Organometallic migration reactions

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Organometallic Migration Reactions

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Abstract: A molecular orbital study of the reaction path for the methyl migration reaction in $CH_3Mn(CO)_5$, the "carbonyl insertion reaction", is the starting point for a general analysis of organometallic migration reactions. The reaction path contains a five-coordinate intermediate and a transition state close in energy to the intermediate. Among the questions studied are the stereochemical course of the reaction, the effect of solvent on the kinetics, possible binuclear mechanisms, the vexing problem of formyl formation by the migration reaction, the effect of changing the migrating group, the migration terminus (carbene, nitrosyl, isonitrile), the effect of other ligands on the metal, and variation of the metal and coordination number.

The general reaction 1, a 1,2 shift of a ligand L to an unsaturated fragment XY, both coordinated to a metal M, is of
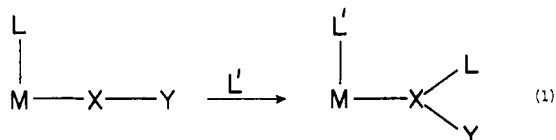
obvious synthetic value. As such, it has drawn the attention of chemists from the early days of organometallic chemistry on, and has been the subject of numerous synthetic and mechanistic investigations.[1-4] The case XY = CO has been popularly called the carbonyl insertion reaction. It is a key step in many homogeneous catalytic transformations,[4-7] and possibly in some heterogeneous processes as well.[8-10] Theoretical analyses of this crucial process are lacking, with the important exception of a recent paper by Howell and Olsen.[11] We have attempted a general analysis of a model system for carbonyl insertion, using the extended Hückel method.[12] To sharpen the questions which were the challenge for our study it is perhaps worthwhile to review some of the experimental findings and mechanistic conclusions.

Since the discovery of prototype reaction 2 in 1957,[13] the

$$RMn(CO)_5 + L \longrightarrow R\overset{O}{\overset{\|}{C}}Mn(CO)_4L \qquad (2)$$
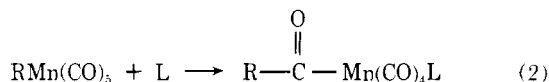
following points have emerged: (1) The kinetics of the reaction are first order in $RMn(CO)_5$, though sometimes there is an incoming ligand dependence. (2) Donating solvents can accelerate the overall reaction rate. (3) A coordinatively unsaturated intermediate appears to be involved. (4) The entering ligand occupies the position previously occupied by the alkyl group, cis to the acyl. Thus the reaction is really an alkyl migration rather than a carbonyl insertion. (5) The acyl CO originates from the original coordination sphere of the metal.

Further studies have extended the scope of the reaction: (6) There is in general no restriction on the transition metal involved, and many different coordination environments allow this reaction type. (7) There is some selectivity as to the nature of the migrating group. In particular the formation of formyl derivatives by H migration has been desired, and the reasons for its apparent absence have been the object of considerable speculation. (8) Substitution patterns on the metal center influence this migration.

A rationalization of the known features of the reaction was the first focus of our study. What is the nature of the postulated intermediate? What factors govern the stereochemical course of the reaction—CO insertion vs. alkyl migration? What role is played by the solvent? We felt that if we could understand these basic aspects we should be able to make predictions as

to the effect of different metal centers and ligands of differing σ and π donating capability on the ease of the migration. This would help the design of systems in which this synthetically useful reaction could be facilitated in cases in which it is difficult or unobserved.

We begin our study with the search for an approximate reaction path by which a methyl group migrates to a carbonyl, eq 3, to give an acyl complex. The computational method used
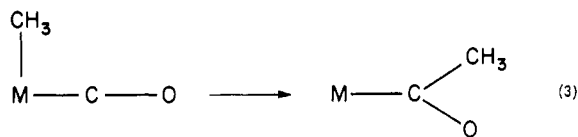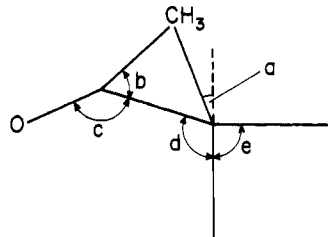

is the extended Hückel procedure[12] with parameters specified in the Appendix. The reader should be aware that processes in which bond breaking and re-formation occur are on the borderline of what may be reliably treated by this approximate MO method. We have nevertheless been able to study effectively such insertion reactions in the organic realm,[14,15] and in one organometallic migration related to this one, the olefin insertion reaction.[16] Proper care must be taken to buttress any computational results by qualitative symmetry and bonding arguments, and this we will do.

Potential Energy Surface for the Rearrangement of $CH_3Mn(CO)_5$ to $CH_3C(O)Mn(CO)_4$. The migration reaction is not restricted to a single metal nor a certain coordination environment. But certainly its most common manifestation is for octahedral d^6 complexes. To extract the general features of the reaction path we have chosen $CH_3Mn(CO)_5$, which is also the example most exhaustively studied experimentally.[13,17]

A full optimization of all degrees of freedom was not carried out, nor would we expect it to lead to a good reaction path from the extended Hückel method. But extensive exploratory calculations led to the following conclusions:

1. It is reasonable to maintain C_s symmetry throughout the reaction, and indeed we will refer to this plane as the migration plane.

2. Methyl group rotation about its local threefold axis is not a significant factor in the reaction.

3. A slight tilting up, 20°, of that carbonyl group which gets the methyl, **1** → **1′**, costs approximately 0.5 eV in the
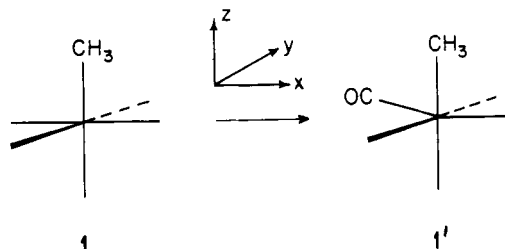
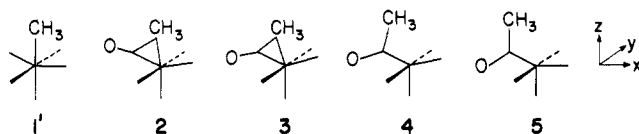**Table I.** Angular Parameters for the Migration Reaction Path[a]

	1	1'	2	3	4	5
a	0	0	10	20	30	35
b	50	65	72	85	100	110
c	180	180	170	155	145	135
d	90	110	110	110	110	110
e	90	90	95	100	95	90

[a] Angles, in degrees, are defined in the drawing.

ground-state geometry, but causes substantial stabilization in the middle of the reaction path.

4. A good representation of the many-dimensional reaction path is given by a two-dimensional slice in which the Cartesian coordinates of the methyl carbon (relative to Mn at the origin) are plotted, and all other crucial degrees of freedom of the molecule allowed to relax at each point. This is shown in Figure 1.

5. Representative points along the reaction path are **1'**, **2**, **3**, **4**, and **5**. These are drawn schematically below. Certain characteristic angles in the migrational plane are associated with these geometries. Their optimized values are listed in Table I.

Structure **1'** is the energy zero for Figure 1, with the crucial carbonyl bent up by 20° to "anticipate" the migrating methyl group. At point **2** the migration is already underway—the total overlap populations between the methyl carbon and the metal or the carbonyl groups are comparable. Structure **3** will be identified as the transition state. In the region of **4** the surface is flat. Just a slight stabilization leads to a five-coordinate unsaturated intermediate **5**, a distorted square pyramid. The characteristic acyl shape is not fully reached in **5**.

The energy profile that one obtains along the dashed line reaction path in Figure 1 is drawn below. The energy difference
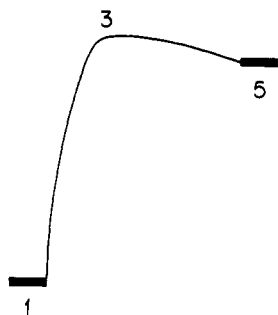
between **1** and **3**, the calculated activation energy for the process, amounts to 0.85 eV or ~20 kcal/mol. Experimental estimates range between 12 and 17 kcal/mol.[18,19] An indirect indication that this reaction path is a reasonable one is to be found in Figure 2, which shows the evolution of the overlap populations to the methyl carbon as the migration proceeds. These change quite smoothly.
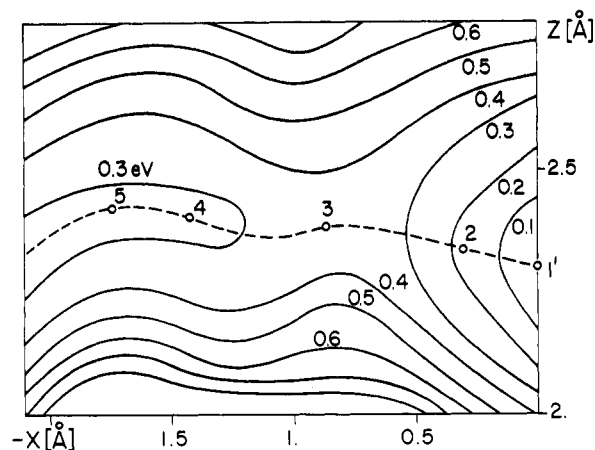
Figure 1. A two-dimensional cut in the migration plane of the many-dimensional surface for the transformation of **1'** to **5**. The axes are the Cartesian coordinates of the C atom of the migrating methyl group. The metal is at the origin. The zero of energy is at **1'**.

