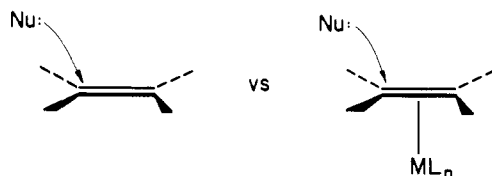


## Activation of a Coordinated Olefin toward Nucleophilic Attack

Sir:

While a nucleophile does not add with ease to an unactivated double bond, it may react readily with an olefin coordinated to a transition-metal center. Many organometallic complexes have

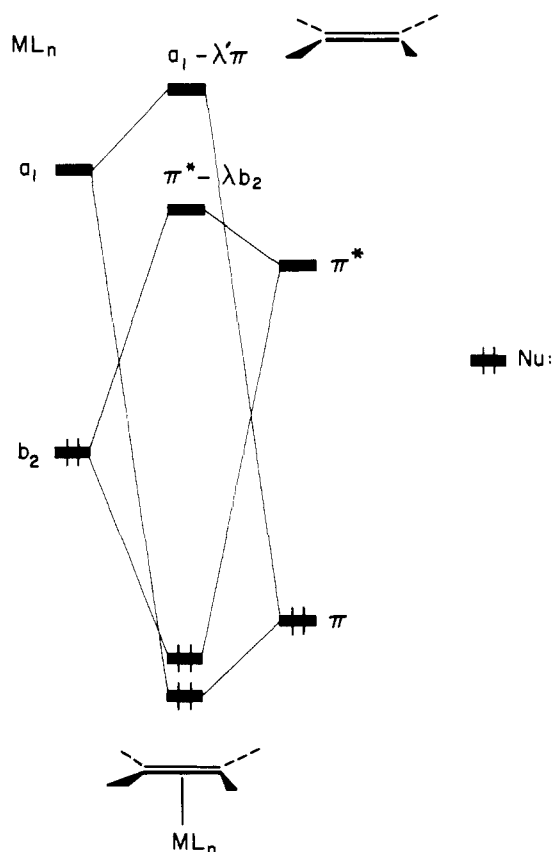


been found to react in this way—some dicationic [e.g., CpRh(PMe<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)<sup>2+</sup>],<sup>1</sup> monocationic [e.g., CpFe(CO)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)<sup>+</sup>,<sup>2</sup> Cp<sub>2</sub>WMe(C<sub>2</sub>H<sub>4</sub>)<sup>+</sup>,<sup>3</sup> Cp(CO)<sub>3</sub>W(C<sub>2</sub>H<sub>4</sub>)<sup>+</sup>] or even neutral [Fe(CO)<sub>4</sub>(olefin),<sup>5</sup> Pd, or PtXY<sub>2</sub>(olefin)<sup>6</sup>]. Since these substrates interact with a wide variety of neutral and anionic nucleophiles, it seems that the electrostatic attraction between the organometallic complex and the nucleophile, while certainly helpful, cannot be the only driving force for the reaction.

A first look at the reaction, in fact, reveals more factors pointing to olefin deactivation on coordination than activation. Whatever the ML<sub>n</sub> metal fragment coordinated (and we have examined d<sup>6</sup> CpML<sub>2</sub> and ML<sub>5</sub>, d<sup>8</sup> ML<sub>4</sub> and ML<sub>3</sub>, and d<sup>10</sup> ML<sub>2</sub>), the essentials of a Dewar-Chatman-Duncanson model of olefin bonding<sup>7,8</sup> are obtained. As indicated schematically below, the ML<sub>n</sub> fragment has a high-lying filled orbital of b<sub>2</sub> symmetry to interact with ethylene π\* and a more or less low-lying vacant a<sub>1</sub> orbital to mix with π. Often mixing with other filled or vacant orbitals will perturb this oversimplified picture, but its essentials remain.

It has been reasoned that the metal, acting much like an electron-attracting substituent, deprives the unsaturated ligand of a part of its π-electron density, and thus activates it toward the nucleophile.<sup>9</sup> That may be so, but the reverse flow, back-donation from metal to olefin, should counteract the effect. A frontier orbital analysis provides further insight into the course of the reaction.

