 18-e complexes considered so far are compared in Table 2.

In sharp contrast to the reaction energy of the Ru complexes, methyl addition to [Mo(CO)$_6$] is calculated to be only slightly exothermic ($\Delta E_{B3LYP} = -7.9$ kcal/mol). Extrapolation from the CCSD-T energies even yields a slightly *positive* enthalpy for this reaction ($\Delta H^{\circ}_{CCSD-T} = +0.6$ kcal/mol). This is substantially less favorable than addition to free CO ($\Delta\Delta E_{B3LYP} = 12.1$ kcal/mol), implying that coordination of CO in this prototypical d^6 metal carbonyl inhibits its reaction with the alkyl radical. On the other hand, ΔE_{B3LYP} for methyl addition to [Pd(CO)$_4$] is −21.8 kcal/mol, 3.9 kcal/mol less favorable than that of addition to [Ru(CO)$_5$], but still slightly more exothermic than addition to free CO ($\Delta E_{B3LYP} = -19.9$ kcal/mol). Thus the reaction energy of alkyl radical addition to metal carbonyls is very sensitive to the electronic configuration of the metal.

In any attempt to elucidate the factors that contribute toward differentiating the thermodynamics in the given reactions, several different thermodynamic cycles can be envisaged. The utility (if any) of such cycles depends on the general correlation (if any) of the energetics of the individual reaction steps with the reaction energy. For example, since the addition is (at least formally) oxidizing in the metal, we first considered the electron-transfer cycle of eq 3.

$$[M(CO)_n] + [CH_3] \rightarrow [M(CO)_n]^+ + [CH_3]^- \rightarrow [M(CO)_{n-1}COCH_3] \quad (3)$$
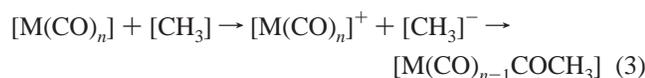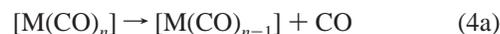
The calculated trends in the ionization energy of the homoleptic carbonyl complexes: IE = 192 (Mo) < 172 (Ru) > 186 (Pd) (in kcal/mol Table 2), are found to match their methyl radical

(38) Bernhardt, E.; Willner, H.; Breidung, J.; Buhl, M.; Jonas, V.; Thiel, W.; Kornath, A. *J. Phys. Chem. A* **2003**, *107*, 859.

Figure 7. Geometry and SOMO in the TS of methyl addition to [Mo(CO)$_6$] (**6**), [Ru(CO)$_5$] (**1**), and [Pd(CO)$_4$] (**8**), and their B3LYP energies relative to separate reactants ($\Delta E^{\ddagger}_{B3LYP}$).

affinity trends: $-\Delta E_{B3LYP} = 7.9$ (Mo) < 25.6 (Ru) > 21.8 (Pd) (in kcal/mol), with the more easily oxidized metal−carbonyl having the greater driving force to add the methyl radical. However, for [Ru(CO)$_3$(dmpe)] the ionization energy is much smaller than that of **1** (137 vs 172 kcal/mol). On the basis of the IE alone, one would expect methyl addition to [Ru(CO)$_3$-(dmpe)] to be much more exothermic than addition to **1**, yet it is only 1.5 kcal/mol more so ($\Delta\Delta E_{B3LYP}$). Thus, while IE is presumably a relevant parameter in determining the thermodynamics of the given reaction, it is not systematically the dominating one in governing the reaction energy trends.

