$F)_2][Co(COD)_2]$ (2.026–2.090 Å)[38] and $Co(MeCN)_2$(diethyl fumarate)$_2$ (2.060 (9) Å).[32]

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Supplementary Material Available: A stereodrawing of the unit cell and tables of anisotropic thermal parameters, hydrogen atom coordinates, and additional bond distances and angles for the complex $Na[Co(CO)_2(DF)_2]\cdot THF$ (9 pages); a table of observed and calculated structure factors for the complex $Na[Co(CO)_2(DF)_2]\cdot THF$ (15 pages). Ordering information is given on any current masthead page.

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Understanding Reactivity Trends by Structural and Theoretical Studies of Distortions in Ground-State Reagents

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Distortions of the carbonyl ligands in $RM(CO)_n$ ($M = Mn$, $n = 5$; $M = Co$, $n = 4$) are examined by studying published structural data. The more electropositive the R group, the more the equatorial CO groups are found to bend toward the R group. The results can be understood in terms of a simple model: for example, in $RMn(CO)_5$ the more electropositive the R group, the more the $Mn(CO)_5$ group departs from the octahedral structure expected for a d^6 system and approaches the distorted trigonal bipyramidal (TBP) or square pyramidal (SP) geometry expected for a d^8 configuration. In a similar way the TBP $RCo(CO)_4$ undergoes distortions leading toward d^{10} tetrahedral geometry when R is electropositive. The effect is found to be more pronounced for late transition metals and for TBP over O_h coordination modes. EHT calculations validate and amplify this simple model and are used to identify the main orbital interactions. On Bürgi–Dunitz ideas, the above distortions are correlated with the carbonyl insertion into a M–R bond for which larger reaction rates are found for more electropositive R groups. These results suggest that the electronic factors that favor distortion also favor the insertion reaction. Distortion analysis allows us to understand why nucleophiles sometimes substitute and sometimes abstract R in $RCo(CO)_3$.

Introduction

An important goal in chemistry is understanding the factors that affect reaction rates and product ratios as the structure of the reaction partners is changed. In order to do this, we need to identify and understand key electronic and steric effects in the transition state. Such an analysis is particularly difficult because few experimental studies are available that give a detailed insight into the structural or electronic properties of the transition structure. Direct spectroscopic study is not possible and thus only indirect evidence can be used. High-level quantum chemical calculations have been done to determine the geometries and energies of transition structures. However, in the case of organometallic systems such studies are still difficult and certain well-marked reactivity trends remain unexplained.

In this paper, we describe a method for gaining a better understanding of electronic effects that influence chemical reactions by a combination of structural and theoretical studies. Bürgi and Dunitz showed how a quantitative comparison of a series of structural data can help define reaction pathways.[1] For example, a study of the N···C═O spatial arrangements in several molecules containing a carbonyl function and an amino group was used to define the reaction path of the addition of nucleophiles to a carbonyl function. Several other organic reactions (S_N2, isomerization, proton transfer) were analyzed in a similar manner.[1,2] In contrast, similar investigations in the area of organometallic reactions are still scarce. To our knowledge two studies have been conducted: hydrolysis of hexacoordinated Ni complexes[1] and oxidative addition of a C–H bond to a metal.[3] Another study examined the relationship between structure and activation energy, providing an estimate of transition-state structures in the ring inversion of (*s-cis*-η^4-butadiene) complexes.[4] In each of these examples, structures frozen in the crystalline state were considered to be successive snapshots of a reaction pathway. Theoretical studies have supported this view.[5] However, few attempts have been made to analyze the factors that make a structure freeze in the crystal on a

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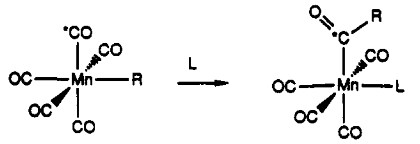
more or less advanced point on the reaction path and compare them with those factors affecting the rate of reaction in solution. In this work we attempt to fill such a gap and make a bridge between structural deformations in the starting material and reactivity in solution.

The CO insertion reaction is one of the best known examples of insertion and is a reaction of fundamental significance in organometallic chemistry.[6] The reaction is a key step in alkene hydroformylation, which is practiced commercially on a very large scale. The most widely studied example of CO insertion is shown in eq 1. The reaction has received considerable attention owing to its importance in organometallic chemistry. One noticeable aspect of the reaction is that the rate of CO insertion increases as R becomes less electronegative.[7] This has been reproduced in theoretical studies[8] and interpreted in terms of thermodynamic properties.[8a]



(1)

Metal carbonyl complexes of the form $RM(CO)_n$ ($M = Mn$, $n = 5$; $M = Co$, $n = 4$) exhibit systematic distortions of the equatorial CO groups (CO_{eq}) toward R. On Bürgi–Dunitz ideas, we correlate this distortion with the carbonyl insertion reaction. We postulate that the insertion reaction will proceed more easily if the structural distortion in the starting complex is larger, on the grounds that the factors that favor the distortion are also likely to stabilize the transition state for the reaction. We use theoretical methods to understand the electronic factors that favor the distortion and to show why similar factors might facilitate the insertion reaction. We will also examine how activation energies are affected by these electronic factors and to what extent steric factors may dictate the distortion. These geometries have already attracted the interest of several theoretical groups.[9-11] The distortion has been examined by Elian and Hoffmann[10] for both the hexa- and the pentacoordinated complexes. More sophisticated methods have also been used, especially in the case of hydride (R = H) complexes.[11] However, no systematic study including the influence of the ligand field, the character of the metal, and the nature of the spectator ligands has been performed.

