polarization with **2** shows that here $k_{ET} \gtrsim 1 \times 10^{10}$ s^{-1}.

Rate of excitation energy transfer involves the interaction of the two locally excited states $\Psi_R\Psi_{S*}$ and $\Psi_{R*}\Psi_S$.[6,7,19] Since this interaction strongly decreases with carbonyl–carbonyl distance, it is not surprising that k_{ET} is much larger for the 1,5-dione than for the 1,7-dione. As far as we know the only data available on rate of intramolecular $^1n\pi^*$ energy transfer in aliphatic diketones are those of Lissi et al.[20] Interestingly, the rates they find for a series of nonrigid 1,4-diones ($\sim 2 \times 10^8$ s^{-1}) are much lower than that for the 1,5-dione **2**.

Although the reported measurements represent only a first step in the investigation of CPL as a probe for intramolecular energy transfer, the technique seems quite promising. Objects for further study are the extension of the dynamic range of the method by adding quenchers to affect τ_F and the influence of temperature and solvent. Further interesting possibilities include the study of intermolecular energy transfer in racemates from the dependency of $G_L - G_R$ on concentration and, as suggested at Groningen University,[21] the use of chemiexcitation to create the *meso*-dione's locally excited state in high enantiomeric excess.

Acknowledgment. We are grateful to J. P. M. van der Ploeg for the synthesis of **2** and to Dr. H. J. C. Jacobs for stimulating discussions.

Registry No. *meso*-**1**, 83998-83-8; *trans*-**2**, 83998-84-9; *trans*-**2a**, 83998-85-0; *trans*-**4**, 29365-79-5; *trans*-8-acetoxy[4.3.0]nonane-3,4-dione, 83998-86-1; bicyclo[3.3.0]octane-3,7-diol-3-carboxylic acid, 83998-87-2.

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A Theoretical Prescription for Reductive Coupling of CO or CNR Ligands

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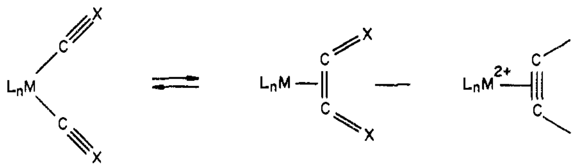
Reactions that lead to carbon–carbon bond formation are always an attractive synthetic prospect. Especially valuable for such transition-metal catalyzed reactions are carbonyls or isocyanides, which are ubiquitous ligands. So let us think about the electronic requirements for coupling two CO or CNR ligands on a transition-metal center, reaction 1.[1]



1 X = O, NR

Many coordination numbers, geometries, metals, and electron counts could be envisaged and have been examined by us. We focus our discussion here on the seven-coordinate d^4 case, following an experimental observation—the only well-explored instance of C–C bond formation among thousands of carbonyl and isocyanide complexes occurs in the $[Mo(CNR)_6X]^+$ system.[2,3] Here the isocyanides couple in the presence of Zn and acid, with net addition of two H atoms to form $\{Mo[(CNHR)_2](CNR)_4X\}^+$, X = halide.