Another straightforward thermodynamic cycle for radical addition to an M−CO bond is that of eq 4, which implicitly expresses the relative thermodynamics as the sum of M−CO bond dissociation and M-acyl bond formation.

$$[M(CO)_n] \rightarrow [M(CO)_{n-1}] + CO \quad (4a)$$

$$[M(CO)_{n-1}] + \cdot C(O)CH_3 \rightarrow [M(CO)_{n-1}(COCH_3)] \quad (4b)$$

The calculated trends in the M−CO bond dissociation energy, BDE = 38.2 (Mo) > 26.4 (Ru) > 9.3 (Pd) (in kcal/mol, Table 2),[39] are clearly different from the trends of the reaction energy for methyl addition. Similarly, while the difference in the reaction energy of methyl addition to the two Ru complexes is negligible, the difference in the CO BDEs of the two Ru complexes is quite large (ΔBDE = 7.8 kcal/mol, Table 2). Such lack of correlation is perhaps not surprising in that the energy of the radical addition process is dependent on the difference between the M−CO bond strength and the strength of the product M-acyl bond. If both of these correlate in the same direction with simple parameters such as the electron-donating ability of the metal center, the dependence of their *difference* on such parameters is not expected to follow a simple relationship.

TS of Methyl Addition to 18-e Metal Carbonyls. The data pertaining to the geometry and energy of the TSs of methyl addition to the 18-e complexes considered thus far are presented in Figure 7 and in Table 3.

Despite the poor thermodynamic driving force for methyl addition to [Mo(CO)$_6$], the reaction barrier for this reaction is calculated to be relatively small ($\Delta E^{\ddagger}_{B3LYP} = 9.0$, or $\Delta E^{\ddagger}_{CCSD-T}$

(39) The given CO BDE trends parallel the experimental and previously calculated ones. See for example: (a) Li, J.; Schreckenbach, G.; Ziegler, T. *J. Am. Chem. Soc.* **1995**, *117*, 486 and references therein. (b) van Wullen, C. *J. Chem. Phys.* **1996**, *105*, 5485.

Table 3. Comparison of the Activation Energy of Methyl Radical Addition to d⁶, d⁸, and d¹⁰ Metal Carbonyls, and the Distortion Energies Needed to Reach the TS*[a]*

reactant	$\Delta E^{\ddagger}_{B3LYP}$	$\Delta E^{\ddagger}_{CCSD-T}$	$\Delta H^{\circ\ddagger}_{B3LYP}$	$\Delta E_{distort}$
free CO	0.8	5.3	1.8	
[Mo(CO)₆]	9.0	11.6	10.5	6.9
[Ru(CO)₅]	6.4	9.3	7.4	4.3
[Ru(dmpe)(CO)₃]	7.3		8.3	4.1
[Pd(CO)₄]	3.2	6.4	4.4	2.7

[a] Units are in kcal/mol. $\Delta E^{\ddagger}$ is the electronic activation energy relative to separate reactants. $\Delta H^{\circ\ddagger}$ is the activation enthalpy evaluated at 298 K and 1 atm, $\Delta E_{distort}$ is the B3LYP energy needed to distort the geometry of the reactants to their parameters in the respective TSs.

= 11.6 kcal/mol), only slightly greater than the barrier of addition to [Ru(CO)₅] (6.4 (B3LYP) or 9.3 (CCSD-T) kcal/mol). For the reaction of [Pd(CO)₄] on the other hand, the activation energy is calculated to be quite low, 3.2 (B3LYP) or 6.4 kcal/mol (CCSD-T). This is 3.0 kcal/mol *lower* than the activation energy of the reaction of [Ru(CO)₅], although addition to [Pd(CO)₄] is 4 kcal/mol less exoergic than addition to [Ru-(CO)₅]. The variations in $\Delta E^{\ddagger}_{B3LYP}$ (2.7–9.0 kcal/mol) are clearly much smaller than those calculated for the reaction energies (−8.4 to −27.1 kcal/mol), and the order ($\Delta E^{\ddagger}$: Mo > Ru > Pd) is different from that of the thermodynamics (ΔE: Mo > Pd > Ru). These results can be understood on the basis of the nature of the TS discussed for the reaction of [Ru(CO)₅] which appears to be common to the TS of the other systems. Specifically, the C−C distance between the adding methyl and the incipient carbonyl is long in all the T*S*s: 2.14 (Mo), 2.38 (Ru), and 2.37 Å (Pd). Figure 7 shows that at these distances the SOMO is still localized on the methyl group, and has some contribution from the π*-MO of the bent carbonyl, but with minimal contribution from the metal-based orbitals. Consistently, the spin densities on the metal in these TSs are small: 0.10 (Mo), 0.05 (Ru), and 0.05 (Pd). Thus the factors that could potentially differentiate the thermodynamics of metal−acyl formation, such as the ionization energies and M−CO and M-acyl bond energies are unlikely to have the same discriminatory impact in the TSs. Instead, the variations in the activation energies are expected to depend on the energy needed to distort the geometry of the starting-metal carbonyls to the respective geometries in the TSs, which involves bending of the M−CO bond to nearly the same extent: M−CO angle = 151° (Mo), 149° (Ru), and 145° (Pd). Indeed the distortion energies, $\Delta E_{distort}$ (calculated at the B3LYP level), are quite similar to the activation energies ($\Delta E^{\ddagger}_{B3LYP}$), as seen in Table 3.