Table I. Distortion Data for $RM(CO)_n$ ($M = Mn$, Re, $n = 5$; $M = Co$, $n = 4$)

R	label[a]	$\delta\theta_{obs}$,[b] °	$\delta\theta_{cone}$,[c] °	χ[d]	ref
M = Mn					
H[e]	a	7.2	8.8	7.17	12
GeH_3	b	7.0	11.3	7.52	13
$SnMe_3$	c	5.6	7.8	7.47	14
$GeBr_3$	d	5.0	6.0	8.30	15
CH_3	e	4.7	10.8	7.37	16
SiH_3	f	4.5	6.0	7.20	13
$Mn(CO)_5$	g	3.4	1.9		17
$SnPh_3$	h	3.3	-0.8	8.02	18
SiF_3	i	2.9	4.8	10.58	19
$Si(SiMe_3)_3$	j	2.6	-5.9	7.36	20
$SnCl_3$	k	2.2	7.8	8.74	21
CF_3	l	2.1	7.0	10.90	22
Cl	m	1.7	11.3	9.38	23
M = Re					
GeH_3		7.0	13.0	7.52	24
CH_3		6.0	12.3	7.37	24
SiH_3		4.0	9.3	7.20	24
Cl		1.2	13.5	9.38	25
M = Co					
f	n	19.4			26
$[Et_3NH]^+$	o	15.9	15.7	7.54	27
$Au(PPh_3)$	p	12.3			28
$Ag(L^2)$[g]	q	11.9			28
H	a	9.7	7.8	7.17	29
SiH_3	f	8.3	5.8	7.20	30
GePhMeNp[h]	r	6.4	2.0	7.94	31
GeH_3	b	6.2	10.8	7.52	32
$SiCl_3$	s	4.8	3.3	8.88	33
SiF_3	i	4.4	2.0	10.58	34
$GeCl_3$	t	3.0	8.8	8.91	35

[a] Labels in Figure 1. [b] Observed distortion. [c] Cone angle distortion. [d] Group electronegativity. [e] Neutron diffraction structure. [f] R = noncoordinating ligand, $[Me_3PSiMe_3]^+$; $Co(CO)_4$ is thus $[Co(CO)_4]^-$. [g] $L^2 = Me_2AsC_6H_4(AsMe)C_6H_4AsMe_2$. [h] Np = 1-naphthyl.

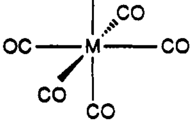
Table II. Experimental and Calculated Distortions for $HM(CO)_n$

	$[HCr(CO)_5]^-$	$HMn(CO)_5$	$[HFe(CO)_4]^-$	$HCo(CO)_4$
$\delta\theta_{obs}$[a]	5.4	7.2	9.1	9.7
$\delta\theta_{calc}$[b]	2.7	4.9	9.0	9.9

[a] Experimental values taken from the literature (see text). [b] Calculated values using regular octahedral or TBP structure with hydridic parameters on the H (*Hii* = -11.6 eV).

Results and Discussion

(a) Documenting the Distortion. We have chosen to examine formally octahedral d^6 $RM(CO)_5$ (M = Mn and Re) (1) and formally trigonal bipyramidal (TBP) d^8 $RM(CO)_4$ (M = Co) (2). These systems are convenient to study since a large amount of structural data is available in the literature, Table I.[36] The CO_{eq} distortion from an



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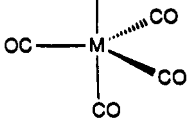

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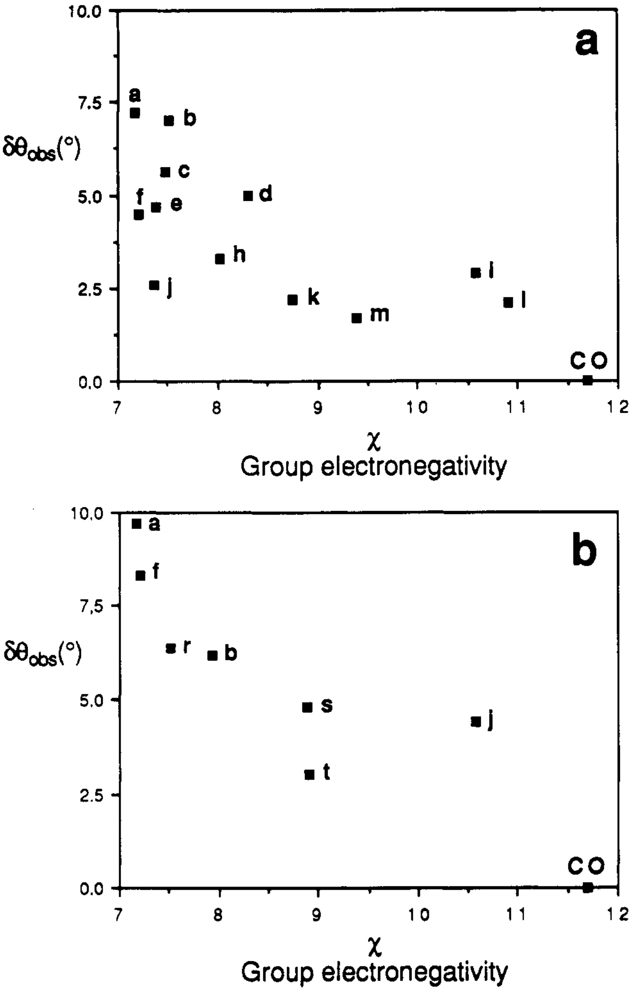
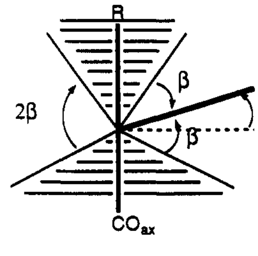


Figure 1. Plots of group electronegativity (χ) versus observed distortion ($\delta\theta_{obs}$, deg) for (a) $RMn(CO)_5$ and (b) $RCo(CO)_4$. Labels for R groups are given in Table I. On each plot R = CO is included as a reference point where no distortion occurs ($\delta\theta_{obs}$ = 0°).

idealized geometry is reported as $\delta\theta_{obs}$, which is the average of the angular distortions of the CO_{eq} groups from their octahedral (or TBP) positions in the direction of the axial R group.

