

γ are weakly varying functions of ΔE , it can be predicted on the basis of eq 4 that if the assumptions made above are appropriate, a linear relation should exist between $\ln k_{nr}$ and E_{em} . From the results shown in Figure 1 there is obvious agreement between theory and experiment. The agreement is not surprising given the assumptions involved and the nature of the excited states. The excited states appear to share a common deactivating mode. The results of investigations of low-temperature emission spectra of $\text{Os}(\text{bpy})_3^{2+}$ and several related complexes of the type $\text{Os}(\text{bpy})_2\text{L}_2^{2+}$ ^{3b,11} all show vibrational progressions of approximately 1300 cm^{-1} corresponding to ligand-based skeletal stretching vibrations¹² and appear to be the dominant deactivating modes, ω_M .¹³ The assumption of a low-temperature limit is clearly appropriate for a vibration having $\hbar\omega_M = 1300\text{ cm}^{-1}$ since $\hbar\omega_M/k_B T > 6$.^{5a}

Inherent in the success of eq 4 is the assumption that variations in V are relatively small for the series of excited states. Clearly, V will not be constant, but it appears in the intercept as $\ln V^2$. Variations in V , which are in the range ca. $30\text{--}100\text{ cm}^{-1}$ from eq 1, must be too small to affect the linear relationship between $\ln k_{nr}$ and E_{em} noticeably. The importance of significant changes in V may appear in the enhanced lifetimes in Table I for phen complexes compared to analogous bpy complexes. The lifetime enhancements of approximately a factor of 3 are almost entirely due to the faster radiationless decay of the bpy excited states. The similarity in slopes in Figure 1 suggests similar deactivating modes and S values for the two series and that radiationless decay rate differences come from a decrease in the electron tunneling matrix element for the phen complexes.

A third assumption is that S , which is a measure of excited-state distortion in the deactivating mode or modes, is constant. Preliminary Franck-Condon analyses on the emission spectra of these complexes using standard procedures¹⁵ show that systematic variations in Δ_M^2 and hence in S do occur as E_{em} increases. However, the variations are relatively small and act only to modify slightly the observed slopes and intercepts of the plots of $\ln k_{nr}$ vs. E_{em} and not the conclusions reached here. Further work on the quantitative evaluation of V , Δ_M^2 , and S is currently in progress.

The smaller but still significant variations in the radiative rate constants in Table I should also be noted since it is their interplay with k_{nr} which determines excited-state lifetimes. In particular, as the luminescence is moved to higher energy, k_r becomes more important in determining excited-state lifetimes. Radiative decay rate constants are predicted to increase approximately as the cube of the emission energy, provided that the integrated intensity of the charge-transfer absorption remains constant.¹⁶ The data in Table I are in agreement with this prediction, and it appears that there exist satisfactory theoretical bases for accounting in a detailed way for relative excited-state lifetimes in this series of compounds.

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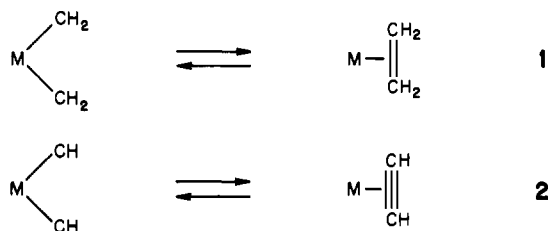
On Coupling Carbenes and Carbynes

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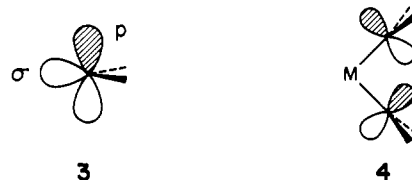
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Let us think about the electronic requirements for transition-metal-catalyzed linking of two carbenes to an olefin, **1**, two carbynes to an acetylene, **2**, or the reverse reaction, the direct dismantling of a coordinated ethylene or acetylene. A wide range



of coordination numbers and geometries could be envisaged, but the essence of the reactions is revealed by examining the naked metal case and then restoring the other ligands. Figure 1 shows a level correlation diagram for reaction 1 for $M = W$ and no ligands. The two methylenes are put in a conformation appropriate to the final geometry of the coordinated olefin.¹

