On the Conformation and Structure of Organometal Complexes in the Solid State: Two Studies Relevant to Chemical Synthesis

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Dedicated to Professor Jack Dunitz

Conformational preferences of two classes of organometal complexes have been surveyed by inspecting the Cambridge Structural Database (CSD). Lewis acid carbonyl complexes demonstrate a variety of coordination geometries, depending on the electronic and steric requirements of the carbonyl ligands and the nature of the Lewis acid. Similarly, the solid-state conformation of various π-bonding ligands in metal acyl, metal nitrosyl, metal acetylene, and metal imido complexes is revealed. These insights have stimulated the development of a conformational model that is based on considerations of π-bond hybridization and frontier molecular orbital theory. The analyses are relevant to the mechanism and transition structures of many synthetically important transformations. A deeper understanding of the conformational properties of organometal complexes, based on accurate structural information, will likely expedite the design and improvement of metal-mediated processes.

1. Introduction

Soon after the advent of X-ray crystallography, it became clear that crystal structures can uncover more than just a simple picture of the covalent connectivity of molecular entities.[1] The realization of the potential of X-ray crystallography in providing information regarding two central questions in chemistry—namely, reactivity and the three-dimensional conformation of molecules—rapidly led to the foundation of the powerful field of structural chemistry.[2] In organic chemistry, perceptions of bonding and reactivity have benefited from this structural approach enormously. Although many of the important questions remain unanswered, many of the ground-state physicochemical properties of molecules can be predicted fairly reliably by the structural theory of organic chemistry. At first, it seemed implausible that static, crystalline species could reveal any information regarding the dynamics of transition states. However, the pioneering work of *Dunitz, Bürgi*, and coworkers in the early 1970s showed that, in certain instances, even these parameters can be derived from the inspection of a family of crystal structures.[3] Hence, this approach came to be known as the "structure–reactivity correlation" method.[4]

Today, largely due to the efforts of the Cambridge Crystallographic Data Centre[5] and partly due to the ready availability of powerful and efficient computing machines, thorough searches of more than 70 000 crystal structures of organic, inorganic, and organometallic compounds can be achieved with reasonable ease and speed. Attracted by the wealth and accuracy of the information provided by crystal structure analyses, an ever-growing number of organic chemists now utilize this powerful tool to infer mechanistic and conformational hypotheses based on structural data.[6]

This approach has been particularly fruitful in the study of weak interactions such as hydrogen bonding[7] and donor–acceptor interactions of Lewis acid–Lewis base pairs.[8]

In this review we shall describe how analyses of crystal structures led to the formulation of principles and hypotheses regarding the conformational preferences of two classes of organometal complexes. First, we report on recent insights into carbonyl–Lewis acid complexation. Next, the influence of π bonding on the conformation of a variety of ligands attached to transition metals will be addressed. In both instances the original search of the Cambridge Structural Database (CSD) was prompted by a simple question regarding the conformation of a complex or an intuitive hunch about the origins of an unusual observation. Unfortunately, even after careful inspection of numerous crystal structures, the answers to the original questions were not altogether transparent. However, during this exercise many important lessons were learned and some of the missing links in the context of the more general problem were pinpointed. It is hoped that these observations will not only lead to a better understanding of the conformational properties of organometal complexes, but also guide future efforts in related areas of research.

2. Carbonyl–Lewis Acid Complexation

A Lewis basic carbonyl group can be activated through coordination to a metal-centered Lewis acid, with profound reactivity and stereochemical consequences. In the context of asymmetric synthesis, many of the Lewis acid–mediated reactions are known to proceed with improved stereoselectivities as compared to their non-catalyzed counterparts, and, most recently, a variety of chiral Lewis acids have been used as remarkably efficient catalysts for carbonyl addition processes.[9] Although the origins of many of the effects brought about by Lewis acids are still poorly understood, it is clear that the conformational preferences of the Lewis acid carbonyl complex are ultimately responsible for determining the stereochemical course of Lewis acid–mediated reactions. In

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Sections 2.1–2.3, some of the crystallographic studies on the complexes of Lewis acids with organic carbonyl ligands will be discussed. The relevance of the crystallographic data to the general conformational biases of such complexes will be the focus of this discussion.