A distinct trend is apparent: the CO_{eq} tends to distort toward the R group to an increasing extent as the R group becomes more electropositive but keep essentially ideal octahedral (or TBP) positions when the R group is electronegative. In order to see the correlation in a more quantitative manner we have used the group electronegativity scale, χ_R, proposed by Huheey.[37] A general trend (Figure 1) is apparent despite some scattering of points. Strongly electronegative R groups, such as Cl, CF_3, or Cl_3Sn, tend to give small distortions, while more electropositive groups, such as H, CH_3, and GeH_3, tend to give the largest distortions. Comparing groups that have similar electronic characteristics is more difficult, for example, CH_3, SiH_3, and GeH_3. It is commonly accepted that the heaviest element should be the most electropositive and, according to this argument, GeH_3 should induce the largest $\delta\theta_{obs}$, which is the case. However, the ordering of CH_3 and SiH_3 is less clear. It is often thought that SiR_3 has electron-accepting capabilities either via its π^* orbitals (arising from combinations of Si–R σ^* orbitals) or through the presence of d orbitals on the metal; our simple correlation cannot incorporate such effects.

Electronegativity scales are semiempirical and the effect of an R group may not be adequately represented by a single parameter (as we saw for SiH_3). An obvious factor to consider in a search for a better correlation is the steric effect. Is this of any importance in determining the distortion? First, it is clear that it is not the steric effect that dictates the distortion. For example, in *trans*-$(PPh_3)Mn(CO)_4(SnPh_3)$, where the two axial ligands are of similar size, the CO_{eq} bends toward the more electropositive $SnPh_3$ group ($\delta\theta_{obs}$ = 3.3°).[38] Similarly in the hexacoordinated metallacycle $Fe(CO)_3(PPh_3)(CH_2)_4$, the two axial CO ligands bend toward the more hindered carbon, which is trans to the carbonyl group.[39] In order to determine the importance of steric factors we use the cone angle[40] and include the value $\delta\theta_{cone}$ in Table I. This value is the expected distortion of CO_{eq}, assuming that they will lie midway between the steric cones of the two axial ligands as illustrated in 3.[41] The correlation between the size of the ligand and the distortion is poor,[42] although on the whole, $\delta\theta_{obs}$ does not exceed $\delta\theta_{cone}$. This is probably because $\delta\theta_{cone}$



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defines the region in which CO_{eq} may reside without undue steric problems. However, some interesting examples of the relevance of the steric factors exist for known bulky groups such as $SnPh_3$ or $Si(SiMe_3)_3$. In these complexes, the CO_{eq} groups distort toward R ($\delta\theta_{obs} > 0$) even though we would have seen distortion away from R ($\delta\theta_{cone} < 0$) if steric factors were dictating the shape of the complexes. Hence we can see that steric factors are not the main contributors to the distortion. Thus for a large variety of *cis*-$RR'M(CO)_4$, the CO ligands bend toward the more electropositive of the two R groups.[39,43,44] They can, however, play a fine tuning role in a distortion determined predominantly by the electronic nature of the R group.

Considering the above limiting factors, we can see that the electronegativity/distortion correlation curves we presented in Figure 1 are satisfactory. We should bear in mind that the distortions are small and have been measured by various techniques. Searching for a better fit would be unrealistic.

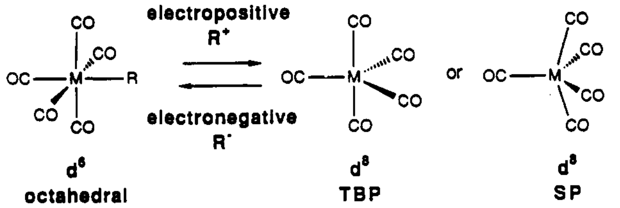
The ligand field influences the magnitude of the distortion. Thus the values of $\delta\theta_{obs}$ obtained for the $RCo(CO)_4$ system are generally slightly larger than those for the same R group in the $RMn(CO)_5$ system. Decreasing also the number of CO ligands on the complex may even enhance the distortion. Thus in TBP (triphos)RhMe(CO) the angle between the axial RhMe and equatorial RhCO bonds is only 79.1° ($\delta\theta_{obs} = 10.9°$).[45] An additional example is provided by the mixed heteronuclear cluster $(CO)_4CoSnPh_2Mn(CO)_5$, which contains both ligand fields.[46] The $CO_{eq}s$ in both metal carbonyl fragments distort toward the Sn; $\delta\theta_{obs}$ for the $Co(CO)_4$ fragment is about 9° but $\delta\theta_{obs}$ for the $Mn(CO)_5$ fragment is only 3°.

That the distortion is not confined to carbonyls is illustrated by an X-ray crystal structure of $Co(CO)H(PPh_3)_3$,[47] which shows that the three equatorial phosphines bend toward the hydride. In the series $MHL'(PPh_3)_3$ the equatorial phosphines distort away from their ideal TBP positions, toward the electropositive hydride and away from L′ (L′ = CO, N_2, $PPh(OEt)_2$, PF_3, NO, Cl, PPh_3).[47] However, in general, the distortion of equatorial ligands appears to be larger with L = CO than with other equatorial ligands.

Finally the nature of the metal may also influence the magnitude of distortion. The consideration of hydride complexes is especially informative since they give large distortions. In the manganese and cobalt hydrides the values for $\delta\theta_{obs}$ are 7.2° and 9.7°, respectively. These values are larger than in the corresponding isoelectronic complexes: $[HCr(CO)_5]^-$, 5.4°,[48] and $[HFe(CO)_4]^-$, 9.1.[49] Although we have only a limited series at hand, this suggests that later transition metals may induce larger distortions for a given coordination mode.

(b) Understanding the Distortion. We will now discuss the causes of the distortions on the basis of theoretical ideas. Although a molecular orbital explanation of the distortion has already been provided,[10] it does not incorporate the influence of the ligands, the metal, and the ligand field. Our study will deal with all of these aspects. We describe EHT calculations[50] that show the origin of the electronegativity/distortion trend observed in the structural data. We will discuss the octahedral manganese system in detail first and then extend the theory to the TBP cobalt system. The distortion itself is derived from the same electronic effects in both coordination modes.