So far we have discussed the computed structural and energetic features of a possible reaction path. For further insight we must learn how the individual orbitals are modified and see if there is a controlling level or levels.

Electronic Features of the Insertion Reaction. It is instructive to carry out the insertion reaction along the computed reaction path, but removing the metal and its ligands. The critical interactions of the frontier orbitals, the carbonyl lone pair σ_{CO} and its π^*, with the methyl anion lone pair $\sigma_{CH_3^-}$ are shown in **6**. The dominant feature of this diagram is a four-electron
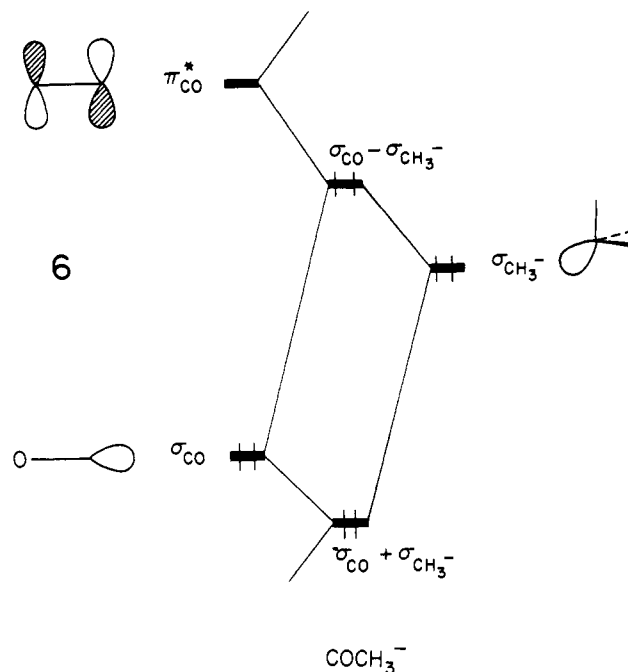
destabilizing interaction between $\sigma_{CH_3^-}$ and σ_{CO}. This is partially relieved by mixing in π^*_{CO}, which allows the antibonding lobes to hybridize away from each other, as shown in **7**. Nevertheless, the net effect is destabilizing. From the acyl
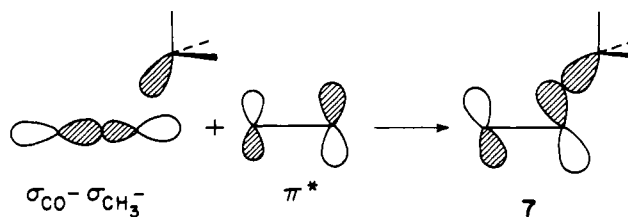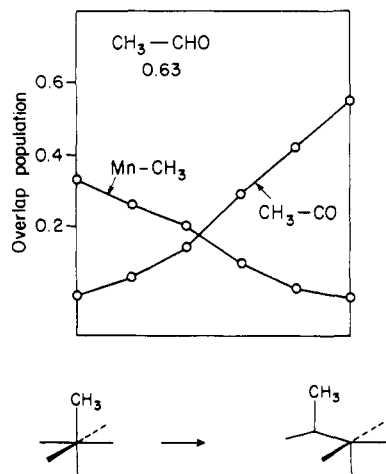
Figure 2. Computed total overlap population of the Mn–CH_3 and CH_3–CO bonds along the reaction path, 1 to 5.
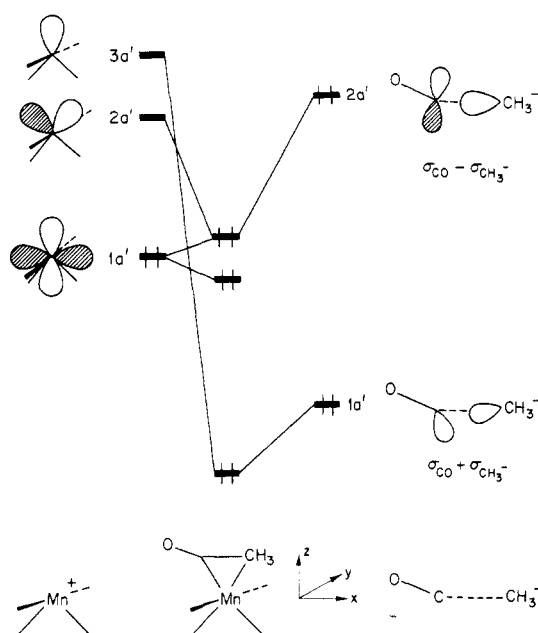

Figure 3. Schematic interaction diagram for $Mn(CO)_4^+$ and the transition state structure of the acetyl anion, to compose 3. Only selected orbitals in the migration plane are shown.

Figure 4. Orbital evolution along the reaction path. Structures 1, 3, and 5 are shown.

8

While Figure 3 showed the interaction in the transition state region, Figure 4 shows the evolution of the levels throughout the entire migration reaction. There are two identifiable contributors to the total activation energy. The major part of the barrier is due to the rise in energy of that a′ orbital which is identifiable as the Mn–CH_3 σ bond in the reactant and is transformed into an orbital of the intermediate 5 which is

side and a localized viewpoint the HOMO 7 might be identified as an oxygen lone pair, but in fact it is quite delocalized as shown.

A Walsh diagram for the uncatalyzed reaction indeed shows that the major part of the destabilization of this system is tied up with the "σ_{CH_3}--σ_{CO}" highest occupied molecular orbital (HOMO) of 6. Next we bring up a C_{2v} $Mn(CO)_4^+$ fragment, for simplicity focusing on interactions[20] in model structures 1, 3, and 5. The orbitals of an $M(CO)_4$ fragment are well known.[21] For a d^6 fragment there are two good acceptor orbitals, approximately described as symmetric and antisymmetric combinations of hybrids pointing toward the missing octahedral sites. In 1, where CO and CH_3^- are still separated ligands, their well-directed donor functions provide strong stabilizing interaction with the metal.

The critical ligand arrangement in which metal stabilization must be extremely effective is in the high-energy region of 3. An interaction diagram for this structure is shown in Figure 3. Indeed the orbitals of partially formed CH_3CO^-, shown in 6, interact very well with those of $Mn(CO)_4^+$. Note especially in Figure 3 the stabilization of the HOMO of 6, σ_{CH_3}--σ_{CO},
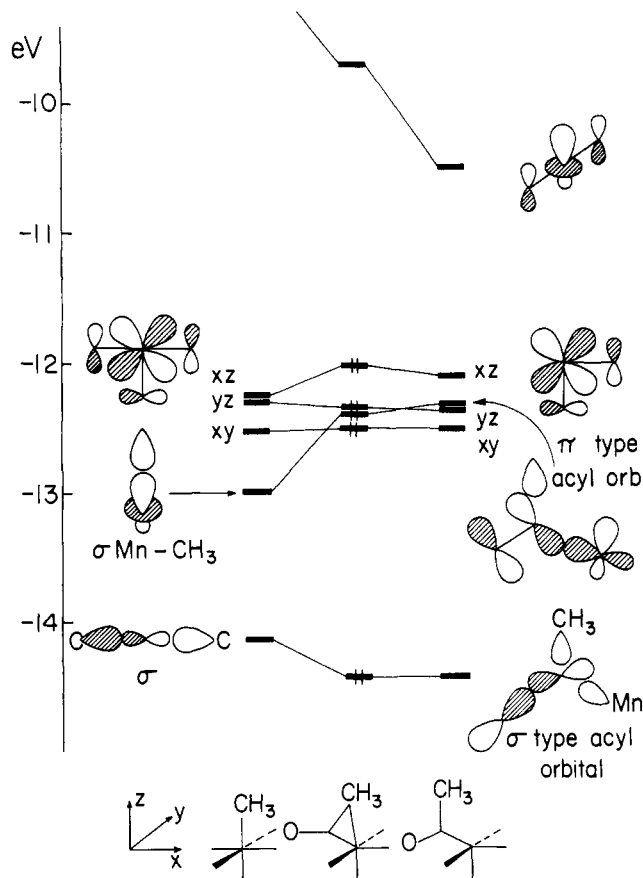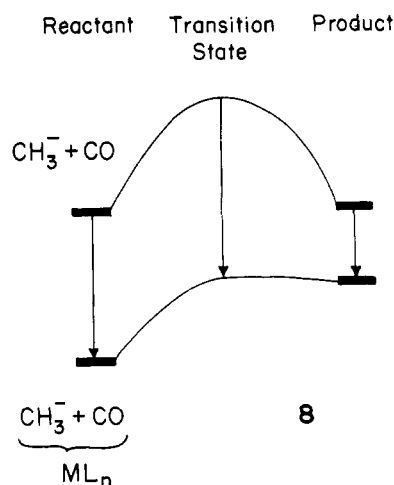
by mixing with the out of phase hybrid combination, 2a′, of $Mn(CO)_4^+$.