Each methylene contributes a σ and p orbital, **3**.² Two methylenes bring to $M(\text{CH}_2)_2$ in- and out-of-phase combinations of these σ and p orbitals. Three of these four combinations find a metal partner to interact with—they are $1a_1$, $1b_2$, $2a_1$ as seen in Figure 1. The fourth combination, $2b_2$, **4**, having too many nodes,



is of the wrong pseudosymmetry to interact effectively with any metal s, p, or d orbital. Above these four orbitals lie three metal d's, unaffected by the methylenes. Higher still are some metal-carbene antibonding combinations, $4a_1$, $3b_2$, $5a_1$, hybridized at the metal to point away from the carbenes.

On the olefin side we have $1a_1$, the CC σ bond, and $2a_1$ and $1b_2$, the two combinations responsible for metal-olefin bonding. Note the π and π^* components here.³ Above these lie four metal orbitals as well as $2b_2$ and $5a_1$, antibonding partners to $1b_2$ and $2a_1$.

The level correlations are straightforward. The critical orbital, $2b_2$, is carbene-carbene antibonding. As the carbenes near each other, this level goes up in energy, sharply so. It must correlate to a CC σ^* or π^* level, and no metal mixing can assuage its destabilization. Metal interaction can keep one b_2 orbital ($1b_2$) down in energy but not two.

At this point a convention for electron counting must be established. If the carbenes and the olefin are treated as neutral,

(1) This may not necessarily be the equilibrium orientation of the two carbenes—that being set by either steric factors (as it seems to be in the known biscarbene complexes, to be referenced later) or by electronic factors: the two acceptors will avoid, if possible, competing for the same metal d orbital. See, for instance: Burdett, J. K.; Albright, T. A. *Inorg. Chem.* **1979**, *18*, 2112-2120 and references therein. Be that as it may, the ethylene precursor geometry must be attained early on in the reaction.

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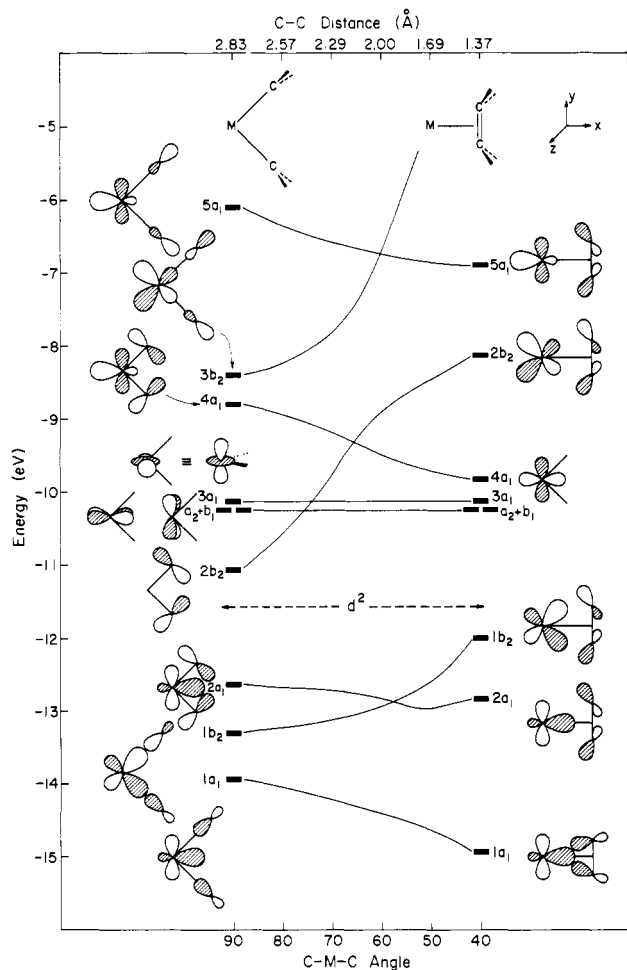
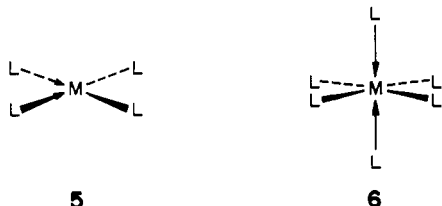


Figure 1. Evolution of frontier orbitals of $W(CH_2)_2$ as a function of C-W-C angle. The energies are taken from an extended Hückel calculation. Note the nonlinear CC distance scale at the top. The filling of levels for a d^2 case (carbenes neutral) is indicated.

the electron counts are as shown in Figure 1. The reaction encounters a level crossing, is "forbidden", for all electron counts greater than d^2 .