Distortion from the Octahedron to the Square Pyramid: d^6 $HMn(CO)_5$. Rather than go straight to the theoretical studies, it is easier to start our discussion by considering a much more immediately accessible idea illustrated in eq 2. Consider the species $RM(CO)_5$ in which we make R very electronegative. R is then strongly coordinated to the metal and the formally d^6 ML_6 species is predicted to have an ideal octahedral structure, i.e., $\delta\theta_{obs}$ is near zero. On the other hand, if R is very electropositive, the R group can be considered to act as a weakly coordinating cation, leaving the d^8 $M(CO)_5$ anion, which, like other pentacoordinate d^8 species, would be expected to have a TBP geometry, for which $\delta\theta$ is 30° (for each of the two distorting CO_{eq}) or, alternatively, a square pyramid (SP) with an angle between the basal and apical ligands greater than 90° ($\delta\theta > 0°$).[51] Elian and Hoffman[10] have clearly shown that the d^8 TBP and SP structures were both more stable than a d^8 square planar pyramid. For the molecules described here, a preference for TBP or SP will depend on the specific ligand set or local symmetry considerations. Symmetry can be even lower if only one CO_{eq} is distorted. All these distortions have a common origin, therefore no attempt will be made to differentiate between them.



(2)

Calculations have been carried out on $Mn(CO)_5H'$ (4), in which the change in relative electronegativity of H′ is simulated by changing the energy of its 1s orbital. Taking standard hydrogen parameters ($H_{ii} = -13.6$ eV) as a reference value, a more electronegative or electropositive center is modeled by making H_{ii} less than or greater than −13.6 eV, respectively. Three types of distortions can be considered, the first being the distortion of a single CO_{eq} (C_s symmetry) in the horizontal (xz) plane. The second maintains C_{2v} symmetry as two CO_{eq} groups are allowed to change position in the xz plane. The third distortion maintains C_{4v} symmetry since all four CO_{eq} groups are allowed to move in a concerted manner. Calculations on these each of these three distortions in 4 show that there is always a total energy minimum at a value of $\delta\theta > 0$ (i.e.,

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(43) (a) Lindner, E.; Eberle, H.-J.; Hoehne, S. *Chem. Ber.* **1981**, *114*, 413. Lindner, E.; Eberle, H.-J. *J. Organomet. Chem.* **1980**, *191*, 143. Lindner, E.; von Au G. *Z. Naturforsh.* **1980**, *35B*, 1104; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 824. Distortions of lower magnitude are found when L = phosphine in place of oxyphosphines: Lindner, E.; Zinsser, F.; Hiller, W.; Fawzi, R. *J. Organomet. Chem.* **1985**, *288*, 317. Lindner, E.; Funk, G.; Hoehner, S. *Chem. Ber.* **1981**, *114*, 2465. (b) Rapid CO insertion into the Mn–C σ bond has also been observed for these complexes: Lindner, E.; Eberle, H.-J. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 73.

(44) Lindner, E.; Jansen, R.-M.; Hiller, W.; Fawzi, R. *Chem. Ber.* **1989**, *122*, 1403.

(45) Thaler, E. C.; Folting, K.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 2664.

(46) Bir'yukov, B. P.; Struchkov, Y. T.; Anisimov, K. N.; Kolobova, N. E.; Osipova, O. P.; Zakharov, M. Y. *J. Chem. Soc., Chem. Commun.* **1967**, 749.

(47) Whitfield, J. M.; Watkins, S. F.; Tupper, G. B.; Baddley, W. H. *J. Chem. Soc., Dalton Trans.* **1977**, 407.

(48) Darensbourg, M.; Slater, S. *J. Am. Chem. Soc.* **1981**, *103*, 5914.

(49) Smith, M. B.; Bau, R., *J. Am. Chem. Soc.* **1973**, *95*, 2388.

(50) EHT calculations were carried out by using the weighted H_{ij} formulation: Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686. At $\delta\theta = 0°$ species 4–6 are regular octahedra with Mn–C = 1.84 Å, C–O = 1.14 Å, and Mn–H = 1.6 Å. $HCo(CO)_4$ was calculated by using Co–C = 1.84 Å, C–O = 1.14 Å, and Co–H = 1.6 Å. Normal H parameters were used for hydrides H and H_c ($H_{ii} = -13.6$ eV, $\zeta = 1.3$) and only H_{ii} was varied for H′. The parameters for Mn and Co were taken from: Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 7240.

(51) Burdett, J. K. *Molecular Shapes*; Wiley: New York 1980; p 189.

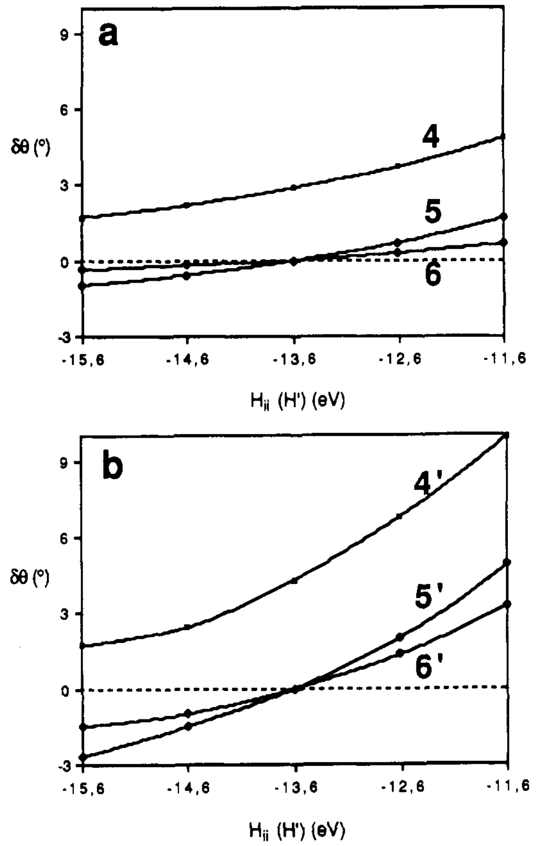
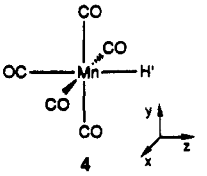


Figure 2. Plots of calculated $\delta\theta$ (deg) at the energy minimum with changing H' electronegativity as represented by H_{ii} (eV) for (a) 4–6 for the octahedral d^6 manganese systems, and (b) 4'–6' for the TBP d^8 cobalt systems.