In 5 the acyl anion is nearly fully formed. It has an excellent donor orbital, but only a single one. The result is a drastic decrease, revealed by our fragment molecular orbital (FMO) analysis,[20] in the net stabilization provided by the metal. The overall effect of the metal on the acyl formation process is shown in 8.

primarily acyl in character. A smaller part of the barrier is caused by the xz a′ orbital, which loses one π-type overlap in the course of the migration. One orbital is stabilized in the course of the reaction, becoming the σ-type acyl orbital, but it does not compensate entirely for the destabilizations encountered by the two higher a′ orbitals. Changes in the a″ orbitals, antisymmetric with respect to the reaction plane, and in the "core" levels below -15 eV are unimportant.

In the course of the migration a low-lying vacant orbital is created. This is of course the acceptor orbital of a five-coordinate d^6 fragment, mainly metal z^2 in character.[21] It is important to the subsequent argument that this orbital is not established until the intermediate **5** is approached, and in particular is not at low energy in the transition state region of structure **3**.

Kinetics, Solvent Effects, and Acid–Base Catalysis. Let us write a mechanism

$$RMn(CO)_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [RCOMn(CO)_4]$$

$$\xrightarrow{k_2(+L)} RCOMn(CO)_4L \quad (4)$$
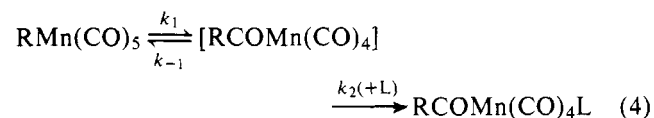
for the migration reaction, involving an intermediate. Many kinetic investigations have made it clear that a kinetic law with a stationary state condition could be applied.[17-19,22-25] This leads to an expression

$$k_{\text{obsd}} = \frac{k_1 k_2[L]}{k_{-1} + k_2[L]} \quad (5)$$

for the overall rate constant of the reaction. Our intermediate, structure **5**, is not separated by a substantial barrier from transition state **3**. Taken at face value this implies that k_{-1} should always make a significant contribution to k_{obsd}. Equation 5 will not simplify and a ligand dependence will always remain. That is what is in fact observed in most cases[18,22] with the exception of those experiments conducted in strongly polar, donating solvents, where a solvent effect—to be discussed below—dominates.

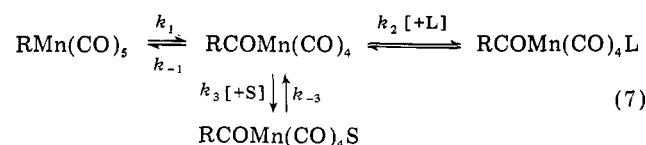A direct second-order reaction of type

$$RMn(CO)_5 + L \xrightarrow{k_2} RCOMn(CO)_4L \quad (6)$$

$$k_{\text{obsd}} = k_2[L]$$

in which the back reaction has been neglected has been excluded experimentally in an investigation on the four-coordinate platinum system.[26] While there is no corresponding experimental evidence of such a direct nature for the octahedral Mn case, our theoretical calculations on Pt, to be presented later, show no substantial difference from Mn. In the latter case a direct second-order reaction would occur only if the transition state **3** were stabilized by the incoming ligand. But the calculations show only repulsive interaction in the region of **3**. To have two-electron stabilization there one would need a low-lying acceptor orbital in the $RCOMn(CO)_4$ moiety. But Figure 4 showed that the requisite acceptor orbital is not created until the transition state for the reaction is passed, not until the region of structures **4** and **5**. The incoming ligand stabilizes the intermediate, but not the transition state for the reaction.

Solvent molecules are in principle no different from the incoming ligand considered up to this point. In d^6 pentacoordinate square pyramidal complexes the sixth site is available for interaction with almost any electron-carrying substrate.[27] Even weakly donating solvents could therefore interact with our intermediate **5**, but as argued above that should have no effect on the transition state **3**. Yet different solvents do provide a kinetic acceleration up to a factor of 10^4, which appears to parallel the donating capability and not the dielectric constant

of the medium.[18] We have to assume that a general mechanism of type 7 is at work.

$$RMn(CO)_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RCOMn(CO)_4 \underset{}{\overset{k_2\,[+L]}{\rightleftharpoons}} RCOMn(CO)_4L$$

$$k_3\,[+S] \downarrow \uparrow k_{-3} \qquad\qquad (7)$$

$$RCOMn(CO)_4S$$

The exact kinetic expression for this extended mechanism is complicated, but it seems unlikely that the solvent can actually accelerate the overall reaction. In case the solvent complex is really tight, $k_{-3} \sim k_1$, then such very strongly donating solvents will retard the overall rate. This is observed for third-row transition metals, where THF is a worse medium for the reaction than halogenated hydrocarbons.[26] In some such cases the solvent complexes are so stable that they have been isolated.[28] It should be noted that in either kinetic extreme the overall reaction is first order.

Another observation in these complexes of the second- or third-row transition metals, all of which involve halogens as ligands, is that the solvent dependence of the overall reaction rate is smaller than for complexes of the first transition series, without halogen ligands. The explanation here may be that the complexes themselves provide good donating sites, and the solvent molecules do not compete well. We are suggesting, and this is speculative, the intervention of bridged dimers of type **9** or **10**. Dimers with bridging halogens are common in Rh, Ir,


M = Ir, Rh

9

M = Pd, Pt

Ac = acyl   L = phosphine

10
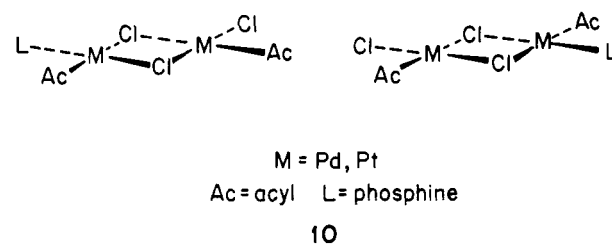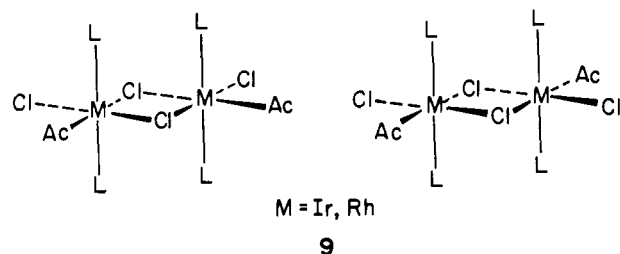
Pd, and Pt chemistry.[29] Complexes relevant to our reaction must contain acetyl ligands. Such complexes have been proposed in migration reactions of Ir,[28,30] and a structure is available for a dimeric Rh acetyl complex which is bridged by iodines.[31]

In alkyl migrations of the first transition series halogens are not normally present in the coordination sphere. Nevertheless, one can think of weakly bound dimeric structures with bridging acyls, e.g., **11**, as possible stabilized intermediates. Under

11
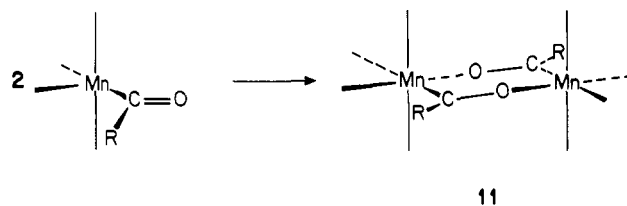
proper kinetic conditions these would be capable of competing with solvent assistance. A model calculation on the interaction of two molecules of **5** to yield **11** indicates a stabilization of 11 kcal/mol upon dimerization, a number that should be viewed

cautiously. While only some bridging acyl complexes have been characterized,[32a-c] to our knowledge, many complexes are known in which the COR⁻ is replaced by another four-electron donating group, for instance, PR₂⁻. The recently published structure of **12**, with a planar inner ring,[32d] is an interesting

12
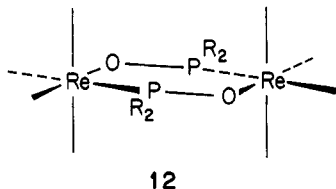
example. Dimeric intermediates have been implicated in a number of other organometallic reactions.[33]

As we discuss the possible stabilization of the transition state by external influences, we must consider the possibility of acid catalysis. In the organic realm the effect of electrophiles on carbonyl reactions is well known experimentally[34] and has been analyzed theoretically as well.[35] In the organometallic area related to the migration reaction we have the direct observation of some formyl and acyl ion pairs[36,37] as well as studies indicating ion pairing effects upon migration rates.[24,38-40] In cluster catalysis[41] AlCl₃ enhances Fischer–Tropsch processes, which undoubtedly involve alkyl migrations.

We have investigated the influence of attaching Li⁺ or H⁺ to the acetyl oxygen in the transition state structure, **13**. The

13
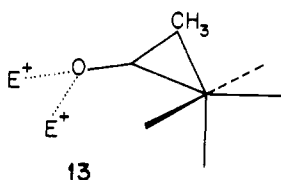
position of the electrophile E⁺ optimizes collinear with the CO bond, but all E⁺–O–C angles from 180 to 120° are catalytically active, in the sense that the energy of the crucial destabilized orbitals is lowered. The effect is not large, 0.15 eV on the crucial σ_{CH_3}--σ_{CO} orbital of **6**, but may be experimentally important.