Methyl Addition to Unsaturated Metal Carbonyls. Radical addition to electronically and coordinatively unsaturated complexes might be expected to lead to behavior very different from that of the 18-e systems considered above. In particular, metal addition to the metal center of 18-e complexes does not compete with addition to their CO ligands, and it is of interest to know if this applies to unsaturated systems as well. In this section we examine briefly the energetics of methyl addition to the closed shell 16-e fragments resulting from CO dissociation from the homoleptic metal carbonyls and to the square planar d⁸ [Rh-(CO)₄]⁺ and the 17-e square pyramidal d⁷ [Tc(CO)₅] complexes. In this series both the metal−acyl and the metal−alkyl products were located and characterized as true minima on the potential-energy surface. The energies of these products relative to the separate reactants are given in Table 4.

Table 4. Comparison of the Reaction and Activation Energy of Methyl Radical Addition to Representative Unsaturated Metal-Carbonyl Complexes*[a]*

reactant	B3LYP Results			CCSD−T Results		
	$\Delta E_{CO-add'n}$	$\Delta E_{M-add'n}$	$\Delta E^{\ddagger}_{CO-add'n}$	$\Delta E_{CO-add'n}$	$\Delta E_{M-add'n}$	$\Delta E^{\ddagger}_{CO-add'n}$
Free CO	−19.9		0.8	−11.1		5.3
[Mo(CO)₅]	−23.4	−20.2	6.1	−22.0	−26.0	8.2
[Ru(CO)₄]	−25.0	−30.7		−22.3	−37.3	
[Pd(CO)₃]	−21.7	−7.2	1.5	−14.1	−8.0	4.5
[Rh(CO)₄]⁺	−27.0	−15.9		−18.0	−17.2	
[Tc(CO)₅]	−31.0	−48.0		−29.1	−57.4	

[a] $\Delta E_{CO-add'n}$ and $\Delta E_{M-add'n}$ are the electronic energies for formation of the acyl and alkyl products from separate reactants, respectively, and are given in kcal/mol without ZPE corrections. $\Delta E^{\ddagger}_{CO-add'n}$ is the electronic activation energy for direct C−C bond formation.

Both the B3LYP and CCSD-T calculations predict methyl addition to a coordinated carbonyl in the given unsaturated complexes to be thermodynamically more favored than addition to free CO. The energies of addition to the 16-e Ru and Pd fragments (−25.0 and −21.7 kcal/mol, respectively, B3LYP) are remarkably close to those of the corresponding parent 18-e complexes (−25.6 and −21.8 kcal/mol; Table 3). In contrast, methyl addition to [Mo(CO)₅] (−23.4 kcal/mol) is much more exothermic than addition to [Mo(CO)₆] (−7.9 kcal/mol). This appears to follow, at least in part, from the presence of an η²-type bond between the CO of the acyl group and Mo in the Mo−acyl product that is not present in any of the other acyl products. At the B3LYP level, methyl addition to [Rh(CO)₄]⁺ has a slightly greater exothermicity than addition to the Ru fragment ($\Delta\Delta E$ = 2.0 kcal/mol) but this is reversed at the CCSD−T level ($\Delta\Delta E$ = −4.3 kcal/mol). Finally, the exothermicity of methyl addition to a carbonyl of [Tc(CO)₅] (which affords a closed shell-five coordinate 16-e product) is somewhat but not dramatically greater (−31.0 kcal/mol, B3LYP results) than that of the 16- or 18-e species investigated.