CO distorted toward H'). The most symmetric C_{4v} distortion is the most convenient to discuss and only these results are presented in detail here; the results for the C_{2v} and C_s distortions are very similar and are found to be controlled by the same electronic effects.[52]

In order to differentiate between σ and π effects of the spectator ligands on the distortion process, we chose to examine the d^6 complexes $Mn(CO)_5H'$ (4), *trans*-$[HMn(CO)_4H']^-$ (5), and $[HMn(H_{eq})_4H']^{5-}$ (6). Figure 2a shows



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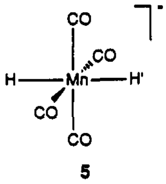

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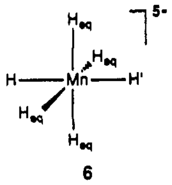
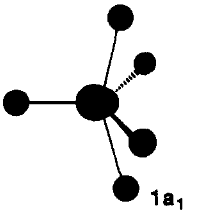


6

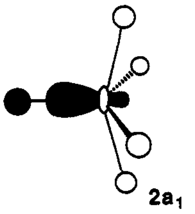
the change in $\delta\theta$ as a function of the energy of the 1s orbital of H' (H_{ii}) for 4–6. In 4, the CO$_{eq}$ groups always bend toward H' for any H' 1s energy value and the distortion increases as H' becomes more electropositive. In 5 and 6, the CO$_{eq}$ groups bend toward H' when its 1s orbital energy of H' is above −13.6 eV (i.e., more electropositive) and away from H' when its 1s orbital energy is below −13.6 eV. The distortion away from the octahedral ($\delta\theta$ = 0°) structure increases with the difference in electronegativity between the two transoid H and H' ligands. The distortion increases in the order 6 < 5 < 4 for a given H' center. Therefore, the distortion appears to increase with the difference of electronegativity of H' and the ligand trans to it, which is in agreement with the structural data presented in Table I and Figure 1a. The distortion also increases with the presence of a π-acceptor group cis to H', which is consistent with larger $\delta\theta_{obs}$ for carbonyls than for phosphines.[47]

In order to understand the factors responsible for this behavior we need to separate the σ from the π-components of the distortion. The calculations for 6 show that although the distortion toward the more electropositive axial ligand is much smaller than those obtained for 4 and 5, there must nevertheless be a small σ component favoring the distortion. We therefore take the approach of examining 6 to determine the σ effects followed by an examination of 5 to find the effects of cis-π acceptors. Finally we discuss the bonding in 4 where a π acceptor has been introduced trans to H'.

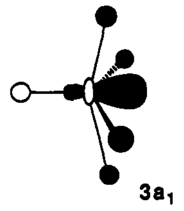
Complex 6 can be constructed from the two fragments $[HMn(H_{eq})_4]^{4-}$ and H'$^-$. The metal fragment molecular orbitals relevant to our problem are the two lower σ-bonding M–H orbitals (1a$_1$ and 2a$_1$), the three nonbonding orbitals originating from the t$_{2g}$ of the octahedron, and the σ-type hybrid (3a$_1$), which is the LUMO of the fragment for a d^6 electron count. The two lower σ orbitals are both hybridized toward H but differ in the phases between H and H$_{eq}$. The 1a$_1$ is a linear combination of s and z and is in-phase for all the hydrides, as shown in **7a**, while 2a$_1$ is a linear combination of z^2 and z and is out-of-phase between H and H$_{eq}$ as shown in **7b**. The 1a$_1$ orbital favors



7a



7b



7c

distortion toward H since this increases the in-phase interaction between H$_{eq}$ and both the metal and the H orbitals. The 2a$_1$ orbital favors distortion away from H since this simultaneously reduces the out-of-phase interaction between H$_{eq}$ and H and increases the in-phase interaction between H$_{eq}$ and the hybridized metal orbital. The effects of these orbitals effectively cancel each other out and they will not be considered further. The nonbonding orbitals originating from the t$_{2g}$ set of the octahedron (not shown) favor $\delta\theta$ = 0°. The LUMO of the complex, 3a$_1$, is also a linear combination of z^2 and z, this time hybridized away from H as shown in 7c. It is stabilized by moving H$_{eq}$ away from H ($\delta\theta$ > 0°) since this displacement decreases the out-of-phase overlap between H and H$_{eq}$ and also makes the interaction M–H$_{eq}$ less antibonding.[53] The corresponding Walsh diagrams have been presented by Elian and Hoffmann.[10]

The occupied orbital of H' will interact with 1a$_1$, 2a$_1$, and 3a$_1$. Making H' more electropositive (i.e., raising the energy of its occupied orbital) increases the interaction between H' and 3a$_1$ and will transfer more electrons into 3a$_1$. Displacement of H$_{eq}$ toward H' is thus more favored. Full occupancy of 3a$_1$ by two electrons (the d^8 ML$_5$ complex) is thus the extreme case of electron transfer. In contrast, totally emptying the 3a$_1$ orbital maintains a preference for an undistorted octahedral structure.

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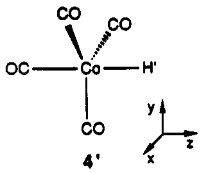
[52] For regular H' energy values (−13.6 eV) these total energy minima come at H-Mn-CO$_{eq}$ angles of 86.2° (C_s symmetry), 86.4° (C_{2v} symmetry), and 87.1° (C_{4v} symmetry).

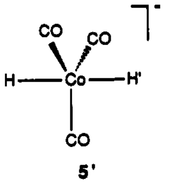
[53] Moving H$_{eq}$ toward the nodal cone of z^2 in 7c on any side of the metal would be stabilizing. Additional stability is reached by moving H$_{eq}$ toward the large lobe of the metal orbital since H$_{eq}$ and the p component on the metal are thus in phase.

A consequence of replacing the H_{eq} ligands in **6** by CO to give **5** is that π effects may come into play. The H′ 1s orbital can only mix with fragment orbitals of a_1 symmetry. The introduction of π-acceptor ligands cis to H′ stabilizes the LUMO of the metal fragment $[HMn(CO)_4]^+$ by incorporation of the high-lying π^*_{CO} as shown in **8**.[54] The incorporation of π^*_{CO} increases the preference for distortion compared to **7c**, since this will also increase metal to π^*_{CO} back-bonding, and we see a larger distortion in **5** than in **6**.