How is the transition state affected by the approach of an acid? We have mentioned earlier that an alkyl group attacking CO has to overcome destabilizing interactions between the alkyl lone pair and the carbonyl lone pair. The carbonyl lone pair is not entirely localized at the carbon. An electrophile attacking at the oxygen will also affect the energy of this orbital. It will lower it, as indicated schematically below. This
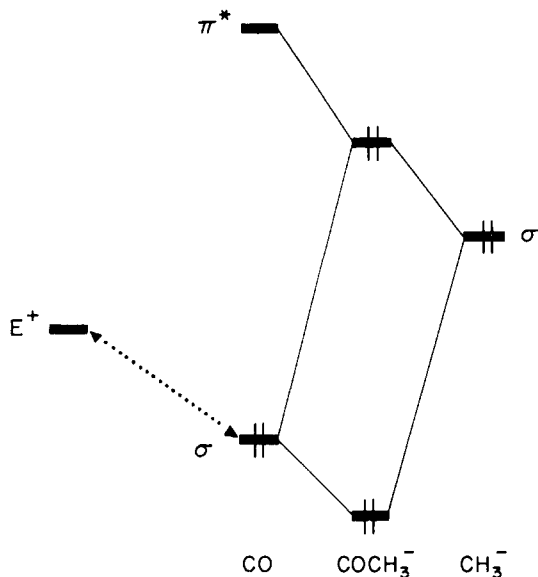

will decrease the four-electron destabilizing interaction with σ_{CH_3}- and, in a second-order way, allow the increased mixing of the latter with π^*_{CO}.

As we mentioned above, the effect on the transition state is not large. There is a greater effect on the intermediate **5**, which provides another way that the reaction may be influenced. The intermediate is stabilized by some 14 kcal/mol (relative to the absence of an electrophile) while the transition state is stabilized by only 3 kcal/mol. k_{-1} in our kinetic expression (eq 5) is decreased, which would accelerate the reaction.

We have discussed in some detail the influences which may be exerted upon the transition state for the migration reaction. But we have not yet exhausted the geometrical possibilities available to the intermediate.

The Five-Coordinate Intermediate. Any time that one has a five-coordinate complex one has to worry about its susceptibility to polytopal rearrangements.[42] The intermediate **5** that we calculate appears to lack low-energy pathways to other square pyramidal or trigonal bipyramidal isomers, and that by itself is a matter of some interest.

The interchange of acetyl methyl and oxygen orientations within a square pyramid, a seemingly simple process, can in principle be accomplished in two ways: by rotating around the metal to acetyl bond, **14a**, or by a motion of the acetyl ligand to the vacant site, **14b**. The first of these is a difficult process,


14a

14b
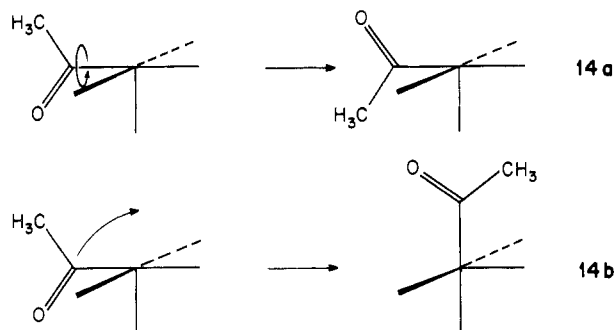
requiring some 20 kcal/mol in our calculation. This is primarily a steric effect, for in principle a single-faced π acceptor in the basal site of a square pyramid should prefer a so-called ba‖ orientation of its acceptor orbital.[42]

The other process, **14b**, is physically distinguishable from the rotation, and there is some precedent for considering it.[43,44] Figure 5 shows a potential energy curve for this motion. Notice the prominent minimum with the acetyl group slightly bent up toward the vacant coordination site. It is interesting to trace the origin of this preference. An orbital correlation diagram leads to a controlling orbital, the highest occupied MO. A fragment analysis shows this orbital to be derived from the acetyl HOMO discussed previously with an antibonding admixture of the Mn(CO)₄⁺ donor orbital and a bonding component of the Mn(CO)₄⁺ acceptor function. This partitioning is useful, for it allows an understanding of the deformation—it minimizes the repulsive component which is shown in **15**. (The


15
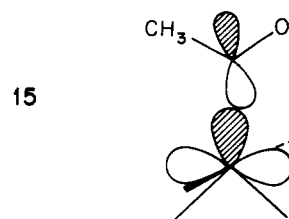
point of view is changed here. It is from the front, with the Mn(CO)₄ unit rotated by 45° in the plane of the paper.) Note that the σ lobe on the acetyl carbon is pointed toward the oxygen side. The antibonding interaction in **15** is minimized by a clockwise motion of the acetyl group, as shown in **16**.

16
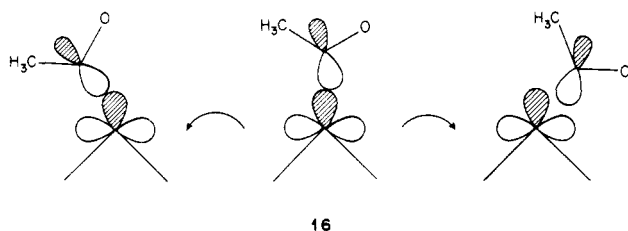
This deformation is peculiar to the acyl ligand. Other ligands may show different preferences. For instance, a study of the related motion in $Mn(CO)_4Br$ shows the trigonal bipyramid favored.[44] This would be a point near the middle of Figure 5 or **16**, and is set by maximizing π donation from a Br^- lone pair to the antisymmetric $Mn(CO)_4^+$ acceptor orbital. In the acetyl case the analogous π-donating component is small and less effective.

At this point we note the unique structure, reported by Eisenberg and co-workers,[45] of **17**, a five-coordinate Rh-


17
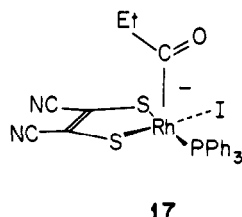
(I)-acyl complex. The geometry is square pyramidal, with the acyl group apical. In our calculations on isomers of $CH_3COMn(CO)_4$ the acetyl group prefers the basal site by 0.65 eV, and we are in the process of carrying out calculations on the particular ligand set of **17**.

Trigonal bipyramidal d^6 ML_5 structures should be high spin, with their low-spin states unstable with respect to deformation toward a square pyramid. As the five ligands are made nonequivalent, the driving force for distortion from a trigonal bipyramid will be somewhat reduced. Most d^6 five-coordinate structures can be interpreted in terms of a square-pyramidal environment.[46] But there are some exceptions, for instance, the structure **18a**.[47a] A five-coordinate acyl complex structure
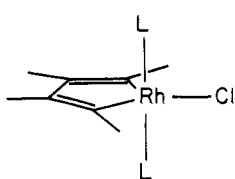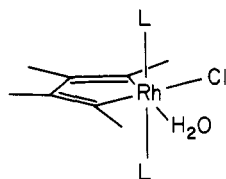

18a, L = SbPh₃   **18b**, L = AsPh₃

has recently been reported.[47b] Our calculations on $Rh(PH_3)_2Cl_2(CH_3CO)$ favor a structure, albeit distorted, closer to the square pyramidal extreme. The trigonal bipyramidal alternatives had small HOMO–LUMO gaps and would be candidates for high-spin ground states. There is still further doubt that trigonal bipyramidal structures could appear in solution, since a structure closely related to **18a,b** shows that even the weakly donating water molecule may occupy the sixth coordination site.[48]

Still another deformation of an acyl complex that had to be examined is a decrease in the Mn–C–O angle, or a sliding along of the acyl ligand toward a dihapto structure, **19**. Structures of this type are known for Cp_2MR, M = Ti, Zr,[49] and a compound electronically related to **19**, the $R_2N=CH_2$ complex **20**, has been structurally characterized.[50] Even $Fe(CO)_4$-(C_2R_2)[51] may be viewed as analogous if the ligand is taken as $C_2R_2^{2-}$.
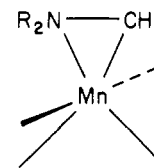
Our attempts to trace the bending surface from **5** to **19** led
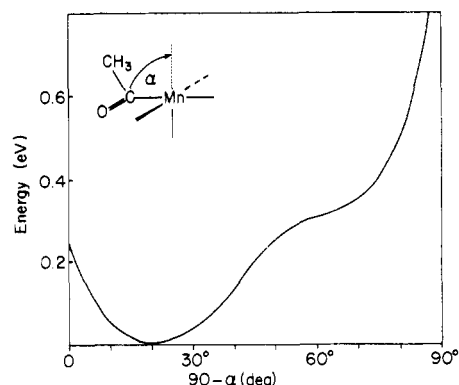
Figure 5. Bending surface of the acetyl group in the migration plane around the $Mn(CO)_4^+$ C_{2v} fragment. The energy zero refers to structure **5**.
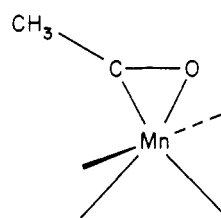


19   **20**

only to a steady increase in energy. Yet an interaction diagram shows nothing qualitatively wrong with the η^2 structure **19**. The difference lies in a quantitative factor—the overlap match of the fragment orbitals is significantly worse in **19** than in the calculated optimum intermediate structure. The situation is reversed in the Cp_2M complexes.

