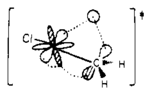
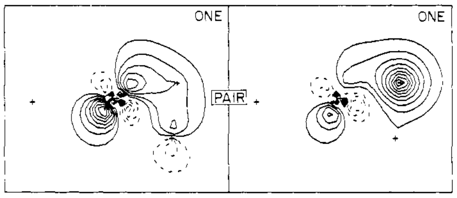
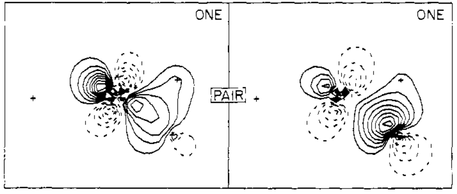


a) Ru-H Bond to C-H Bond Pair



b) Ru-C Sigma Bond Pair



c) Ru-C Pi Bond to Ru dπ Lone Pair

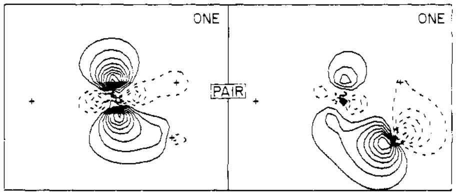


Figure 2. GVB(3/6)PP one-electron orbitals near the transition state (Θ(H-Ru-C) = 50.0°). (a) Orbital pair describing the Ru-H bond of the reactant **1** and the C-H bond of the product **2**; (b) orbital pair describing the Ru-C σ-bond for both **1** and **2**; (c) orbital pair describing the Ru-C π-bond of **1** and the Ru dπ lone pair of **2**. Contours are shown at intervals of 0.05 au.

smooth transition from an Ru-H to a C-H bond may be possible, since the in-plane carbon p-orbital is oriented correctly for formation of the in-plane C-H bond. Indeed, at the highest level of theory examined, we find that the CH_2 insertion into Ru-H proceeds with a low activation barrier (11.5 kcal/mol) and is thermodynamically favorable, with an exothermicity of 7.1 kcal/mol, as displayed in the reaction coordinate of Figure 1. Notice that the transition state occurs approximately halfway between reactants and products, as expected for a reaction which is nearly thermoneutral (Hammond postulate).

Figure 2 shows the orbitals near the transition state [Θ(H-Ru-C) = 50°]. Here we see that the Ru-H bond smoothly converts into the C-H bond (Figure 2a), while the Ru-C σ-bond (Figure 2b) does not change significantly. At the transition state, the Ru-C π-bond (Figure 2c) has begun to move out of the way of the incipient C-H bond and already has substantial Ru d lone-pair character.[12] The Ru-C and Ru-H bonds at the transition state have lengthened significantly from their values in **1**, increasing from 1.87 to 1.93 Å for Ru-C and from 1.65 to 1.77 Å for Ru-H.

The exothermicity, activation barrier, and transition-state geometry were calculated at five levels of theory, as shown in Figure 1.[13] The geometries along the reaction coordinate were predicted by analytic gradients of Hartree-Fock wave functions,[14] with all geometrical parameters optimized at each H-Ru-C angle.[15] In the highest level of theory considered (the bottom curve of Figure 1), we optimize the six active orbitals (the orbitals actively involved in the insertion, namely, the Ru-H and the Ru-C σ- and π-bond pairs) self-consistently for a full six-electron CI within those six orbitals (all occupations of six electrons in six orbitals—the GVB(3/6)CI-MCSCF level). This level allows a balanced description of the three bond pairs changing during the reaction. Higher level, extended basis dissociation-consistent CI calculations[16] on various dissociation processes involving these species[13] suggest that the true exothermicity is 10.4 kcal/mol, in good agreement with our MCSCF calculations.

In conclusion, we have shown that alkylidene migratory insertions can be quite facile, proceeding with a low activation barrier. These calculations provide the first quantitative evidence for the feasibility of this elementary reaction (previously postulated based on experimental results,[4-8] but never directly observed). These results suggest that for Ru, the reverse reaction of α-hydrogen elimination is subject to a barrier of 18.6 kcal/mol. This is consistent with the fact that α-H eliminations most often occur for the early transition metals. Work in progress on the related reaction of CH_2 insertion into an Ru-alkyl bond suggests an exothermicity of 4.9 kcal/mol. The activation barrier will probably be higher than that for H due to the necessary reorientation of the alkyl upon migration from Ru to CH_2.[17] The alkyl migration differs primarily from the hydride energetics because the incipient C-C bond is weaker than the incipient C-H bond. While our calculations suggest that late transition metals undergo CH_2 insertion with relative ease, early metal alkylidenes have been observed that do *not* insert into M-R bonds. We believe that this is due to the much greater strength of the M-C π-bond for the early transition metals.[18]

Acknowledgment. This work was supported by the Shell Development Co., Houston, TX, and the National Science Foundation (Grant CHE83-18041). E.A.C. gratefully acknowledges the support of a National Science Foundation Predoctoral Fellowship (1982-1985).