Table 4 shows that the energy difference between the metal−alkyl and metal−acyl products varies substantially among the different complexes, primarily reflecting a large variability in the metal−alkyl addition enthalpies. For the Mo fragment, the two addition products have comparable energies, and their order depends on the method used in the calculation ($\Delta\Delta E_{B3LYP}$ = 3.4 or $\Delta\Delta E_{CCSD-T}$ = −4.0 kcal/mol). For the Ru fragment, the five coordinate 17-e alkyl product is significantly lower in energy than the acyl product ($\Delta\Delta E_{B3LYP}$ = −5.7 or $\Delta\Delta E_{CCSD-T}$ = −15 kcal/mol). In the reaction of the Pd fragment on the other hand, the Pd−alkyl product is quite high in energy ($\Delta\Delta E_{B3LYP}$ = 15 or $\Delta\Delta E_{CCSD-T}$ = 5.9 kcal/mol). Perhaps unexpectedly, the B3LYP level predicts that [Rh(CO)₄Me]⁺, which belongs to the more common class of five-coordinate 17-e complexes, is 11 kcal/mol higher than the unusual four-coordinate 15-e acyl product, although the difference between the two is reduced to 0.9 kcal/mol at the CCSD-T level. Finally, [Tc(CO)₅Me] is about 20 kcal/mol lower in energy than [Tc-(CO)₄(MeCO)]. This is intuitively appealing in that [Tc-(CO)₅Me] is a six-coordinate 18-e octahedral species.

In studying the kinetics of the given reaction, we could locate true TSs for direct C−C bond formation only for the Mo and Pd 16-e fragments. The corresponding B3LYP activation energies are +6.5 (Mo) and +1.9 (Pd) kcal/mol. As before, a large part of these activation energies can be attributed to the requirement of distortion in the geometry of the fragment to

Table 5. Activation and Reaction Parameters for Cyclohexyl Radical Addition to Free CO and Representative 18-e Metal Carbonyls[a]

reactant	activation parameters			thermodynamic parameters		
	$\Delta E^{\ddagger}_{B3LYP}$	$\Delta H^{o\ddagger}_{B3LYP}$	$\Delta G^{o\ddagger}_{B3LYP}$	ΔE_{B3LYP}	ΔH^{o}_{B3LYP}	ΔG^{o}_{B3LYP}
free CO	1.1	2.2	11.6	−14.7	−11.3	−0.4
[Mo(CO)$_6$]	5.5	6.7	15.6	−2.2	1.0	11.2
[Ru(CO)$_5$]	7.9	9.4	19.7	−18.5	−15.2	−4.3
[Ru(dmpe)(CO)$_3$]	8.6	10.1	22.2	−19.3	−15.8	−2.3
[Pd(CO)$_4$]	2.4	3.7	13.5	−16.0	−13.7	−1.8

[a] Units are in kcal/mol. ΔE values are for the electronic energies for the transformation from separate reactants to the products or TSs and are given without ZPE correction, and ΔH^{o} and ΔG^{o} are the activation and reaction enthalpies and Gibbs free energies, respectively, evaluated at 298 K and 1 atm.

Scheme 2. Proposed Mechanism for Cyclohexane Photocarbonylation[a]
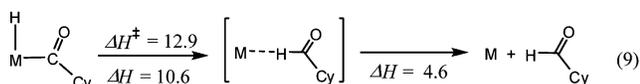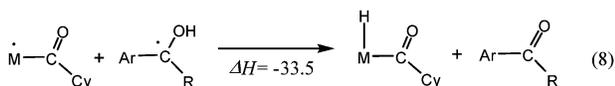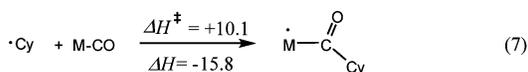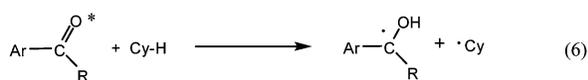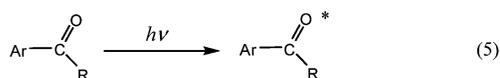
[a] Enthalpies are calculated at the B3LYP Level for M−CO = [Ru(CO)$_3$(dmpe)] and ArC(O)R = acetophenone (in kcal/mol).