2.1. Conformational Issues

Factors that may influence the reactivity and conformation of Lewis acid carbonyl complexes can be classified broadly into three categories. The primary question in analyzing a Lewis acid carbonyl complex concerns the mode of coordination. Both η^1 (σ) bonding and η^2 (π) bonding of Lewis acids to carbonyl ligands are observed (Fig. 1), and, as
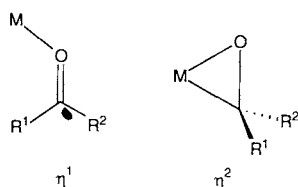
Fig. 1. σ (left) vs. π (right) bonding in Lewis acid carbonyl complexes.

will be seen, crystallographic studies seem to provide fairly straightforward rules for the prediction of each mode of coordination.

Second, the exact location of the Lewis acid with respect to its carbonyl ligand is of interest. Specifically, knowledge of the range and limits of several parameters, such as the Lewis acid–oxygen distance r and the angles θ and ϕ in Figure 2, is an obvious requirement for the prediction of the structure of these complexes.
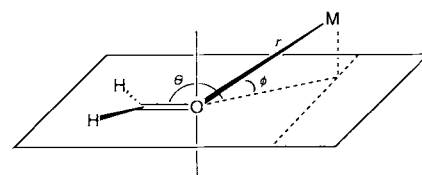

Fig. 2. Definition of the parameters r, θ and ϕ.

Third, the effect of Lewis acid coordination on the inherent conformational preferences adjacent to the carbonyl group should be considered. In particular, how is the s-cis–s-trans equilibrium of α,β-unsaturated carbonyls or the energy

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profile for the rotation about the CO–C$_\alpha$ bond of nonconjugated carbonyls affected by Lewis acid complexation (Fig. 3)?
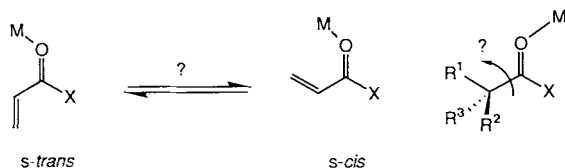

s-*trans*   s-*cis*

Fig. 3. How is rotation about the CO–C$_\alpha$ bond of carbonyls influenced by Lewis acid coordination?

2.2. Crystal Structures of Lewis Acid Carbonyl Complexes

2.2.1. Cationic Alkali-Metal Lewis Acids

Some of the earliest inquiries into such questions were performed by *Dunitz, Seebach,* and co-workers. In their report of the crystal structure of the LiBr–acetone complex, these researchers discussed the conformational biases of alkali–metal carbonyl complexes.[10] In particular, the LiBr–acetone complex assumes a dimeric form in the solid state, in which each lithium ion is coordinated by two molecules of acetone through the carbonyl lone-pair electrons with a bent, planar geometry in a tetrahedral environment (Fig. 4). The
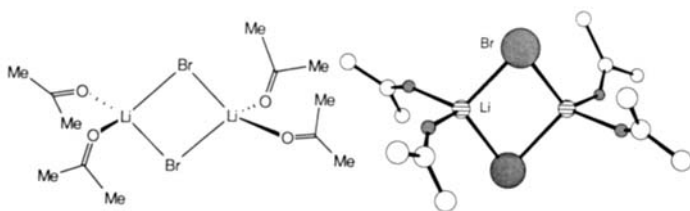

Fig. 4. Crystal structure of LiBr–acetone complex [10].

Li–O bond length is 2.0 Å, the Li–O–C angle 145°. In order to determine the generality of these observations in other alkali-metal carbonyl complexes, the researchers also conducted a general search of the Cambridge Structural Database. Of the nine crystal structures that were analyzed in this study, six contained Li$^\oplus$, two Na$^\oplus$, and one K$^\oplus$ as the Lewis acid bound to the carbonyl ligands. The coordination angle θ for Li$^\oplus$ (cf. Fig. 2) was consistently found to be less than 180° (120–156.3°), but large distortions from planarity ($\phi \neq 0°$) seemed to occur randomly. Furthermore, the Li–O bond distance showed no linear dependence on the Li–O–C–X dihedral angle.