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[12] By the point at which Θ(H-Ru-C) = 40.0°, the Ru d lone pair is fully formed. (The equilibrium geometry of $ClRuCH_3$ has an H-Ru-C angle of 23.2°.)

[13] Full details to be published elsewhere. A valence double-ζ quality basis was used.

[14] Hartree-Fock (HF) calculations are known to predict accurate geometries. As a test, we optimized the geometry of **1** at both the HF and GVB-RCI(3/6) levels and found that the two geometries were very similar (e.g., all bond lengths and angles differed by at most 0.03 Å and 11.9°, respectively); see ref 11.

[15] The geometries of **1** and **2** were optimized with no restrictions except the retention of C_s symmetry (lower symmetry cases were found to be higher in energy; ref 11).

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Carbyne-Carbyne Ligand Coupling on a Single Tungsten Center

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The coupling of two carbyne ligands on a single transition-metal center has been analyzed theoretically by Hoffmann, Wilker, and Einsenstein.[1] These authors concluded that the reaction should be allowed for systems containing six electrons in the metal-ligand π-orbitals. In Fischer-type carbyne complexes, e.g., $[(W{\equiv}CPh)Br(CO)_4]$ (**1**), there are six electrons in metal-ligand π-orbitals.[2] The carbyne complex **1** is derived from tungsten hexacarbonyl, itself a six-π-electron system, by transformation of a carbonyl ligand into a carbyne ligand. Since the number of π-electrons is not changed during this reaction, a second transformation of one of the remaining carbonyl ligands in **1** into a carbyne ligand should lead to a tungsten bis(carbyne) system with

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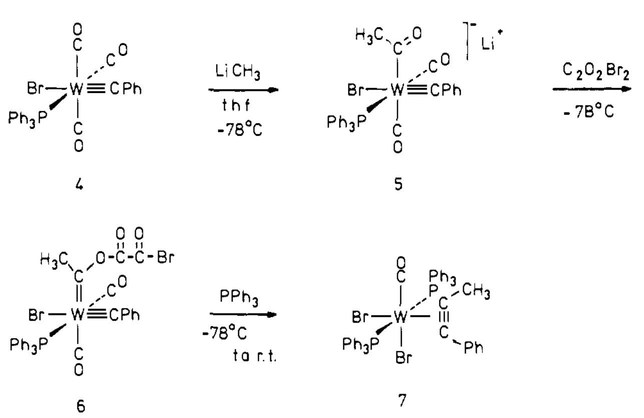
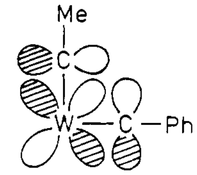
six metal–ligand π-electrons. According to Hoffmann et al. this configuration should result in the formation of a tungsten acetylene complex. Here we would like to report the realization of this situation.

Complex **1** is prepared by reaction of $W(CO)_6$ with phenyl lithium and oxalyl bromide.[3,4] The intermediate tungsten acyl complex is isolated as its tetramethylammonium salt $[NMe_4][W(C(O)Ph)(CO)_5]$ (**2**). The carbonyl ligands in **1** have been demonstrated by Fischer to undergo attack by organyl lithium reagents to give tungsten acyl complexes of the type $Li[(W{\equiv}CPh)Br(C(O)R)(CO)_3]$ (**3**).[5] These compounds, at least in principle, contain the requisite components for the generation of a second carbyne ligand within a tungsten carbyne complex. However, complexes **3** are very thermally labile. Since it is known that bis-substituted carbyne complexes of the type $[(W{\equiv}CPh)Br(CO)_2L_2]$ are significantly more stable than the monosubstituted derivatives $[(W{\equiv}CPh)Br(CO)_3L]$,[6] it appeared likely that the stability of complexes **3** would increase with the introduction of an additional donor ligand. Consequently, we considered monosubstituted carbonyl tungsten carbyne complexes as a suitable starting point for the potential synthesis of a tungsten bis(carbyne) system.