reach the TS ($\Delta E_{distort} = 5.7$ (Mo) and 1.1 (Pd); in kcal/mol). For methyl addition to the Ru and Rh complexes, the potential energy surface is complicated by the presence of direct interaction between the methyl SOMO and a nonbonding metal orbital even at long M−C distances. A detailed account of the energy surface of methyl addition to square planar complexes will be presented elsewhere.

Thus, this section demonstrates that alkyl radical addition to bound CO is not impacted strongly or in any systematic manner by coordinative unsaturation at the metal center. Furthermore, the calculations reveal that competition between addition to the metal center vs addition to the carbonyl carbon becomes important in unsaturated complexes, but the thermodynamic preference between these two is very dependent on the specific metal system.

Relevance to Alkane Carbonylation. The ability of photoexcited aryl ketones to generate free alkyl radicals by hydrogen atom abstraction from alkanes is a well-known process (eqs 5 and 6, Scheme 2). Boese and Goldman have shown that under high pressures of CO, irradiation of aryl ketones in cyclohexane produces cyclohexaldehyde without the need of a metal carbonyl. However, the photocarbonylation becomes more efficient under 1 atm CO in the presence of d[8] metal carbonyls such as [Ru(dmpe)(CO)$_3$] (0.7−7.0 mM) than in the presence of even 70 atm CO in the absence of any metal carbonyl.[16] On the other hand, no increase in the carbonylation rates was observed when d[6]-[Mo(CO)$_6$] was used as a potential cocatalyst.[40] A reaction sequence accounting for the role of the d[8]-metal carbonyls in

mediating photocarbonylation was proposed on the basis of the observed kinetics of the process and other mechanistic experiments, and is reproduced in Scheme 2.[16]

Calculations on the reaction between the cyclohexyl radical and the various 18-e metal carbonyls considered before were conducted at the B3LYP level, and the results are summarized in Table 5. As found for the reaction with the methyl radical, cyclohexyl radical addition to free CO is more rapid than addition to any of the metal carbonyls studied. However, for the cyclohexyl radical, the exothermicity of addition to free CO is calculated to be quite low ($\Delta H^{o}_{B3LYP} = -11.3$ kcal/mol; yielding $\Delta G^{o}_{B3LYP} = -0.4$ kcal/mol). Given that the presence of even a small steady-state concentration of photolytically generated free alkyl radical will lead to fast reaction with the hydroxyalkyl radical, as well as to bimolecular alkyl radical reactions such as dimerization and β-hydrogen abstraction, the low exothermicity of the reaction of free CO suggests that the reversibility of this reaction is an important factor impeding alkyl radical carbonylation in the absence of a metal carbonyl.

The activation enthalpies for cyclohexyl radical addition to [Mo(CO)$_6$], [Ru(CO)$_5$], and [Ru(dmpe)(CO)$_3$] are 9.4, 6.7, and 10.1 kcal/mol, respectively. Although these barriers are substantially larger than the barrier to addition to free CO, they are still not too high to preclude the reaction. However, cyclohexyl radical addition to [Mo(CO)$_6$] is endothermic ($\Delta H^{o}_{B3LYP} = 1.0$ kcal/mol) and highly endoergic ($\Delta G^{o}_{B3LYP} = 11.2$ kcal/mol). In contrast, the enthalpy of cyclohexyl addition to the ruthenium complexes is calculated to be quite negative (≈ -15.5 kcal/mol), over 4 kcal/mol more exothermic than addition to free CO. Thus in the context of alkane carbonylation, the calculations suggest that the high exothermicity of radical addition to CO bound to the ruthenium complexes is the key to their ability to mediate alkane photocarbonylation.