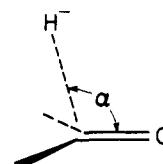
The electrophilic reactivity of the ethylene, free or complexed, toward an approaching external base resides fundamentally in the π\* orbital of the olefin. It is clear from the diagram above that the orbital of the complex which is mostly olefin π\*, the antibonding π\*-λb<sub>2</sub> combination, is both at higher energy and less



localized on the ethylene in the complex.

Thus, by the perturbation theoretical criterion,<sup>10</sup> the reactivity of the coordinated olefin should be decreased. In other words, the π\* orbital of the olefin, already busy stabilizing an occupied ML<sub>n</sub> orbital, is not particularly anxious to accept an extra electron pair from a nucleophile. Additional reactivity provided by the a<sub>1</sub>-λ'π combination is unlikely to make up for the decreased reacting "power" of π\*-λb<sub>2</sub>.

So where does the activation come from? We think it is derived from the potentiality of a geometrical deformation. The study began with the establishment of a reliable index of nucleophilic activity, by analysis of a reaction which has been well-studied experimentally and theoretically. This is the addition of a nucleophile to a carbonyl.<sup>11</sup> Model extended Hückel calculations of H<sup>-</sup> attack on H<sub>2</sub>C=O and H<sub>2</sub>C=CH<sub>2</sub> led us to identify as a useful index the overlap population between the H<sup>-</sup> and the entire unsaturated substrate, computed as a function of approach angle α, at a C...H<sup>-</sup> distance corresponding to moderate interaction, 2.0 Å.



Similar calculations were performed for a variety of olefin complexes in their equilibrium geometries. In every case, the overlap population between H<sup>-</sup> and the ethylene fragment of L<sub>n</sub>M(C<sub>2</sub>H<sub>4</sub>) was less than that in an uncomplexed ethylene. Sometimes the difference was small, as in CpFe(CO)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)<sup>+</sup>, sometimes large, as in (PH<sub>3</sub>)<sub>2</sub>Ni(C<sub>2</sub>H<sub>4</sub>). The schematic analysis

(1) Werner, H.; Feser, R.; Werner, R. *J. Organomet. Chem.* **1979**, *181*, C7-C10.

(2) Rosan, A.; Rosenblum, M.; Tancrede, J. *J. Am. Chem. Soc.* **1973**, *95*, 3062-3064. Lennon, P.; Rosan, A. M.; Rosenblum, M. *Ibid.* **1977**, *99*, 8426-8439. Lennon, P.; Madhavarao, M.; Rosan, A.; Rosenblum, M. *J. Organomet. Chem.* **1976**, *108*, 93-109. Green, M. L. H.; Nagy, P. G. I. *Ibid.* **1963**, *1*, 58-69. Cosslett, L.; Kane-Maguire, L. A. P. *Ibid.* **1979**, *178*, C17-C19.

(3) Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1974**, 761-762.

(4) Beck, W.; Olgemöller, B. *J. Organomet. Chem.* **1977**, *127*, C45-C47.

(5) Roberts, B. W.; Wong, J. J. *J. Chem. Soc., Chem. Commun.* **1977**, 20-21. Baar, M. R.; Roberts, B. W. *Ibid.* **1979**, 1129-1130.

(6) (a) Palumbo, R.; De Renzi, A.; Panunzi, A.; Paiaro, G. *J. Am. Chem. Soc.* **1969**, *91*, 3874-3883. Panunzi, A.; De Renzi, A.; Paiaro, G. *Ibid.* **1970**, *92*, 3488-3489. (b) Shaw, B. L. *Chem. Commun.* **1968**, 464. (c) Green, M.; Hancock, R. I. *J. Chem. Soc. A* **1967**, 2054-2057. (d) Stille, J. K.; Fox, D. B. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 157-161. Stille, J. K.; Morgan, R. A. *J. Am. Chem. Soc.* **1966**, *88*, 5135-5141. Stille, J. K.; Divakaruni, R. *Ibid.* **1978**, *100*, 1303-1304. (e) Moiseev, I. I.; Vargaftik, M. N.; Syркин, Ya. K. *Dokl. Akad. Nauk. SSSR* **1960**, *133*, 377-380. (f) Al-Najjar, I. M.; Green, M. J. *J. Chem. Soc., Chem. Commun.* **1977**, 926-927. *J. Chem. Soc., Dalton Trans.* **1979**, 1651-1656.