The crystal structures of Na$^\oplus$ complexes, however, showed that linear and bent geometries are equally accessible and bending out of the plane of the carbonyl was once again observed (Fig. 5).[11]

The researchers concluded that the potential energy surface for carbonyl coordination to alkali metals is likely to be fairly flat with respect to changes in the M–O–C angle and the M–O–C–X dihedral angle.
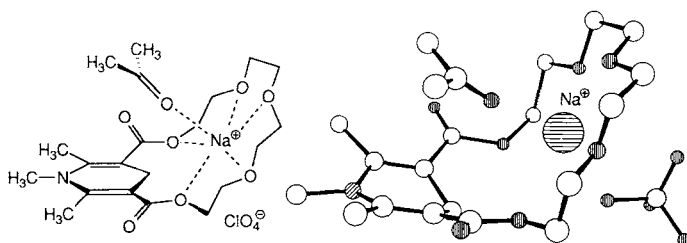

Fig. 5. Linear complexation of a Na$^\oplus$–acetone complex [11].

A more recent search of the CSD for crystal structures of alkali-metal carbonyl complexes also confirmed these results.[12] The average Li–O bond length and the Li–O–C bond angle were found to be 1.99 ± 0.07 Å and 139 ± 3°, respectively. Of the 23 examples found, 9 exhibited coordination by more than 10° out of the plane of the carbonyl group.

Thus, cationic alkali-metal Lewis acids do not exhibit any strong directional preferences upon coordination to carbonyls. In particular, bending toward the π cloud of the carbonyl ($\phi \neq 0$) with no significant lengthening of the M–O bond is commonly observed. Coordination seems to occur from the direction that best satisfies the cation's electron demand and minimizes steric interactions. These, in turn, depend on the coordination number of the cation, the relative size and electronic properties of the ligands, and, in the solid state, on crystal packing forces.

Two remarkable examples of the diversity of Li$^\oplus$–carbonyl coordination can be found in the crystal structures of Li$^\oplus$ bound to the cyclic decapeptides antamanide and perhydroantamanide, reported by *Karle.*[13, 14] In the Li$^\oplus$–antamanide complex (Fig. 6), for instance, lithium was found to
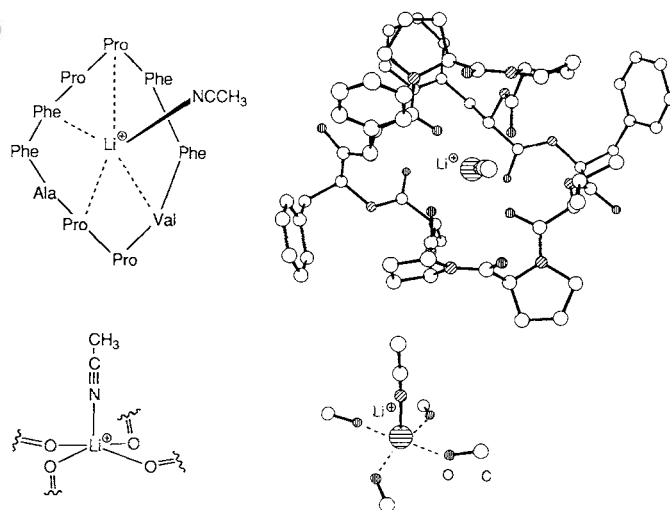

Fig. 6. Crystal structure of Li$^\oplus$–antamanide complex [13].

be pentacoordinated to four carbonyl oxygens and the nitrogen atom of an acetonitrile solvent molecule in a pseudo-square-pyramidal arrangement. In this structure, the Li–O bond lengths and Li–O–C bond angles are similar to the values discussed previously and are consistent with the principles of the foregoing discussion.

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It is interesting to note that ab initio, gas-phase calculations on the Li$^{\oplus}$-carbonyl complexes predict a strong preference for the linear, planar geometry ($\theta = \phi = 0°$), wherein the main source of metal-carbonyl interaction is electrostatic ion-dipole attraction.[15, 16] This discrepancy with the experimental observations may be an artifact of either the assumption of in vacuo conditions or the restriction of 1:1 stoichiometry. Thus, bent geometries may have been predicted had solvent molecules or additional carbonyl ligands been included in these calculations.