Having examined these various structural alternatives, we return to the intermediate structure **5** and seek some structural evidence for its peculiarities, in particular the slight distortion or canting from the idealized square pyramid, the orientation of the acyl plane, and conjugation with the partially formed $CH_3—C=O$ σ system. Such evidence is difficult to find, because most of the known acyl complexes are octahedral and the deformations we seek are prevented by steric contacts. Among lower coordination numbers there is an iminoacetyl Pt complex,[52] **21**, in which this isoelectronic group is oriented
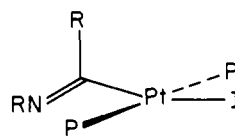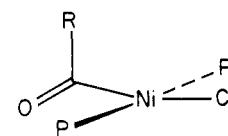
21   **22**

perpendicular to the Pt coordination plane. A substantial rotational barrier around the Pt–C bond is suggested. The acetyl carbon is bent up about 10° from the coordination plane. Another related example is **22**,[53a] with an acetyl C–Ni–Cl angle of 172°, but in this case we cannot extract unambiguously the direction of bending from the given data.[53b] The deviations in the acetyl geometry are, however, in accord with our results. The metal–acetyl distance (1.84 Å) is the shortest found, compared to other first-row transition element acetyl complexes. However, there is a significantly elongated C–CH₃ bond. We find that this is an expected consequence of hyperconjugative mixing with the high-lying acetyl orbital.

Before we proceed to discuss the influence of the migrating group, it is perhaps amusing to note that in an organic reaction which is closely related to our alkyl migration, the Wolff rearrangement (eq 8), the very same question that has been occupying our time, the nature of the intermediate, has been a source of controversy in experimental and theoretical treatments.[54]
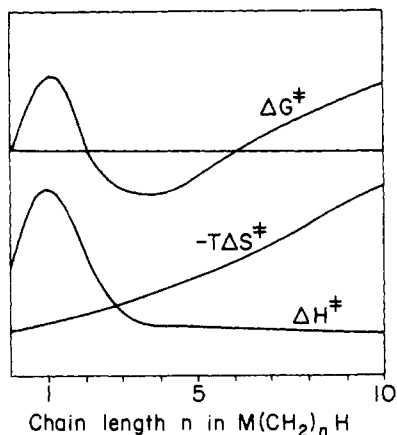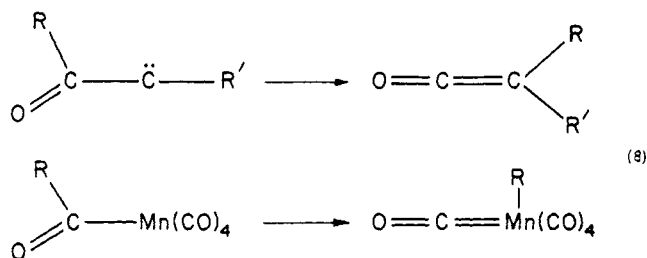
Figure 6. Schematic dependence of the activation parameters for the migration reaction of hydride and n-alkyls as a function of chain length.

Table II. Alkyl Migration Studies

R	σ orbital overlap in $RMn(CO)_5$	fragment ligand σ orbital energy, eV	activation energy, eV
CH_3	0.270	−11.76	0.85
C_2H_5	0.254	−11.34	0.66
$n\text{-}C_3H_7$	0.240	−11.25	0.64

El = Electronegativity
of the migrating
group

Electronic and Steric Effects of the Migrating Group. Having established the main features of the reaction path, we turn our attention to evolving a strategy for perturbing the reaction, first through changes in the migrating group, then by changes in the metal and its ligands. In each case we have made the oversimplified assumption that the reaction path remains the same, and gauged the effect of the perturbation by looking at the effect on the idealized activation energy, the difference between ground state **1** and transition state **3**.

The migrating group could change its σ or π interacting capability. The σ effect may be modeled by changing the energy of the donor orbital—the more electronegative the group, the lower its energy, the poorer a σ donor it should be. If we lower the donor orbital by 2 eV in our calculations, the activation energy rises to 33 kcal/mol. Similarly, if we go from CH_3 to the more electronegative Cl, we calculate an increase in the activation energy to 66 kcal/mol. Thus a poorer σ donor raises the activation energy for the migration, and a better σ donor lowers it.
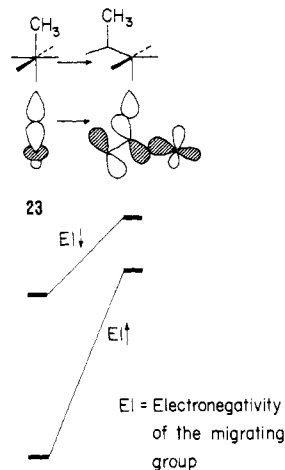
One way to understand the σ effect is derived from an examination of the orbitals—most of the energy change is associated with the conversion of the metal-alkyl σ bond to the acyl π-type orbital, as shown in **23**. The electronegativity change affects the metal-alkyl σ bond more, simply because it has a much greater admixture of the migrating group (methyl). There are other ways to analyze this problem as well.

We now approach the important case of the formyl complex. In our calculations the hydrogen 1s orbital is of lower energy than the methyl lone pair. Thus the hydride ligand is formally a poorer σ donor and the migration of hydrogen should be a more difficult process. But things are not so simple. Indeed, the calculations show that the orbital pictured in **23** does have to climb higher in the H case, nearly 1.45 eV. Yet the total computed activation energy is 0.7 eV, actually smaller for formyl than for acetyl formation! What has happened is that there is a compensating stabilization in one of the lower orbitals, specifically the one that develops into the new C–H bond.

Should we trust the extended Hückel result of comparable

activation energies for formyl and acetyl intermediate formation? There is only indirect evidence that hydride migrations occur.[55] Formyl complexes, the final products of such a migration, are rare,[37,38,56] and those that are known were not prepared by a migrational pathway. Only a thioformyl complex has, to our knowledge, been made in this manner.[57] It may be that our calculations are misleading and higher activation energies for formation of the formyl intermediate should have been obtained. Or the formyl intermediate is in fact formed but is susceptible to homolytic or heterolytic cleavage. Our theoretical method is not the right one for evaluating the possibility of either, but there is some evidence in the literature for both reaction paths. $HMn(CO)_5$ can induce the formation of radicals,[37,56b] and the hydride transferring power of M–CHO has been known.[56c] Though our theoretical case is weak, we actually believe the computed result of a low barrier to a hydride shift.

Let us consider next the catalytically important migration of alkyl anions other than CH_3^-. The chain growth reaction in Fischer–Tropsch processes is supposed to involve alkyl migrations[5,6] of alkyl fragments with increasing chain length. We have made a brief investigation for R = methyl, ethyl, and n-propyl, with results summarized in Table II. There is a trend toward greater ease of migration with increasing chain length. In part it is an electronegativity effect (see the fragment donor energy in Table II), in part the decreasing bond strength in the initial reactant. The latter is due to the increasing delocalization of the alkyl group σ orbital, which has a smaller coefficient on the metal-bonded carbon.

These findings lead us to speculate about some parallels to the Fischer–Tropsch process. Suppose the $\Delta H^{\ddagger}$ for the migration reaction extrapolates as shown in Figure 6. We further assume a decreasing $\Delta S^{\ddagger}$ with increasing chain length, because of the lower probability of longer chains following a selected pathway. The superposition gives $\Delta G^{\ddagger}$. The observed chain length distribution in the Fischer–Tropsch synthesis[5]—except for very high chain numbers—is obtained with the demand that every group which migrates slower than hydride, which stays longer in the metal bound state, has a higher probability of being expelled as a hydrocarbon.

Highly α-branched alkyl groups should migrate still easier

than *n*-alkyl anions, owing to the increased delocalization of the alkyl lone pair. But steric crowding in the transition state is unavoidable and may increase the activation energy. We find this to be a factor in model calculations on *tert*-butyl and trifluoromethyl migrations.

The migration of acyl groups is experimentally some 7–8 kcal/mol less facile[59] than those of methyl. The process is interesting in that catalytic chain growth reactions usually do not involve such steps. The insertion reaction of isocyanide complexes, which we will discuss below, does in fact show multiinsertion steps[60] if the reaction is not controlled through the stoichiometry of the starting materials. For the model acyl
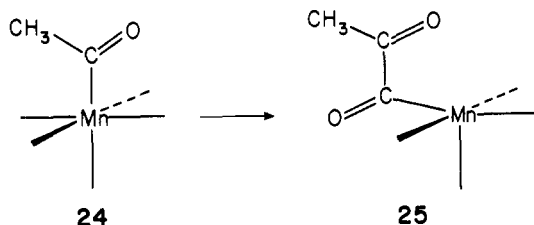
24 → **25**

migration reaction **24** → **25** we calculate an activation energy of approximately 1.05 eV, a little less than the experimental value. The reaction is very similar to the methyl migration, but the newly formed CC bond is considerably weaker.