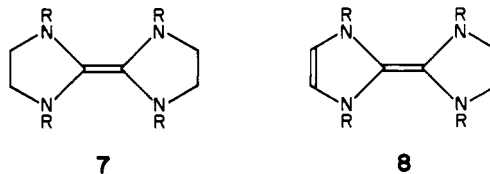
From this basic picture the evolution of the orbitals of a fully coordinated metal may be predicted. If two ligands are added in the plane of the carbenes, **5**, the symmetric (a_1) and antisymmetric (b_2) ligand base combinations interact primarily with $3b_2$ and $5a_1$ on the left of Figure 1, with $2b_2$ and $5a_1$ on the right. The essential level crossing is untouched. If two axial ligands are also added, **6**, the z^2 , $3a_1$, orbital is removed from the picture. Again the level crossings due to b_2 remain. A similar procedure may be followed for any desired metal coordination geometry.



The reaction therefore is controlled by the relative location of the carbene $2b_2$ orbital and the metal a_2 , b_1 , and/or $3a_1$ orbitals. If $2b_2$ is raised in energy and/or if the nonbonding metal d orbitals are lowered in energy so that the metal levels end up lower in energy than the $2b_2$ orbital, the orbital crossings will not take place. The reaction becomes allowed for d^4 and d^6 electron counts (and d^8 for **5**). This can be accomplished by any combination of the following: putting π donors on the carbene, substituting the carbene carbon by a more electropositive atom, making the metal

more electronegative, or putting π acceptors on the metal. When the reaction is "allowed", one would expect a small barrier for biscarbene-olefin interconversion, no judgment being made here as to which side of the reaction is thermodynamically more stable.

There are thousands of known olefin complexes. But only one class of substituted ethylenes cleaves readily to two complexed carbenes. This is **7**, used by Lappert,⁴ and the related **8**, by Öfele,⁵ in the synthesis of numerous biscarbenes of type **5** and **6** as well as biscarbenes of other coordination numbers and electron counts. The electron-donating substituents on the carbene fragments are apparent.



A similar analysis may be made for the carbyne coupling reaction **2**. This process is also forbidden for all electron counts above six (metal d electrons and electrons in carbyne p orbitals combined), unless once again one applies the strategy for interchanging metal and carbyne p levels detailed above. Seven-coordination presents a special case where an electron count of four is optimal. With proper attention paid to the annoying problem of electron counting, the analysis is easily extended to nitrene, oxido, and isocyanide linkups. It encompasses as diverse phenomena as the noninterconvertibility of bound $PhNO$ and $(PhN)(O)$,⁶ the existence of separate $(NR)_2$ and $RNNR$ complexes⁷ and $(O)(CHR)$ and (R_2CO) complexes,⁸ though in very different environments, the photochemically induced cleavage of a dioxo ligand in $(TPP)Mo(O_2)_2$,⁹ and the coupling of two isocyanides to a diaminoacetylene in a seven-coordinate $Mo(II)$ complex.¹⁰ Particularly exciting is the prescription, forthcoming,