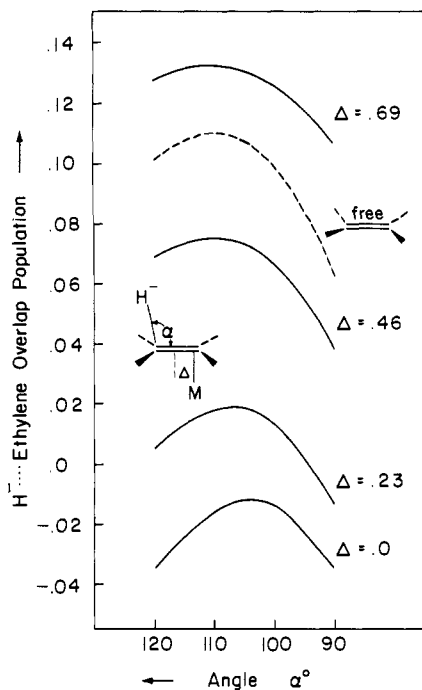
(7) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C71-C79; *Annu. Rep. Prog. Chem.* **1951**, *48*, 112-135. Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939-2947.

(8) Albright, T. A.; Hoffmann, R.; Thibault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801-3812, and references therein.

(9) Davies, S. G.; Green, M. L. H.; Mings, D. M. P. *Tetrahedron* **1978**, *34*, 3047-3077, and references therein.

(10) Heilbronner, E.; Bock, H. "Das HMO Modell und seine Anwendung", Verlag Chemie: Weinheim/Bergstr., Germany, 1968. Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1-9.

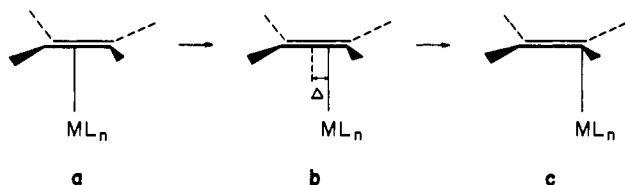
(11) Bürgi, H.-B.; Dunitz, J. D.; Shefter, E. *J. Am. Chem. Soc.* **1973**, *95*, 5065-5067; *Acta Crystallogr., Sect. B* **1974**, *30*, 1517-1537. Bürgi, H.-B.; Lehn, J. M.; Wipff, G. *J. Am. Chem. Soc.* **1974**, *96*, 1956-1957. Bürgi, H.-B.; Dunitz, J. D.; Lehn, J.-M.; Wipff, G. *Tetrahedron* **1974**, *30*, 1563-1572.



**Figure 1.** The  $H^-$ -ethylene overlap population in the model complex  $(CO)_5Fe(C_2H_4)^{2+} \cdots H^-$  as a function of the approach angle ( $\alpha$ ) and the slipping of the ethylene ( $\Delta$ ).

that we presented above, implying deactivation upon coordination, was supported.

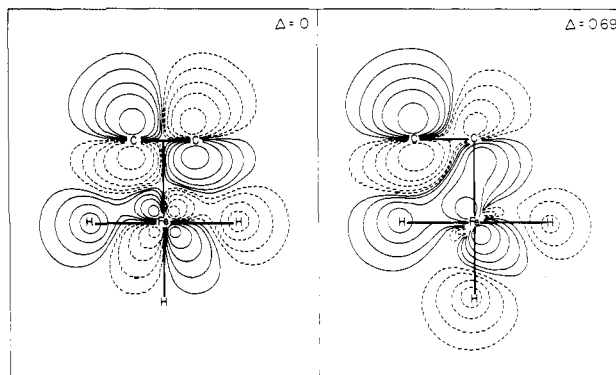
A certain deformation of the complexed olefin, one which has no equivalent in the free molecule, supplies the anticipated but missed activation. This is a slipping of the  $ML_n$  fragment along the ethylene, idealized by a simple displacement from the center,  $\Delta$  in structure b.  $\Delta = 0$  is the symmetrically bonded  $\eta^2 \pi$  complex



while  $\Delta = 0.69$  is in our geometry for a model for an  $\eta^1 \sigma$  complex. The dramatic effect of this motion on the  $H^-$ -olefin overlap population is shown in Figure 1 for the model  $d^6$  complex  $(CO)_5Fe(C_2H_4)^{2+} \cdots H^-$ . When the ethylene is  $\pi$  bonded, the overlap population with  $H^-$  is much lower than that in the free ethylene. As  $\Delta$  is increased, the overlap population rises and eventually surpasses that of the free olefin.<sup>12</sup> There is a d-electron count and coordination number dependence of this activation mode. It takes place in our calculations for  $d^6 ML_5$ ,  $d^8 ML_4$ , and  $d^8 ML_3$ , but not for the  $d^{10} ML_2$ .