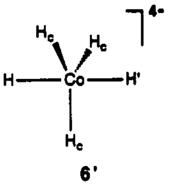
Finally we can replace the axial H with CO, complex **4**, to observe the effect on the distortion of a π acceptor trans to H′. The a_1 orbitals closely resemble those of **5**. In addition the nonbonding xz and yz t_{2g} type mix with the x and y, respectively, in order to optimize the back-bonding interaction with the trans CO, **9**. Since this interaction always has a minimum at $\delta\theta > 0°$, it shifts the total energy minimum toward larger $\delta\theta$ and is thus responsible for the shift in the curve for **4** to larger values of $\delta\theta$ from those of **5** and **6** in Figure 2a. The larger back-donation to the axial CO suggests an increase in the M–CO bond order with increasing distortion. This is consistent with the generally shorter M–C bond length for axial carbonyls in these complexes.



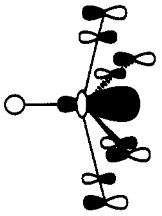
4′



5′



6′



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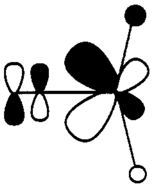
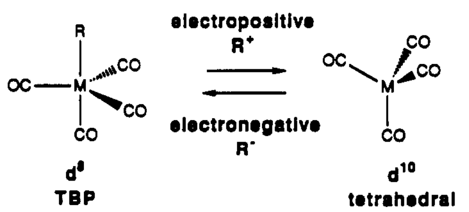


9

Thus we have shown that the electronegativity difference between H′ and the ligand trans to it is important and largely determines the direction of the distortion. The presence of π-acceptor ligands in equatorial positions enhances the distortion via increased participation of the equatorial ligands in the LUMO. A π acceptor in an axial position (trans to H′) enhances the distortion in order to optimize back-bonding from the d block.

Distortion from the Trigonal Bipyramid to the Tetrahedron: d^8 $HCo(CO)_4$. The distortion of a TBP toward a capped tetrahedron can be rationalized by using the same simple model we used for the octahedron, eq 3.



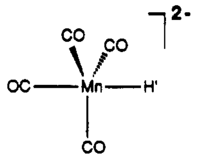
(3)

If we make R very electropositive in a d^8 species, $RM(CO)_4$, R can be considered as a cation weakly coordinated to a d^{10} $[M(CO)_4]^-$ fragment, which would be expected to have a tetrahedral geometry. An electronegative R is strongly coordinated and the complex assumes an undistorted TBP geometry predicted for a d^8 ML_5 species. This model is best illustrated by the Co system since structures exist for the entire range of the distortion from the TBP to tetrahedral $[Co(CO)_4]^-$.[26]

The electronic origin of the distortions in the TBP complexes is very similar to that described above for the octahedral complexes. Figure 2b shows the change in $\delta\theta$ as a function of the energy of the 1s orbital of H′ (H_{ii}) for $HCo(CO)_4$ (**4′**), $[HCo(CO)_3H']^-$ (**5′**), and $[HCo(H_{eq})_3H']^{4-}$ (**6′**). The magnitude of the distortion increases along the series **6′**, **5′**, and **4′** for the same value of H_{ii} for H′. In the same way as was described above for the octahedral system, we find that the distortion in **6′** is controlled by σ effects in the a_1 LUMO corresponding to **7c**. In **5′** this a_1 orbital interaction is amplified by the incorporation of the π effects of the CO_{eq}, similar to the effect described by **8**. In the case of **4′** these interactions are supplemented by an increase in back-bonding between the t_{2g} d block and the axial CO, similar to **9**.

The Octahedron versus the Trigonal Bipyramid. The data in Table I demonstrate that the distortion in the TBP cobalt system is always larger than the distortion in the octahedral manganese system. Figure 2 shows that we can reproduce this trend by calculation. The variation in the magnitude of the distortion can be traced both to the coordination geometries and to the difference in the electronegativity of the two metals.

In order to remove problems in comparing different coordination systems with different metal parameters, we carried out further calculations comparing distortions in octahedral d^6 $H'Mn(CO)_5$ (**4**) and TBP d^8 $[H'Mn(CO)_4]^{2-}$ (**10**). Using regular hydrogen parameters, **4** gives a smaller distortion than **10** ($\delta\theta$ = 2.9° and 4.1°, respectively),[55] which demonstrates that there must be an inherent reason for more distortion in a d^8 TBP over a d^6 octahedron. Walsh diagrams for the two systems were presented elsewhere[10] and we do not include them here. The sums of the energies of all the a_1 orbitals in **4** and **10** both decrease as the CO_{eq} groups move toward H. We find that the slope in **4** is larger than the slope in **10**, which suggests that on the basis of these orbitals alone we would expect exactly the reverse



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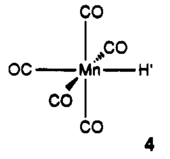

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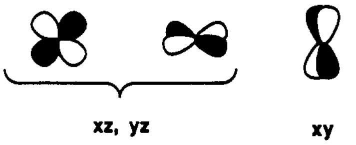

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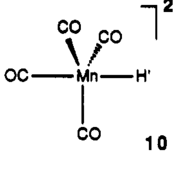

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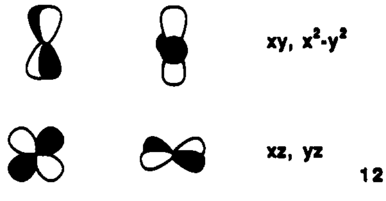

12

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[54] Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4308.

[55] At the energy minimum for TBP $HCo(CO)_4$ using regular hydrogen parameters, $\delta\theta$ = 4.3°.

trend—i.e., more distortion in 4 than in 10. This can be understood in terms of the number of equatorial ligands that distort, moving four ligands will clearly give rise to more stabilization to the a_1 than moving three.