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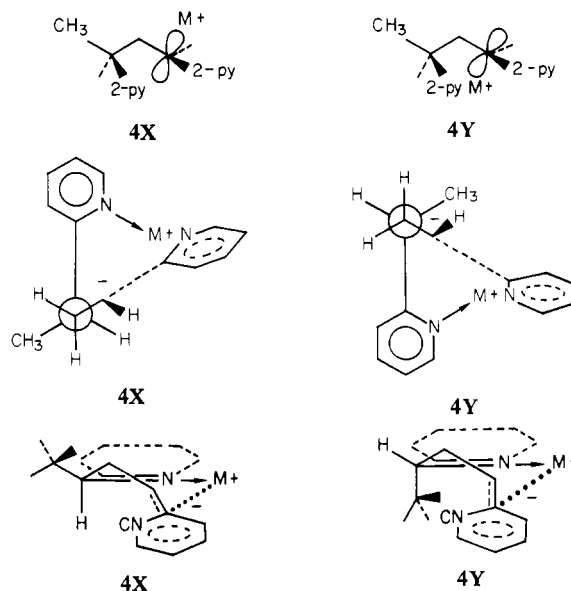
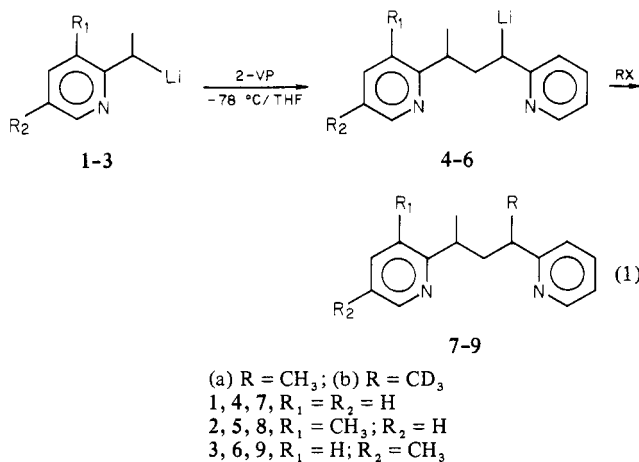
Oligomerization of Vinyl Monomers. 2. Evidence for a Conformationally Restrained Six-Membered Ring Containing Lithium Ion

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There has been much recent interest in stereoselective alkylations of lithiocarbanion salts and similar electrophilic reactions.^{2,3} Several of these have been formulated in terms of an intramolecular coordination of the metal ion by a chelating group, thus



providing an asymmetric environment at the reacting carbanion.^{2,4,5}

We now wish to report evidence for such a scheme involving the addition of 2-vinylpyridine (2-VP) to anions 1-3 at -78°C in THF and sequential methylation according to reaction 1. Previous work^{4a,6} had indicated a very highly stereoselective (>99%) methylation of 4, yielding meso 7. The corresponding methylation in the presence of larger or cryptated and crowned cations had been shown to occur in a largely nonstereoselective manner. The remarkable selectivity of the methylation reaction in the presence of Li or Na ion was ascribed as due to the formation of a conformationally restrained cyclohexene-like ring containing Li ion 4X, which should be preferred over its diastereomer 4Y, generated by exchange of CH₃ and methine H, in which butane gauche and CH₃-nitrogen lone pair interactions are expected to decrease its stability. Substitution of the 3' proton of the chelating pyridine ring by a group of modest size, such as methyl, in 4X is expected to substantially decrease the stability of the chelated complex relative to that of the unsubstituted analogue due to nonbonded interactions with the methylene and the methyl group. Substitution of the 5' proton, however, should have no effect. A similar substitution of the 3' position in 4Y is not expected to lead to severe nonbonded interactions. Accordingly, anions 2 and 3 prepared by reaction of the carbon acid in THF at -78°C with *n*-BuLi were reacted with 1 equiv of 2-VP by slow in vacuo distillation followed by reaction with CH₃I. The products were isolated, separated by preparative medium-pressure liquid chromatography, and analyzed by ¹H and ¹³C NMR spectroscopy and by GC utilizing a 25-m capillary column. The results are shown in Table I.

The 100-MHz ¹H NMR spectrum of 7 in CDCl₃ showed a methyl doublet (δ 1.30) and a methylene multiplet (δ 2.11) characteristic for meso 7.⁶ The corresponding spectrum of 8b showed two methyl doublets at 1.16 and 1.26 ppm in the ratio of 3:1, and the gas chromatogram of the mixture likewise showed a 3:1 ratio of isomers.^{7,8} Corresponding observations were made

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(7) Stereoisomeric relationships were confirmed by mass spectrometry and base-catalyzed epimerization (Table I). The stereoisomers could also be distinguished by the proton chemical shifts of their picoline methyl groups at 1.95 and 2.10 ppm.

(8) The 3:1 ratio of stereoisomers was identical when the crude reaction mixture was directly injected into the GC column so that the ratio of stereoisomers was unaffected by the LC separation.