The reactions subsequent to cyclohexyl addition to coordinated CO in Scheme 2 are all calculated to be thermodynamically favored and kinetically facile for [Ru(CO)$_3$(dmpe)]. First, hydrogen atom abstraction from the hydroxyalkyl radical and the formation of a conventional six coordinate closed shell species (eq 8) is highly exothermic ($\Delta H^{o}_{B3LYP} = -33.5$ kcal/mol; evaluated for ArC(O)R = acetophenone). This reaction is also expected to be fast.[41] The activation enthalpy calculated for the reductive elimination (leading first to a σ-complex, eq 9) is not particularly high (12.9 kcal/mol). The overall reaction enthalpy for conversion of the six-coordinate hydrido-acyl species to free metal fragment and free aldehyde (eq 9) is 15.2 kcal/mol, which affords $\Delta G^{o}_{B3LYP} = +0.5$ kcal/mol when the

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entropy terms are included. Subsequent reaction with CO (eq 10) is highly exothermic (-32.8 kcal/mol) and expected to be fast.

Thus, the calculations support the reaction scheme previously proposed to account for the role of d^8-transition metal complexes in cocatalyzing alkane carbonylation.[16] In particular, strong support is provided for the key step, the attack of a radical on coordinated CO, a reaction which has not previously been proposed. The calculations can be used to explain why d^8-metal carbonyls are effective cocatalysts for alkane photocarbonylation and,[16] and by comparison, why the more common six-coordinate d^6 carbonyls, exemplified by $[Mo(CO)_6]$, are found to be ineffective.[40]

Conclusions

We have used electronic structure methods to investigate how coordination of CO to a transition metal may affect its reactions with alkyl radicals. While this question is of fundamental importance to free radical chemistry in general, a primary motivation in conducting our study has been to understand why d^8-complexes such as $[Ru(dmpe)(CO)_3]$ are effective in cocatalyzing alkane photocarbonylation via a free radical mechanism.[16] To present our results in perspective we have conducted systematic calculations on metal carbonyls representative of several geometries and metal electron configurations. Except for the reaction of $[Mo(CO)_6]$, in all the examples considered, methyl addition to a coordinated CO is found to be $2-10$ kcal/mol more exothermic than addition to free CO. The exothermicity of addition to $[Ru(dmpe)(CO)_3]$ is particularly large, and this has been used to explain why this complex is particularly effective in cocatalyzing alkane photocarbonylation. By the same argument, the low exothermicity of addition to $[Mo(CO)_6]$ can explain why it does not cocatalyze carbonylation.[40]

We have also addressed the effect of coordination of CO on the kinetics of its reaction with an alkyl radical. For all the metal carbonyls considered, the activation energy is found to be greater than that of addition to free CO, though the barriers are still small ($2 < \Delta H^{\circ\ddagger}_{B3LYP} < 10$ kcal/mol). In every case studied, the geometry in the TS is characterized by a long distance between the radical center of the alkyl group and the carbonyl carbon, suggesting that minimal electronic interactions and minimal C—C formation takes place in the TSs. However, the TSs are also characterized by significantly elongated and bent M—CO bonds. Accordingly, the activation energies are close to the energies required for the same distortion of the complexes in the absence of alkyl radical. Interestingly, the calculated activation and reaction energy trends do not satisfy the Evans–Polanyi relationship. Such behavior demonstrates that coordination of unsaturated substrates to transition metal fragments can be a powerful tool in controlling reactivity in free radical chemistry.

The results presented herein should of course be applicable to any reaction in which alkyl radical attacks coordinated CO. In this context we note that several metal-catalyzed radical carbonylation reactions have been reported.[42] To our knowledge, direct radical attack on coordinated CO has not been previously proposed in the context of these systems; our results suggest, however, that it should be at least considered as a possible step in any radical-based metal-catalyzed carbonylation system.

Supporting Information Available: Complete ref 18; tables of Cartesian coordinates and total B3LYP and CCSD-T energies pertaining to methyl addition to all the 18-e complexes considered in the study, including isomers and second-order stationary points not described in the figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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