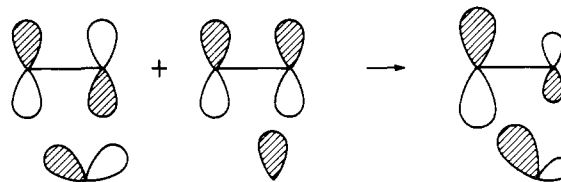
Let us probe the possible origins of the activation through slipping. If one examines the orbitals of the complexed ethylene as a function of  $\Delta$ , one does observe a lowering in energy of the lowest unoccupied molecular orbital (LUMO) as  $\Delta$  increases. However, this stabilizing feature<sup>10</sup> is never large enough to compensate for the dispersion of the LUMO over the various ethylene and  $ML_n$  orbitals. What does increase substantially is the localization of the LUMO of the  $L_nM(C_2H_4)$  complex on the far carbon, as illustrated in Figure 2. This localization is primarily responsible for the superior  $H^-C_2H_4$  bonding at large  $\Delta$ .

The new LUMO of the "slipped"  $L_nM-C_2H_4$  complex can be thought of as a mixture of the unfilled orbitals of the symmetrical



**Figure 2.** A plot of the  $\pi^*-\lambda b_2$  MO in the  $\eta^2 \pi$  complex  $H_5Fe(C_2H_4)^{3-}$  ( $\Delta = 0$ ) and of the LUMO of the  $\eta^1 \pi$  complex  $H_5Fe(C_2H_4)^{3-}$  ( $\Delta = 0.69$ ). The contour values of  $\Psi$  are  $\pm 0.2, 0.1, 0.055, 0.025$ , and  $0.01$ .

species,  $a_1-\lambda' \pi$  and  $\pi^*-\lambda b_2$ . We can write it as  $c_1 a_1 + c_2 b_2 + c_3 \pi + c_4 \pi^*$ , the signs of admixture given below. The LUMO is



dominated by  $\pi^*$ , but the ethylene  $\pi$  contribution in it is important. By itself, the  $H^- \pi^*$  component of the  $H^-$ -ethylene overlap population never surpasses the free ethylene value, at any  $\Delta$ . It is aided, to a variable degree, by the  $\pi$  admixture. The latter is of the correct phase to give a bonding  $H^- \pi$  contribution.

A detailed analysis of the system shows that the mixing of  $\pi$  into the LUMO in the slipped form depends on the energy of the  $ML_n$  fragment  $a_1$  orbital. The higher the  $a_1$ , the less  $\pi$  mixing into the LUMO. In  $(PH_3)_2Ni(C_2H_4)$ , the vacant  $ML_n$   $a_1$  orbital is very high in energy.<sup>8</sup> Consequently, there is little admixture of  $\pi$  into the slipped ethylene LUMO and therefore insufficient activation of the olefin toward the nucleophile.

The detailed analysis, to be published, explores the differences between the various  $ML_n$  fragments. Substituent effects are predictable, e.g., that  $\sigma$  and  $\pi$  acceptors on the metal will increase the activation. But it will take some cleverly designed, conformationally constrained complexes to test our contention that ethylene slipping plays the dominant role in the activation of complexed olefins.<sup>13</sup>

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## Titanacyclobutenes

Sir:

The isolation and structure of titanacyclobutenes of the type  $Cp_2TiCH_2CR=CR$  (**1a**,  $R = Ph$ ; **1b**,  $R = SiMe_3$ ;  $Cp = \eta^5-C_5H_5$ ) are reported. These compounds are prepared by reactions of  $RC \equiv CR$  with  $Cp_2TiCH_2AlClMe_2$  (**2**).<sup>2,3</sup> The acetylenic

(12) The passage to activation occurs only when the slipping is substantial, nearer to a fully formed  $\sigma$  complex. Other geometrical changes in the olefin, not studied by us, certainly take place as the reaction proceeds, so that the activation may in fact occur earlier.

(1) Isolation of **1a** was briefly reported: Tebbe, F. N.; Parshall, G. W.; Ovenall, D. W. *J. Am. Chem. Soc.* **1979**, *101*, 5074-5075.

(2) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611-3613.