The point at which the distortion goes through an optimum must therefore be determined by orbitals other than the a_1 and thus we examine the occupied d block. In 4 the occupied d block consists of the three nonbonding orbitals derived from the t_{2g} set of the octahedron. The two higher orbitals (xz, yz) are degenerate and stabilized by three π^*_{CO} orbitals each; the lower orbital (xy) is stabilized by four π^*_{CO} orbitals, 11. The d orbitals of the TBP are shown in 12. There are two sets of degenerate d orbitals in the TBP system, $x^2 - y^2/xy$ and xz/yz, of symmetry e′ and e″, respectively. Both e′ and e″ are stabilized by back-bonding to π^*_{CO}, but the higher set (e′) is destabilized by antibonding σ interactions with the CO_{eq} groups.

As the CO_{eq} groups are moved in 4, the xz/yz set shows a minimum in energy at $\delta\theta = 1.7^\circ$ due to increased back-bonding to the trans CO, as described above, 9. As the CO_{eq} groups are moved further than the minimum, the curve rises steeply in energy. This destabilization is due to a strong σ-antibonding interaction between the metal and CO_{eq} (together with loss of metal to CO_{eq} back-bonding). The xy orbital is destabilized as the CO_{eq} groups are moved away from $\delta\theta = 0^\circ$, also by loss of metal of CO_{eq} back-bonding.

In the case of 10, $x^2 - y^2/xy$ will be stabilized on distortion due to a reduction in the σ-antibonding interaction with CO_{eq}. In the same way as 4, the xz/yz set will be stabilized initially by increased interaction with the trans CO, similar to 9, and then destabilized by the strong metal CO_{eq} σ-antibonding interaction and the loss of metal to CO_{eq} back-bonding. However, the D_{3h} symmetry is lost upon distortion and, having the same symmetry, the d orbitals are now allowed to mix in such a way as to avoid destabilization. Thus the lower set (formally xz/yz) is maintained at a constant energy by mixing with the higher set (formally $x^2 - y^2/xy$). This mixing causes the higher set to have a minimum at $\delta\theta = 4.1^\circ$ and to be a shallower curve than the equivalent xz/yz in 4. This allows the distortion in 10 to proceed further than that in 4. These features are clearly visible in the published Walsh diagrams.[10]

Thus we see how the coordination geometry influences the extent of the distortion. How will the metal electronegativity affect it? Having already demonstrated that the more electropositive R the greater the distortion, it follows that for the same R and for different metals (in the same coordination mode) the distortion should also depend on the electronegativity of the metal itself. Using a more electronegative metal (i.e., a late transition metal or one with a lower lying LUMO) will have the same electronic effect as using a more electropositive R group and thus favor the distortion. This is the reason why the curves in Figure 2b are steeper than their equivalents in Figure 2a, because the Co systems have lower lying LUMO's than their Mn counterparts. This is borne out by the observations that $HCo(CO)_4$[29] is more distorted than $[HFe(CO)_4]^-$[49] and that $HMn(CO)_5$[12] is more distorted than $[HCr(CO)_5]^-$.[48] The experimental and calculated $\delta\theta$ for these four species are given in Table 2.

M–R Bond Multiplicity. Some attention has been given to the role of potential double-bonding M–R character in the distortion.[9] To examine the effect of double-bonding character we carried out a distortion analysis on a metal carbene complex. We carried out calculations using $[Mn(CO)_5(CH_2)]^-$ (Mn=C = 2.02 Å, C—H = 0.95 Å) and find a minimum in energy at $\delta\theta = 1.0^\circ$, which is in agreement with the virtual absence of distortion in group 6 carbenes.[56a] The unoccupied carbene p orbital interacts with the occupied d block in a similar way to π^*_{CO} and thus disfavors (or reduces) the extent of the distortion. In this way we see how a degree of double-bonding character may disfavor the distortion. In exactly the same way, the partial double bonding in the metal–carbonyl bond will disfavor a distortion toward the CO. However, a small distortion might be observed as in $M(CO)_4(C_2H_2)$ (M = Fe, Ru, Os).[56b]

(c) The Carbonyl Insertion Reaction. The migratory aptitudes of R groups in carbonyl insertion reactions vary as a function of at least two factors. First, the thermodynamics of the system can influence whether insertion takes place at all and, if so, its rate. If the R–M bond is strong, then the insertion will be disfavored. The (RCO)–M bond strength in the product varies relatively little for different R and so the trends of ΔH for eq 1 are dominated by differences in Mn–R bond strengths. In addition, as Collman et al.[57] note, kinetic factors are also involved. Although the benzyl–Mn bond is much weaker than the corresponding methyl bond, the former is much less reactive toward insertion. The acetyl–Mn bond is similar in bond strength to the methyl but no insertion into the M–acetyl bond is observed. CF_3 and Ph are estimated to have equal R–Mn bond strengths, yet the former fails to insert. A comparative study of insertion rates showed that insertion was inhibited by substitution of electron-withdrawing groups on the methyl carbon of $MeMn(CO)_5$.[58] The series $(p\text{-}XC_6H_4CH_2)Mn(CO)_5$ has also been studied and the rate of insertion found to increase from $X = NO_2$ to CH_3 ($NO_2 < Cl < H < CH_3$).[59]

Berke and Hoffmann[8a] analyzed the origin of the variation in activation energy for carbonyl insertion in $MeMn(CO)_5$ with the electronegativity of R and proposed a thermodynamic explanation. Marynick et al. account for the same effect in terms of the more basic R groups interacting more strongly with π^*_{CO} orbitals.[8h] Hoffmann suggested that the activation barrier is a result of the destabilizing interaction between the lone pair of CO_{eq} and the σ hybrid of R^- as they are brought together.[8a] We now propose that the electropositive or -negative character of R should affect the kinetic barrier. The more electropositive R carries less electron density into the vicinity of the M–CO bond and leads to a lowering of the barrier as a result of a decreased four-electron repulsion between the M–R and M–CO σ bonds.

Are Bürgi–Dunitz ideas relevant to this discussion? CO moves very little in the observed ground-state structures. It might be argued that such a small distortion could not significantly lower the barrier. To reach the transition-state structure, however, CO only needs to move by about 10°.[8b] The observed structures show a $\delta\theta$ of 2–7° for each CO_{eq}, which is substantial compared to the required 10°. In addition, thermal motion of the molecule could easily lead to most of the distortion being concentrated in one M–CO motion, allowing attainment of the transition state. Bürgi–Dunitz ideas do therefore seem to apply to this system.