2.2.2. Main-Group and Early-Transition-Metal Lewis Acids

Relative to alkali-metal cations, neutral Lewis acids seem to perform much more consistently. The crystal structure of the BF$_3$-benzaldehyde complex may serve as a representative example (Fig. 7).[17] Here the Lewis acid is placed 1.59 Å
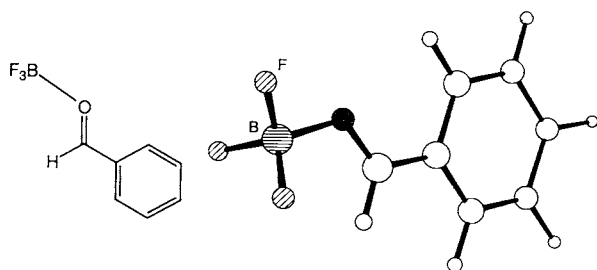
Fig. 7. Crystal structure of BF$_3$-benzaldehyde complex [17].

from the carbonyl oxygen, along the direction of the oxygen lone pair and *anti* to the larger phenyl substituent.[18]

Although crystal structures of other bimolecular complexes of carbonyls with boronic Lewis acids have not been reported, a number of intramolecular chelates have been detected in the solid state.[19–21] In all these cases boron is found to lie in the direction of the carbonyl lone pair with no more than an 11° distortion (ϕ) away from the best plane of the carbonyl group. The average B–O bond length (r) is 1.581 ± 0.019 Å and the B–O–C angle lies between 112 and 119°.

A search of the CSD files for the Al–O = C substructure revealed thirty such interactions with Lewis acidic aluminum atoms from 23 crystal structures.[13] Mean values for the Al–O distances (r) and Al–O–C bond angles were found to be 1.88 ± 0.09 Å and 136 ± 4°, respectively, and aluminum was found to lie within 18° (ϕ) of the carbonyl plane.

The crystal structure of the AlCl$_3$-tetramethylurea (TMU) complex shows a 1:1 adduct (Fig. 8) in which alu-
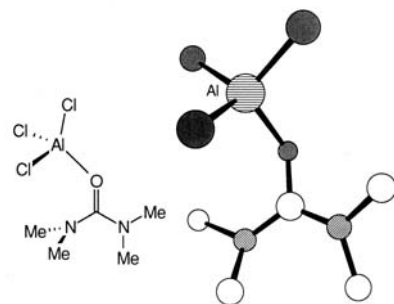

Fig. 8. Crystal structure of AlCl$_3$-TMU complex [22].

minum binds to the carbonyl lone-pair electrons at an angle of 132.5° and at a distance of 1.78 Å.[22] The C–O bond length (1.239 Å) is approximately 0.06 Å longer than that of unbound TMU and 0.03 Å longer than in the corresponding Me$_2$SnCl$_2$-TMU complex. The Lewis acid is slightly out of the plane of the carbonyl, although the dimethylamino group *syn* to aluminum is completely twisted out of conjugation to avoid steric interactions.

Based on the average values revealed in the CSD searches (see above), it may be reasonable to propose that the structure in Figure 8 reflects the "idealized" or low-energy mode of coordination to carbonyls for aluminum-centered Lewis acids. It would be interesting to see how distortions away from such an arrangement may come about. Imposition of steric congestion through bulky substituents is one way to address this question. The crystal structure of the complex formed between (2,6-di-*tert*-butyl-4-methyl)phenoxydiethyl-aluminum and methyl *p*-toluate was recently reported by *Ittel* et al. (Fig. 9).[23] In this structure a pseudo-tetrahedrally
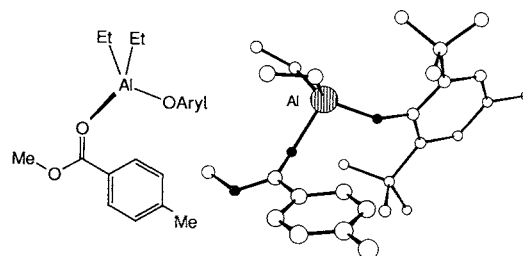

Fig. 9. Crystal structure of Et$_2$Al(OAryl)-methyl *p*-toluate complex [23]. Aryl = 2,6-tBu$_2$-4-Me-C$_6$H$_2$.