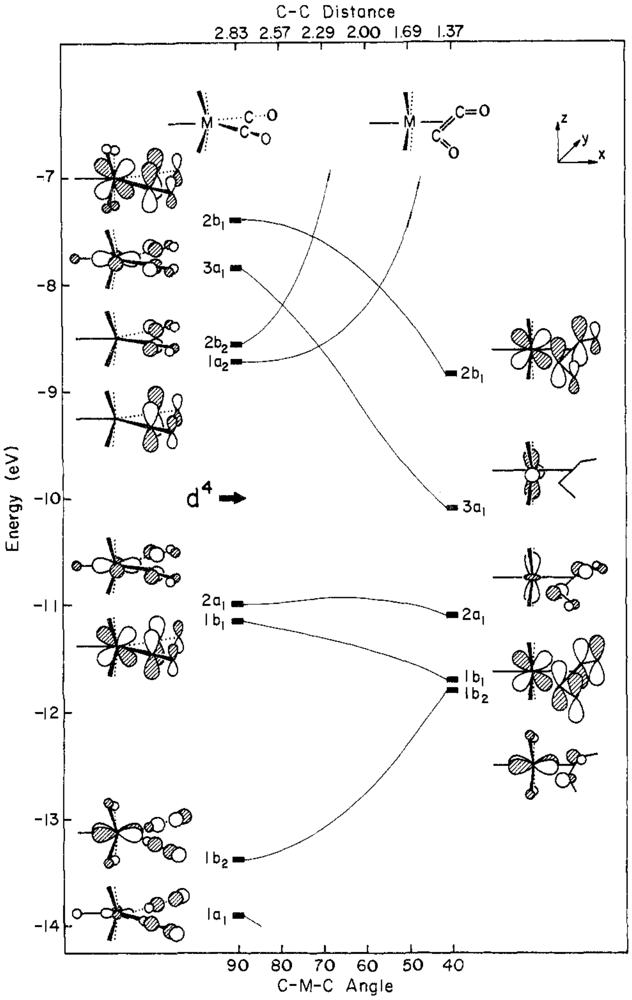


Figure 1. Evolution of energy levels in $H_5W(CO)_2^{3-}$ along an idealized coupling coordinate. The $2a_1$ level is the highest filled one for a d^4 electron count. Note the linear C–M–C angle scale at bottom and the corresponding nonlinear C–C distance scale at top.

Figure 1 shows the extended Hückel correlation diagram for the coupling of two carbonyls on W in a model $W(CO)_2H_5^{3-}$ ion, having a capped trigonal prismatic geometry.[4] The $1a_1$ and $1b_2$

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(1) The analysis is related to our previous study of carbene and carbyne coupling: Hoffmann, R.; Wilker, C. N.; Eisenstein, O. *J. Am. Chem. Soc.* **1982**, *104*, 632–634.

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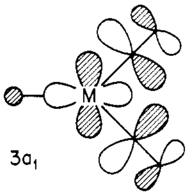
(3) (a) For two examples of carbonyl coupling in binuclear complexes see: Berry, D. H.; Bercaw, J. E.; Jircitano, A. J.; Mertes, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 4712–4715. Bennett, M. J.; Graham, W. A. G.; Smith, R. A.; Stewart, R. P., Jr. *Ibid.* **1973**, *95*, 1684–1686. (b) Reductive coupling of coordinated CO in some highly reduced organometallics has been suggested: Ellis, J. E.; Parnell, C. P.; Hagen, G. P. *Ibid.* **1978**, *100*, 3605–3607. (c) For other examples of coupling coordinated ligands see the footnotes of ref 1. Two fascinating cases of carbyne–carbonyl coupling are to be found in the following work: Fischer, E. O.; Friedrich, P. *Angew. Chem.* **1979**, *91*, 345–346. Churchill, M. R.; Wasserman, H. J.; Holmes, S. J.; Schrock, R. R. *Organometallics* **1982**, *1*, 766–768.

(4) These geometrical assumptions were made. When the reactant geometry is a capped trigonal prism, the C–M–C angle is 90°, the M–C–O angle is 180°, and the C–M–girdle ligand angle is 105°. When the product geometry is an octahedron with the newly formed C_2O_2 occupying one coordination site, the C–M–C angle is 40°, the M–C–O angle is 150°, and the C–M–girdle ligand angle is 90°. These three angles are varied linearly along the hypothetical reaction coordinate. All other angles and bond distances remain constant.

orbitals at the lower left are essentially the W–CO σ bonds, in and out of phase combinations of carbonyl lone pairs with appropriate W hybrids. The $2a_1$ and $1b_1$ orbitals are formally assigned to the metal, though "back-bonding" with carbonyl π^* obviously occurs for these.

Above these orbitals is a substantial energy gap and a group of other metal- and ligand-based levels. Important in the subsequent discussion is the $3a_1$ orbital, **2**. This level is localized mainly on the carbonyls, with an antibonding admixture of metal d.

2

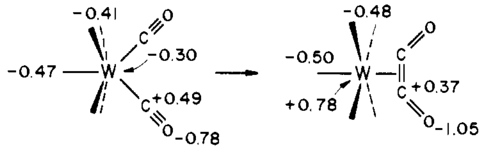


For a d^4 electron count on the seven-coordinate uncoupled side the reaction is nicely allowed. The coupled side is disfavored by 0.9 eV, primarily as a consequence of destabilization of $1b_2$ along the reaction coordinate. Thus the C–C bond formation process in d^4 seven-coordinate carbonyl or isocyanide complexes is a symmetry-allowed reaction, but it emerges in our calculations as an energetically uphill process. How might it be promoted? Two strategies are suggested, focusing respectively on (i) direct reduction and (ii) charge evolution along the reaction coordinate.