The triphenylphosphine-substituted complex $[(W{\equiv}CPh)Br(CO)_3(PPh_3)]$[6] (**4**), is easily accessible in a simple one-pot procedure in the reaction of **2** with oxalyl bromide and triphenylphosphine.[4] Addition of 1 equiv of methyllithium in ether to a cold (−78 °C) solution of **4** in THF results in clean formation of the acyl tungsten carbyne complex $Li[(W{\equiv}CPh)Br(C(O)Me)(CO)_2(PPh_3)]$ (**5**). Complex **5** is stable at temperatures below 0 °C for several hours. Two strong absorptions in the infrared at 1986 and 1916 cm^{-1} indicate the presence of two cis CO ligands; a weak band at 1522 cm^{-1} is observed for the acyl ligand. The ^{13}C NMR spectrum (−80 °C) of **5** exhibits resonances at 315.1 ppm for the carbon atom of the acyl ligand, at 267.2 ppm for the carbyne carbon, and at 217.4 ppm ($^2J_{CP,trans}$ = 47 Hz) and 216.8 ppm ($^2J_{CP,cis}$ = 7 Hz) for the carbonyl ligands. Both the low carbonyl stretch of the acyl ligand and the low-field resonance of the acyl carbon atom indicate a strong carbenoid character of the acyl ligand and thus the possibility of attack by electrophiles at the oxygen atom of the acyl ligand. Upon addition of oxalyl bromide to the orange solution of **5** at −78 °C the color turns deep brown. The low-temperature product is postulated to be $[(W{\equiv}CPh)[{=}C(OC(O)COBr)Me]Br(CO)_2(PPh_3)]$ (**6**). Metal carbene complexes of the type $[(W{=}C(OC(O)COBr)R)(CO)_5]$ have previously been demonstrated to be intermediates in the transformation of tungsten acyl complexes into tungsten carbyne complexes by reaction with oxalyl bromide.[4] After addition of a slight excess of triphenylphosphine at 0 °C and warming of the mixture to room temperature, the color of the solution turns deep blue. Removal of the solvent, washing of the residue with acetone, and recrystallization from CH_2Cl_2/pentane give the blue-green tungsten alkyne complex $[WBr_2(PhC{\equiv}CMe)(CO)(PPh_3)_2]$ (**7**) in 50% yield. **7** was characterized by comparison of its IR and ^1H NMR data with the values reported in the literature[7] as well as by elemental analysis.[8,9]

In the intermediate tungsten carbyne carbene complex **6**, the six metal–ligand π-electrons are sufficient to stabilize independently a metal–carbon triple bond and a metal–carbon double bond. As the bromooxalate dissociates from intermediate **6**, a new electron-deficient methylcarbyne ligand is generated. The two carbyne ligands have to share a pair of electrons in a three-center bond involving two p-orbitals of the carbyne carbon atoms and a d-orbital of the central tungsten atom.





Coupling of the two carbyne ligands likely occurs quickly after or possibly even simultaneously with the dissociation of bromooxalate from the carbene ligand in **6**. The facile formation of coordinated methylphenylacetylene is thus in agreement with the theoretical conclusion by Hoffmann et al.[1]

The stability of the intermediate electron-deficient tungsten bis(carbyne) complex should increase with the introduction of donor substituents at the carbyne carbon atoms.[1] Indeed, stable molybdenum bis(aminocarbyne) complexes with the same formal electron count as the present system have been generated by protonation of electron-rich molybdenum and tungsten bis(isocyanide) complexes.[10] Higher formal electron counts are predicted to make carbyne–carbyne coupling a forbidden reaction, but increasing electronegativity of the metal center should lower the barrier for this process.[1] Recently, a formal carbyne–carbyne ligand coupling reaction has been observed on a palladium center.[11] Irradiation of bis(α-diazomethyl)palladium complexes $[Pd(C(N_2)R)_2(PR'_3)_2]$ with UV light gives rise to acetylene complexes $[Pd(RC_2R)(PR'_3)_2]$. The formation of alkyne ligands from the coupling of carbyne ligands involving several transition-metal centers[12] as well as the reverse of this reaction[13] has been observed

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(9) No products have been detected containing dimethyl- or diphenylacetylene ligands which might arise in case of intermolecular ligand coupling pathways.

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in a variety of systems. Related reactions are the coupling of carbyne ligands with carbonyl ligands[14] as well as the coupling of two carbonyl ligands[15a] and of two isocyanide ligands.[15b]

Acknowledgment. This work was supported by the National Science Foundation (CHE-8411023).