Influence of the Metal Substitution Pattern. The other handle that one has on modifying the activation energy for the migration reaction is through the ligand set on the metal. We have concentrated on NO^+ as a model strong π acceptor, and PH_3 and CH_3 as moderate or strong σ donors which are not π acceptors.

Let us begin with the nitrosyl group. We know of only one alkyl compound of the general type $RM(CO)(NO)L_3$, namely, $CpRe(CO)(NO)R$,[61] but its migratory aptitude appears not to have been investigated. Three isomers, **26a–c**, covering the

26a 0.71 eV   **26b** 0.71   **26c** 0.87
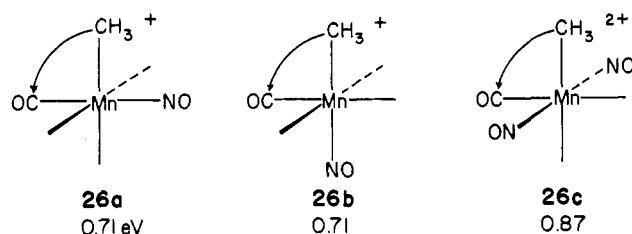
range of stereochemical possibilities were studied. Compound **26c** is disubstituted to retain C_s symmetry, which simplifies the analysis. The computed activation energies are given below the structures, and are to be compared to 0.85 eV for the original pentacarbonyl substituted model. Substitution off the mirror plane has no significant effect. This is easily understood, since the π power of nitrosyls affects only a″ orbitals in the d block, and these are not important in the migration reaction. Although both the σ orbital of the metal–CH_3 bond and the π acyl orbitals of the intermediate are considerably lowered in energy upon NO participation, their relative energy changes are not different from that of the parent $CH_3Mn(CO)_5$.

The cis or trans substituted compounds **26a** and **26b** lower the activation energy for the reaction. The nitrosyl groups in the migration plane are eager to accept the electron density which is released by the loss of one π acceptor in the course of forming the acyl group. This shows up in the calculations, if we plot the electron density shifted to the nitrosyl substituent as the reaction proceeds. Subsequent trapping of the intermediate should lead to *mer* octahedral structures.

Another effect, especially pronounced with multiple NO substitution, is a flattening out of the bending surface in the intermediate; i.e., the motion shown in **27** becomes quite easy. This has the interesting implication that the stereochemical

27
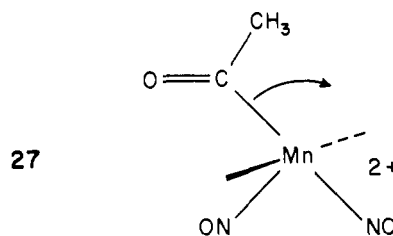
specificity of the migration reaction (methyl to CO) could be decreased upon acceptor substitution.

To model a ligand with weak or moderate σ-donating capability, but a poorer π acceptor than a carbonyl, we chose a phosphine PH_3. The three reactions investigated, along with their activation energies, are shown in **28a–c**. Substitution off

28a 1.04 eV   **28b** 0.94   **28c** 0.84
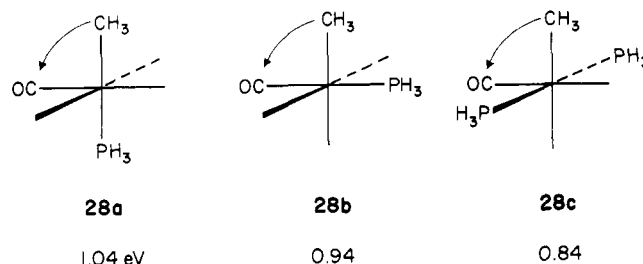
the mirror plane once again has no effect, while there is retardation of the reaction rate upon PH_3 substitution in the migration plane. This is the inverse of the effect computed for the nitrosyl ligand, and is due to the loss of capability for π acceptance along the reaction coordinate. Superimposed on this dominant π effect is a weaker σ donor site preference, which favors an eventual trans arrangement of phosphine and acyl, as in the product of **28b**.

The stronger donor case, modeled by methyl, is still more complicated. Using our conventional transition state geometry, one obtains the same trends as shown for phosphines in **28**, except even stronger. However, there are some experiments, to be mentioned below, which indicate migration with the donors in the mirror plane. This led us to look at the methyl case in greater detail. We reoptimized the transition state, finding significant differences from **3**. (The transition state region for the phosphine case was also reoptimized; no essential difference from **3** was found.) The migrating methyl group resists departure from its initial position, while it is easier to bend the carbonyl group involved in the reaction. The new transition state structure is shown schematically in **29**.

29
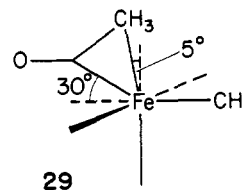
Beginning from *cis*-$(CH_3)_2Fe(CO)_4$ (**30**), and using the reoptimized transition state geometry, we find comparable activation energies for the reaction channels leading to **31** or **32**. But intermediate **31** itself is destabilized, having two strong
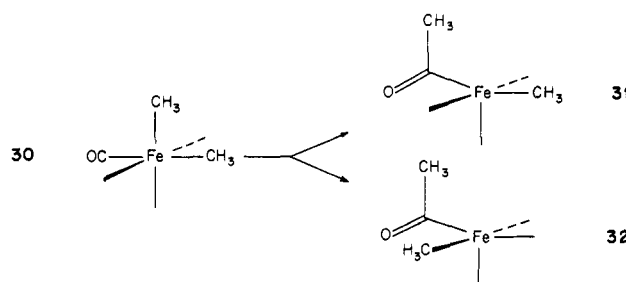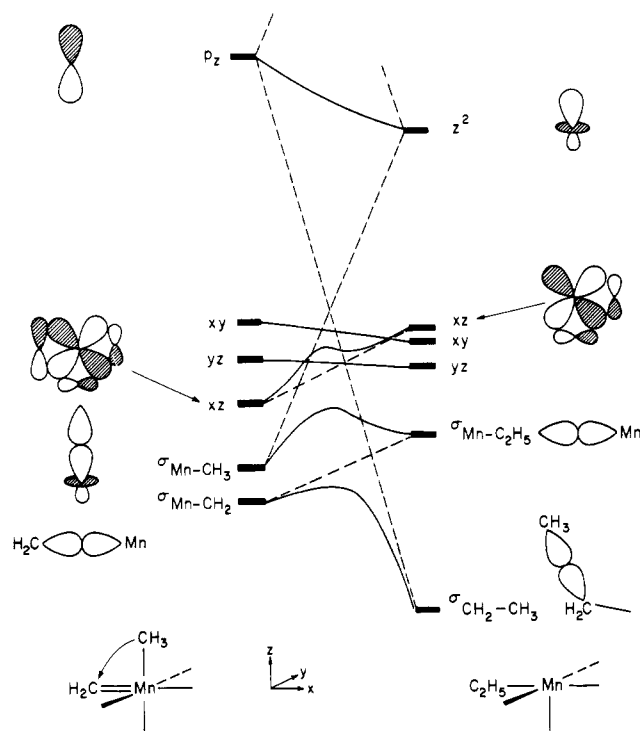
Figure 7. Schematic correlation diagram for reaction **36 → 37**.

donors trans to each other in the basal plane of a square pyramid. Considerably more stable in our calculations is isomer **33**, with the methyl group apical. The precise pathway of rearrangement from **31** to **33** is something we have worried about in great detail, but have not reached a definite conclusion. Weak reversible coordination with a sixth ligand could be involved.

The reason why a hypothetical easy rearrangement from **31** to **33** is important is that its presence or absence will influence our interpretation of the stereochemical course of the reaction. Addition of a ligand to **31** leads to a conclusion of methyl migration, while the trapping of **33** as **34** results in a specific *mer*
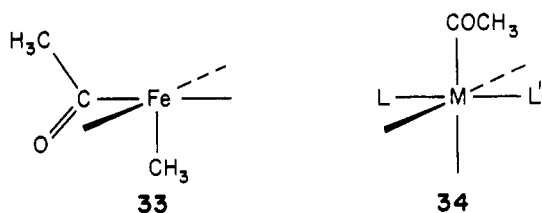
isomer which gives the impression that the reaction is a carbonyl insertion rather than a methyl migration. Several relevant experiments are available. First, the reaction **35** has been
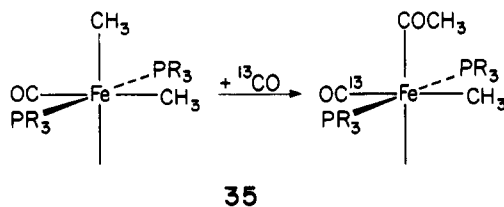
studied.[62] In this case the alternative route having the strong donor out of the migration plane is presumably blocked by phosphine substitution. Second, Maples and Krainhanzel have investigated the reaction[63]

$$cis\text{-}CH_3Mn(CO)_4L \xrightarrow{+L} CH_3COMn(CO)_3L_2 \qquad (9)$$

They found three categories of phosphine donors. One ends up

with *mer* complexes of type **34**, another with facial trisubstituted complexes, the third with isomeric mixtures of both patterns.