At this point it is clear that the distortion and activation energy are determined by the same effect: the more

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(56) (a) See, for example: Casey, C. P.; Burkhardt, T. J.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 2127. (b) Ball, R. G.; Burke, M. R.; Takats, J. *Organometallics* **1987**, *6*, 1918.

(57) Reference 7, p 367.

(58) Slack, D. A.; Egglestone, D. L.; Baird, M. C. *J. Organomet. Chem.* **1978**, *146*, 71.

(59) Kuhlmann, E. J.; Alexander, J. J. *Coord. Chem. Rev.* **1980**, *33*, 195.

electropositive R the greater the distortion and the lower the activation energy. Increasing the distortion should facilitate the insertion. One example of this is the replacement of a σ donor trans to R by a π acceptor, which favors the distortion, as we have shown above, and should favor insertion. This observation has been confirmed experimentally for an iridium system by Kubota et al.[60]

Does this mean that the distortion always helps the reaction to proceed? Such a conclusion should be treated with caution, considering the importance of thermodynamic factors[61] that might inhibit the reaction as has been shown both experimentally[7] and theoretically[8e,h] for R = H. We believe that, everything else being equal, the presence of a distortion is an indicator of a more facile insertion reaction. Facile insertion has indeed been observed recently in complexes presenting noticeable distortion.[43,45]

(d) Distortions in Dinuclear Species. There is considerable potential for carbonyl distortions in dinuclear species or clusters.[62] The structure of $M_2(CO)_8$ species provides one example.[63] The series $Co_2(CO)_8$, $[CoFe(CO)_8]^-$, and $[Fe_2(CO)_8]^{2-}$ has been crystallographically characterized[63] and found to have 2, 1, or 0 bridging carbonyls, respectively. For the unbridged $[Fe_2(CO)_8]^{2-}$ $\delta\theta_{obs} = 6.7°$, and in the singly bridged $[CoFe(CO)_8]^-$ the bridging carbonyl is closer to the Co than the Fe. These differences in apparently isoelectronic structures were rationalized in terms of a variation of the metal–metal distance.[63] Our distortion analysis accounts for the observation in a different way if we consider that a bridging carbonyl represents an arrested insertion into the metal–metal bond. The "insertion" is easier for the more electronegative cobalt than for the iron analogues.

(e) Abstraction versus Substitution in $RCo(CO)_4$. An interesting feature of the chemistry of the $RCo(CO)_4$ system is its behavior with nucleophiles (or Lewis bases). In the case of $HCo(CO)_4$ the proton is lost even to relatively mild bases and the tetrahedral $[Co(CO)_4]^-$ ion forms. The distortion puts $HCo(CO)_4$ almost exactly halfway between a TBP and a tetrahedral structure and may facilitate loss of a proton.

Phosphines may react with $RCo(CO)_4$ in one of two ways. First, substitution chemistry is found indicating that attack occurs at the metal, and, second, nucleophilic abstraction is observed, though less frequently. Literature data show that substitution is observed when the R group is electronegative ($SiCl_3$) (eq 4) but abstraction occurs when R is electropositive ($SiMe_3$, SiH_3) (eq 5).[26] It is surprising

$$RCo(CO)_4 + PR_3 = RCo(CO)_3(PR_3) + CO \qquad (R = SiCl_3) \quad (4)$$

$$RCo(CO)_4 + PR_3 = [Co(CO)_4]^- + R\text{–}PR_3 \qquad (R = SiMe_3, SiH_3) \quad (5)$$

that attack at the Si is disfavored when the Si carries more electron-withdrawing groups. Electron-withdrawing groups would normally be expected to enhance the electrophilicity of Si. The experimental findings therefore show exactly the opposite of what would intuitively be expected.

The explanation we favor comes naturally from the distortion analysis. The abstraction of R^+ leaves a $[Co(CO)_4]^-$ unit, which will be favored when an electropositive R group has caused a distortion of the $RCo(CO)_4$ in the ground state. As we saw above, the distortion is larger for Co than Mn. It is therefore not surprising that the tendency for departure of R as R^+, as manifested by the acidity of the R = H species and the tendency of the R = $SiMe_3$ species to undergo nucleophilic abstraction by PR_3, increases going from Mn to Co. This is contrary to the expectations of a conventional explanation based on the relative electron-withdrawing power of the $Co(CO)_4$ versus the $Mn(CO)_5$ fragment. The Mn complex, having the larger number of CO groups and the higher electronegativity, should, one might think, be more acidic and have a higher tendency to give abstraction chemistry.

Conclusion

We show how theoretical and structural studies can be combined to give useful information about reactions pathways in organometallic chemistry. Distortion analysis in $RM(CO)_n$ (n = 4, 5) show that the more electropositive the R group, the more the CO_{eq} groups are found to depart from the positions they would occupy in an ideal octahedron or TBP. The results can be understood in terms of a simple model. For $RMn(CO)_5$, more electropositive R groups cause the $Mn(CO)_5$ fragment to depart from the regular octahedral structure and approach the distorted TBP or SP geometry expected for a d^8 configuration ($R^+ + Mn(CO)_5^-$). For $RCo(CO)_4$, the more electropositive the R group, the more the $Co(CO)_4$ group departs from the regular TBP and approaches the tetrahedral structure expected for a d^{10} configuration ($R^+ + Co(CO)_4^-$). EHT calculations validate and amplify this simple model. The distortion results from an electron transfer from the R group into the LUMO of the remaining metal fragment, which favors a distorted structure with CO_{eq} bent toward R. The d block serves to limit the extent of the distortion. The distortions we find are thus a response to the electronic nature of the complex. We show that the same electronic characteristics facilitate the CO insertion by lowering the activation energy (diminution of the four-electron repulsion between R^- and CO) and by moving the reactant toward the product structure on the reaction coordinate. Distortion analysis also allows us to understand the otherwise counterintuitive way in which nucleophiles sometimes substitute and sometimes abstract R from $RCo(CO)_4$.

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