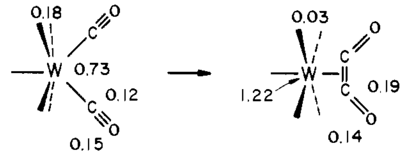
If two electrons were added to the d^4 seven-coordinate complex, they would perforce enter a high-lying orbital. This is not surprising, given that one is beginning with an 18-electron complex. But just a little motion along the reaction coordinate would find the electrons in an orbital that is descending rapidly in energy. The orbital in question is $3a_1$, which is M–C antibonding and C–C bonding and so moves to lower energy as the carbonyl carbons approach either. It would be stabilized further if two protons or other Lewis acids were attached to the electronegative X group bound to carbon in the terminal stages of the coupling, forming a bound acetylene ligand.

The strategy suggested by this is clearly reduction, preferably beginning with a geometry in which the carbonyls or isocyanides have already come part way together. This π-acid ligand proximity is common in seven-coordinate complexes, where C–M–C angles near 70° are observed.[2,5] In general acute angles are promoted by higher coordinate compounds with linear ligands.

Pursuing another line of thought, we show in **3** how the net charges in a d^4 complex evolve along the reaction coordinate and in **4** the distribution of the two electrons in the $1b_2$ orbital, the one rising in energy along the reaction coordinate. The electron-density changes are in principle the basis for a synthetic stretegy: σ and π acceptors, or more electronegative groups, are to be placed where the electron density accumulates, at the sites that grow more negative. Ligands that are σ and π donors, or electropositive groups, facilitate the reaction if put in the sites that grow positive. The problem is obvious—the total electron-density variation is opposite to that of the $1b_2$ orbital-density change. Model calculations in which the ligand or metal electronegativities or donor properties are changed confirm this difficulty. They further indicate that the total charge density effects "win out", but not by much. The effect of the five ligands is small although a better σ or π acceptor as the girdle ligand helps a little. A more electropositive metal definitely lowers the barrier to coupling. This is in accord with the concept of oxidizing the metal while reductively coupling the C≡X ligands. Looking at the system with two electrons more ($3a_1$ occupied), one obtains similar conclusions. Results similar to the above are obtained when isocyanides are considered instead of carbonyls. In support of our strategy is the fact that reductive coupling of $[Mo(CNR)_6X]^+$ complexes best occurs when the redox potential of the Mo(II) → Mo(III) couple is least positive.[6]



3 net charges



4 electron densities in $1b_2$

We look forward to experimental realization of this new reaction type.

Acknowledgment. We thank John Ellis for bringing some relevant work to our attention. Support by the National Science Foundation of the work at Cornell (CHE 7828048) and at Columbia (CHE 8109390) is gratefully acknowledged, as is support by the donors of Petroleum Research Fund, administered by the American Chemical Society, at North Carolina.

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Palladium-Catalyzed Stereocontrolled Cyclization of 1,3-Diene Monoepoxides and Its Application to the Synthesis of 11-Deoxy-PGE$_1$

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Palladium(0)-catalyzed allylic alkylation is a useful synthetic method.[1] The stereoselectivity of this reaction in acyclic systems, however, has not been studied as much as the regioselectivity in both cyclic and acyclic systems.[2] In this communication we report the regio- and stereoselective formation of δ-lactones **5** and **10** by intramolecular nucleophilic displacement of 1,3-diene monoepoxides[3] **1** and **8**, respectively, catalyzed by palladium complexes (Scheme I). If the 1,3-diene monoepoxide moiety serves to control the 1,4 relative stereochemistry between the newly formed carbon bond and the allylic alcohol and also the geometry of the resulting olefin, this overall transformation would be valuable for the synthesis of prostaglandins (PGs). Since one of the major problems in previous syntheses of PGs was the stereoselective generation of the relative stereochemistry between C(15) and C(12), including the geometry of the Δ^{13}-olefin. Regiospecific introduction of an α-side chain to **5** and the conversion of the

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