Varying the Accepting Ligand or the Migration Terminus. There are many unsaturated species other than CO which can bind to transition metals and be involved in α, β shifts. The insertion reactions of these have received less attention, but we think that there are some fascinating mechanistic and synthetic possibilities to be found among them.

There are many known carbene complexes,[64] which are attacked by various kinds of donors, but relatively few intramolecular reactions have been proposed. The process

$$L_nM\text{-}CH_2R \rightarrow L_nM(R)\text{=}CH_2 \qquad (10)$$
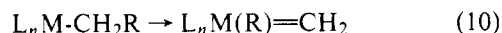
is suggested as the "activating" initial step in the olefin metathesis reaction.[65] Another example might be involved in the following reaction.[66]
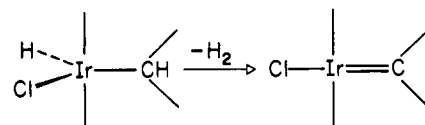
Green has trapped carbene hydride complexes originating from methyl groups, and has stressed the general importance of this reaction type.[67] Also the recent synthesis of simple carbene complexes by Schrock[68] probably involves the conversion of a metal alkyl complex in a similar way.

We have studied such a reaction, or its reverse, which could be called an alkyl activation, on our model manganese system, **36 ⇌ 37**. The calculated activation energy is a remarkably low
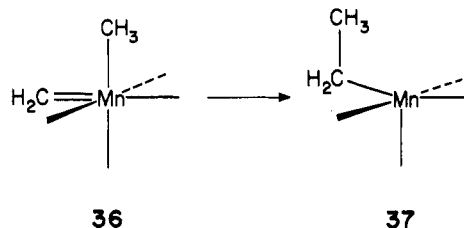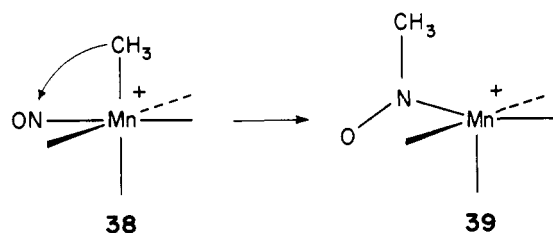

0.2 eV, which is almost the (not very reliable) thermodynamic difference between the two. So one should expect an easy thermal equilibrium of this type, if no further steps, such as migration to CO, disturb it.

A Walsh diagram for the reaction, Figure 7, shows just how finely balanced the reaction is, energetically. In comparison with the otherwise very similar CO system the carbene complex has a much lower lying accepting LUMO, primarily carbene p_z. Its low energy keeps the metal-CH_3 σ orbital from rising along the reaction coordinate and leads to a stable CH_2-CH_3 σ bond.

Another metal ligand system with unusually low-lying acceptor orbitals is the nitrosyl group. Migrations of alkyl or hydride have been observed in several instances.[69] But in neither case has a product with a ligating NOR been observed. Nitroso compound complexes are rare;[70] for instance, $PdCl_2(PhNO)_2$ is known.[70b] Stable alkyl or hydride nitrosyl complexes have been synthesized,[61,71] but little is known of their chemistry with Lewis bases. The reaction of metal alkyls with NO leads usually after an initial migration step to further attachment of NO.[72]

We have investigated the migration **38 → 39**, and found a somewhat higher activation energy (0.92 eV) than in the carbonyl case. But the reasons for this at first sight unexpected result are easy to discover from the correlation diagram of Figure 8. As would have been expected from the carbonyl-carbene argument, the metal-alkyl orbital is in fact kept at low energy. The activation energy arises instead from the rise in energy of the metal xz, as it loses its π bonding with the ni-

trosyl. As the NO distance is elongated in the course of the migration, the energy of the nitrosyl π^* perpendicular to the migration plane drops, in our calculations even below the normal metal acceptor orbital of the five-coordinate intermediate. This explains the high reactivity of nitroso complexes for further attack at the nitrogen.

Another inserting ligand that we have investigated is isocyanide. Many experimental studies of reaction 11 are
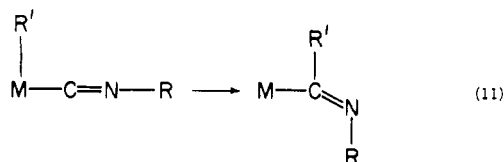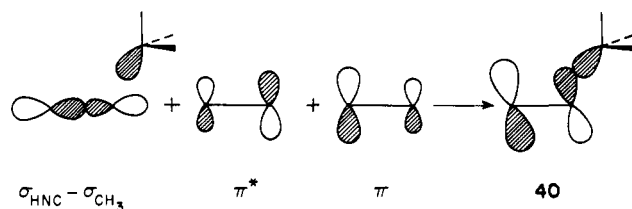

known.[73] Where there is a choice within one molecule, the isonitrile insertion wins out over migration of alkyl to CO.[60b] There are some special features to the reaction: (a) multiple insertion is facile[60] and (b) strong donor solvents appear to inhibit the reaction completely.[73b]

There are also some special features to the theoretical analysis of this migration, carried out along the lines of the carbonyl system. First, the HOMO of the HNC + CH$_3$$^-$ metal system is much more localized on the nitrogen than in the carbonyl case. This is the result of a strong admixture of the isonitrile π orbital, as shown in **40**. Second, fixing an

Mn(CO)$_4$$^+$ fragment to the partially formed iminoacyl group leads to much less stabilization than in the carbonyl case, as a consequence of the low α carbon nucleophilicity expressed in **40**. If we follow the same migration path as we did for the carbonyl, we find an activation energy of 1.8 eV. This is rather high. Third, given that the nitrogen end is emphasized in **40**, one might imagine that a dihapto intermediate, **41**, might be
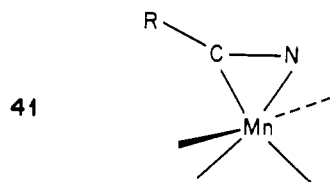
stabilized in this case. In fact we find a local minimum for such a structure, albeit less stable than an iminoacetyl structure analogous to **5**.

The only way we see now to reconcile the experimental findings of a facile reaction in octahedral complexes with a computed high activation energy is by suggesting that the reaction is highly sensitive to acid catalysis. The high-lying orbital **40** is readily stabilized, by some 1.2 eV in our calculation, by affixing an electrophile. In view of the fact that iminoacetyl compounds can be easily protonated to carbene complexes, E$^+$ catalysis is not surprising.[73d,74]

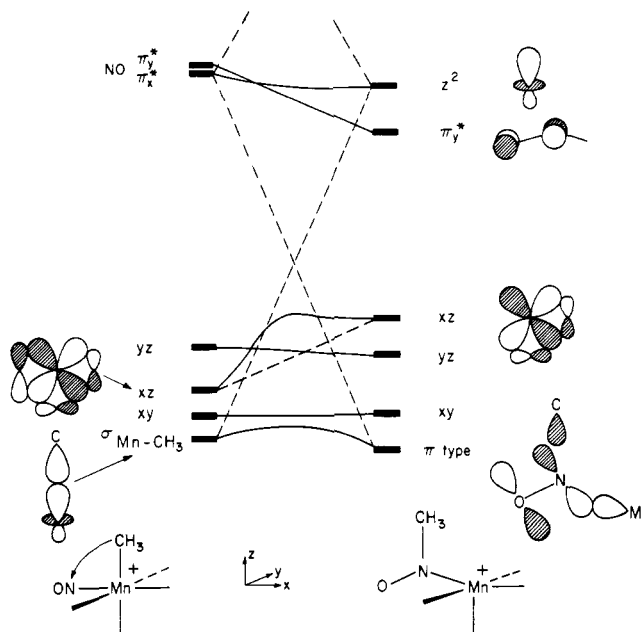**Figure 8.** Schematic correlation diagram for the migration of methyl to nitrosyl, **38 → 39**.

Different Metal Centers and Different Coordination Geometries.

If we replace the Mn in CH$_3$Mn(CO)$_5$ by Re, we change both the electronegativity and the diffuseness (overlapping capability) of the central metal orbitals. This should not affect much the crucial orbital in the reaction, σ_{M-CH_3}-acyl π, because the metal participation at both extremes is roughly the same. But one π interaction is entirely lost in the conversion, which should penalize the Re system more. In our calculations this is worth about 0.2 eV. A σ interaction between metal and CO is also lost, and destabilizes the Re system another 0.35 eV relative to Mn. The computed activation energies are 0.85 eV for Mn, 1.42 eV for Re.