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UV Multiple-Photon Dissociation of $Cr(CO)_6$ to Cr* and CO: Evidence for Direct and Sequential Dissociation Processes

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Gas-phase photodissociation of metal carbonyls to metal atoms and CO is well-known.[1-8] Multiphoton ionization experiments have shown that dissociation of the carbonyls to ground- and excited-state metal atoms is unexpectedly efficient relative to competing ionization processes.[9-13] Because the mechanisms behind metal atom formation are not entirely clear, we have investigated the KrF* laser (248 nm) multiple-photon dissociation of $Cr(CO)_6$ to Cr* and CO in the gas phase. We present evidence that Cr* is formed by two processes: (1) a direct process, where $Cr(CO)_6$ is excited into a dissociative continuum, and (2) a sequential process, where a $Cr(CO)_4$ intermediate photoproduct absorbs an additional photon to produce Cr*.

We monitored formation of Cr* by detecting the emission obtained upon unfocused KrF* laser irradiation of ~20 mtorr of $Cr(CO)_6$ contained in a flow cell. Laser fluences ranged from 3 to 40 mJ cm^{-2}. Emission normal to the laser beam was dispersed by a monochromator (resolution 0.5–2 Å) and detected by a photomultiplier tube in conjunction with a boxcar integrator. Standard lamps were used to calibrate the optical system.

KrF* laser photodissociation of $Cr(CO)_6$ produces a rich Cr emission spectrum. Emission from more than 40 states was detected.[14] The relative populations[15] of the Cr* states follow a statistical distribution.[8] Emission is not quenched by CO, Ar, and He at pressures from 1 to 10 torr (except for two states, see below). The laser-fluence-dependence of the emission intensity indicates that production of Cr* occurs via both two-photon and three-photon processes. All states of Cr* for which ΔE_{298} of formation[16] from $Cr(CO)_6$ is less than the energy of two photons (115 kcal/mol each) are indeed formed by a two-photon process, whereas all other states are formed by a three-photon process.

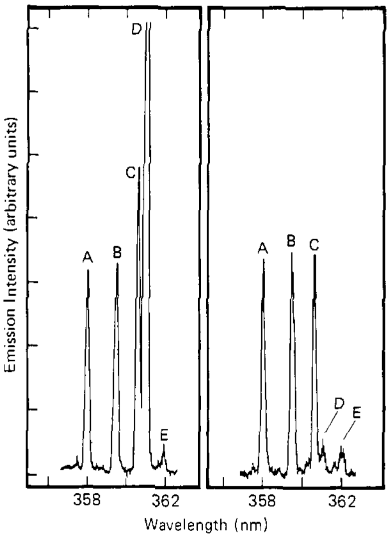

Figure 1. Cr emission spectrum at 2-Å resolution, showing quenching of $Cr(t^5F^o_{1,2})$ emission (peak D) by CO. At left, $p_{CO} = 1$ torr; at right, $p_{CO} = 5$ torr. Peak assignments are as follows, with the upper state energy vs. the a^7S_3 ground state noted in parentheses: (A) $y^7P^o_4 \rightarrow a^7S_3$ (27 935 cm^{-1}); (B) $y^7P^o_3 \rightarrow a^7S_3$ (27 820 cm^{-1}); (C) $y^7P^o_2 \rightarrow a^7S_3$ (27 729 cm^{-1}); (D) $t^5F^o_{1,2} \rightarrow a^5G_{2,3}$ (0.56-Å spacing not resolved) (48 210 and 48 218 cm^{-1}); (E) $x^5H^o_7 \rightarrow a^5G_6$ (48 140 cm^{-1}).

One-photon KrF* laser photodissociation of $Cr(CO)_6$ gives predominantly,[18,19] or exclusively,[20] vibrationally hot $Cr(CO)_4$, suggesting that Cr* may be formed in our experiments by reactions 1 and 2. If Cr* formation proceeds by this pathway, however,

$$Cr(CO)_6 + 1h\nu \rightarrow Cr(CO)_4{}^{\dagger} + 2CO \tag{1}$$

$$Cr(CO)_4{}^{\dagger} + 1(2)h\nu \xrightarrow{k_2} Cr^* + 4CO \tag{2}$$

quenching of Cr* emission by added CO might be expected to occur by competition of reaction 3 with reaction 2. Only five

$$Cr(CO)_4{}^{\dagger} + CO \xrightarrow{k_3} Cr(CO)_5 \tag{3}$$

of the Cr* states we detected are thermodynamically accessible from $Cr(CO)_5$ with the observed fluence dependence;[21] thus, quenching of Cr* emission should be readily apparent if $k_3[CO] \gtrsim k_2$.[23] These rates should in fact be comparable: at a CO pressure of 10 torr,[24] $k_3[CO] \approx 5\text{–}7 \times 10^7\ s^{-1}$, k_2 is not known, but we estimate[25] that $k_2 \approx 5 \times 10^7\ s^{-1}$ at a typical laser fluence of 20 mJ cm^{-2}. The lack of quenching thus indicates that for-

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