Thus the migration reaction should be more difficult as one proceeds down a group. Iridium complexes[30a,75,76] show this effect, Rh complexes to a lesser extent.[47b,77] Typical of these is the Ir complex **42**, for which only the reverse migration proceeds under moderate conditions.[76]
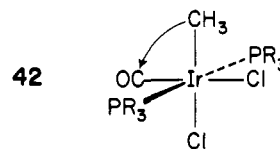
Very often one observes, as in **42** above, that in migrating systems the donors are arranged perpendicular to the migrational plane. If one envisages removing these ligands, which have no effect on the migration, one can see that square planar complexes should show the same features that we have described for CH$_3$Mn(CO)$_5$. These are d^8 systems, not d^6, but the two extra electrons sit in an orbital perpendicular to the migration plane. The complexes investigated usually involve phosphine or arsine substituents.[26,78] The arsine cases, for which kinetics were studied, show the same kinetic behavior as the Mn system.

Migrations are also known for seven-coordinate complexes,[79] but we have not analyzed these. Much more amenable to calculation and widespread are five-coordinate d^8 systems, such as CH$_3$Co(CO)$_4$. The most stable ground-state configuration should be a trigonal bipyramid with the alkyl donor axial.[42] Let us first consider what the acyl intermediate may look like. The orbitals of a C_{3v} pyramidal Co(CO)$_3$$^+$ fragment[80] are well known—the upper three, which carry two

Table III. Parameters Used in EHT Calculations

| Orbital		H_{ii}, eV	ζ_2	ζ_2	$C_1{}^a$	$C_2{}^a$
Mn	3d	−11.59	5.15	1.90	0.5320	0.6490
	4s	−8.63	1.80			
	4p	−5.06	1.80			
Fe	3d	−12.2	5.35	1.8	0.5366	0.6678
	4s	−8.86	1.9			
	4p	−5.12	1.9			
Co	3d	−12.11	5.55	2.1	0.5679	0.6059
	4s	−8.54	2.			
	4p	−4.76	2.			
Rh	4d	−12.5	4.29	1.97	0.5807	0.5685
	5s	−8.09	2.135			
	5p	−4.57	2.1			
Re	5d	−12.66	5.343	2.277	0.6359	0.5677
	6s	−9.36	2.398			
	6p	−5.96	2.372			
Ir	5d	−12.17	5.796	2.557	0.6698	0.586
	6s	−11.36	2.5			
	6p	−4.5	2.2			
Pt	5d	−12.59	6.013	2.696	0.6334	0.5513
	6s	−9.077	2.554			
	6p	−5.575	2.554			
C	2s	−21.40	1.625			
	2p	−11.40	1.625			
N	2s	−26.00	1.95			
	2p	−13.40	1.95			
P	3s	−18.60	1.60			
	3p	−14.00	1.60			
O	2s	−32.30	2.275			
	2p	−14.80	2.275			
F	2s	−40.0	2.425			
	2p	−18.1	2.425			
Cl	3s	−26.30	2.033			
	3p	−14.20	2.033			
H	1s	−13.60	1.30			

^{a} Coefficients for the double ζ expansion.
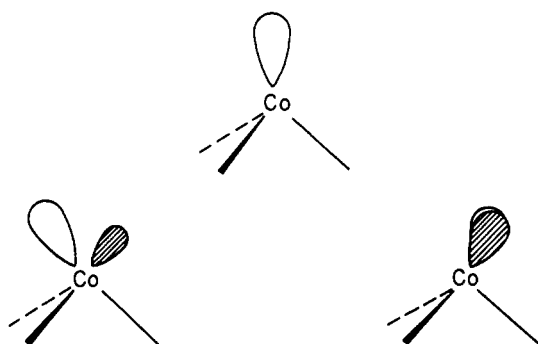
electrons, are shown below. The best accepting lobe is trans to one CO group. From our previous considerations on acyl orientations we would conclude that the preferred geometry is **43**. This is confirmed by detailed calculations. But **43** can relax still further, because the two cis CO groups repel one of the d orbitals, **44**. An opening of their angle leads to a near square-

43   **44**   **45**
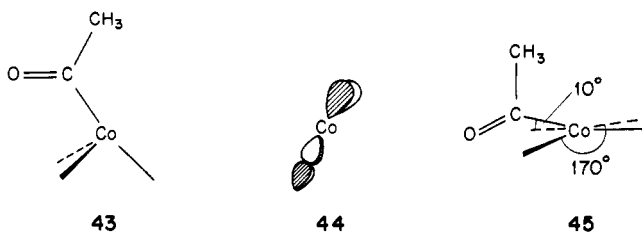
planar intermediate structure **45**. This was already proposed by Osborn and Shapley,[81] and is presumably close to the deformation observed for $CH_3CONi(PMe_3)_2Cl$.[53] In order to get to such an intermediate by alkyl migration one can consider

one possibility seriously, which is starting from a trigonal bipyramidal structure with the alkyl in the equatorial position, **46**. The necessary motions are indicated by the arrows. So,

46
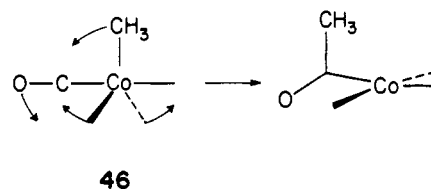
before an alkyl migration can occur, the methyl must pseudorotate from the more stable axial position. We have calculated that the pseudorotation takes about 13 kcal/mol. Ab initio calculations come up with about 8 kcal/mol.[82] Migration from the equatorial position faces only a very small kinetic barrier, because a great deal of energy is set free from the relaxation of the two CO groups in the equatorial plane. The orbital transformations are otherwise very similar to the octahedral case. The energy profile appears below.

The migration is apparently determined by the pseudorotation barrier. The calculated energy profile, showing only a small thermodynamic difference between ground state and intermediate, is consistent with the experimental observation of Breslow and Heck that $CH_3Co(CO)_4$ shows a ketonic band in solution assigned to an acetyl-cobalt-tricarbonyl species.[83a] Almost indistinguishable from the above path is a migration from a square pyramid with the methyl group in the apical position, but two initiating pseudorotations are necessary.[84]

A direct CO insertion from the axial position of the trigonal bipyramid, the ground state, as in **47**, has to pass structures resembling a rotational isomer of **45** which is about 15 kcal/
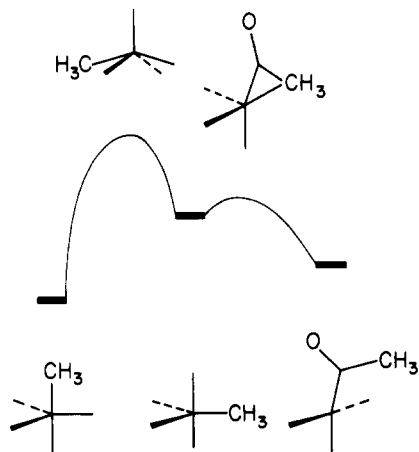
mol higher in energy. The final word has not yet been said about this reaction— if the reader thinks that the geometrical problem is complicated, he or she should take a look at the problems we faced in evaluating associative mechanisms for the olefin insertion reaction.[16]

47
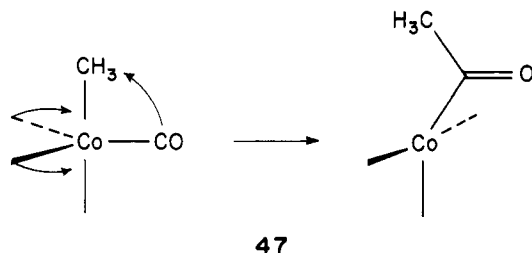
Let us now turn to chemistry. Because of the rapidity of the reaction, the alkyl migration in $RCo(CO)_4$ has not been really investigated in full kinetic detail. Only phosphine-substituted complexes are sufficiently slow that their mechanistic details have been studied.[85] It is believed that the primary characteristics are similar to those in the octahedral Mn system.[83b]

A very special case are the anionic isoelectronic complexes, **48**, whose kinetics have been studied. A strong counterion ef-

48
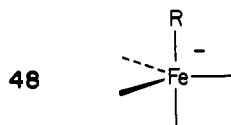
fect has been established.[24,38-40,86] We attribute this in part to Lewis acid catalysis, in part to the lowering of the pseudorotational barrier to put the alkyl group in an equatorial position. We think that the latter effect is a consequence of direct weak coordination of the electrophile to the metal in the square pyramidal conformation. Insertions in square-planar Ni-alkyl complexes[53] could proceed via this five-coordinate pathway. Cases of migration in five-coordinate d^8 Ni complexes are known.[87] Alkyl migration in Pd^{II}, Rh^I square-planar complexes is also proposed to operate via initiating associative steps.[78c,88]

Our separate studies on the olefin insertion reaction[16] sound a cautionary note in that they indicate that, at least in Pt chemistry, one must take seriously reactions proceeding from a dissociative three-coordinate intermediate.

Appendix

The parameters used in the extended Hückel calculations[14] are given in Table III. They were taken for the most part from earlier work (Co,[80] Pt,[16] Re,[89] Ir,[90] Rh,[91] Mn[92]). H_{ii} values for iron were obtained from quadratic charge iteration on $Fe(CO)_4(CH_3)_2$. Fe exponents came from the work of Basch and Gray.[93] The main group parameters are standard ones. All geometries were examined without further charge iteration. The weighted H_{ij} formula[94] was used. For the model calculations the $Mn(CO)_4$ framework had Mn-C 1.853 Å and C-O 1.134 Å.

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