coordinated aluminum is positioned 1.89 Å from the carbonyl ligand. The Al–O–C angle of 145.6° is on the more linear end of the Al–O–C angle spectrum, but, more interestingly, the Al–O–C–C torsion angle (49.9°) shows considerable bending toward the π plane. Clearly, this distortion from the idealized structure is a result of the unusually bulky di-*tert*-butylphenoxide ligand on the Lewis acid, coupled with the fact that in Z aromatic esters both sp^2 lone pairs are fairly hindered. Notice that other available mechanisms for relief of steric strain were not employed. Either twisting of the phenyl substituent or alteration of an idealized Z-ester conformation could have accommodated a more planar Lewis acid complex, but neither occurs to any considerable extent (τ(O-C-C-C) = 12.1°, τ(O-C-O-C) = 4.1°). Furthermore, a linear Lewis acid complex would also avoid steric interactions with the carbonyl substituents, but this mode of coordination seems to be excluded as well. These results suggest that the energetic barrier for out-of-plane bending of the Lewis acid is less steep and probably lower than the barrier for either E/Z ester isomerization, rotation about the phenyl-carbonyl C–C bond, or *in-plane distortion to a linear structure*. The latter proposition is in sharp contrast to theoretical predictions.[24]

Ittel's crystal structure (Fig. 9) also supports a model proposed by *H. Yamamoto* et al. for the complexation of bulky aluminum Lewis acids to carbonyls.[25] These researchers have attributed the preponderance of axial attack of nucleophiles on cyclohexanones such as **1** (formation of **3**), in the

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presence of the Lewis acid MAD, to out-of-plane complexation (2), as depicted in Figure 10.
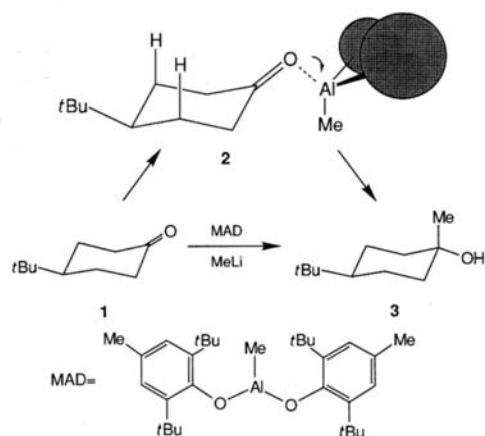

Fig. 10. Out-of-plane complexation of MAD to carbonyls leads to axial attack of nucleophiles on cyclohexanones such as 1 [25].

When a Lewis acid possesses two empty coordination sites, another degree of complexity is added to the structural issues discussed above. Titanium(IV) Lewis acids, for example, show a strong preference for a six-coordinate, octahedral arrangement. Thus, the acid:carbonyl stoichiometry for these complexes is often 1:2 or, when only a single equivalent of the carbonyl base is present, dimeric structures with bridging ligands are observed. The crystalline 1:1 adduct of $TiCl_4$ and ethyl acetate, for example, contains dimeric units of two octahedrally coordinated titaniums with bridging chlorine atoms (Fig. 11).[26] The 2.03-Å-long Ti–O bond is almost
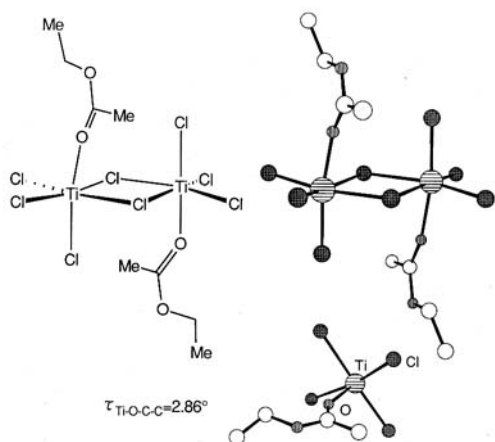
Fig. 11. Crystal structure of $TiCl_4$–ethyl acetate complex [26]. Bottom right: Side view of in-plane titanium coordination.

coplanar with the carbonyl group (τ(Ti-O-C-C) = 2.86°) and the Ti–O–C angle is 152°.

These values agree well with the average Ti–O bond lengths and Ti–O–C bond angles derived from searches of the CSD files (mean Ti–O = 2.14 ± 0.07 Å), though the Ti–O–C angle is on the wider side of the observed range (mean Ti–O-C = 125 ± 12°).[12] The Z conformation of the ester is retained (τ(O-C-O-C) = 2.6°) due to syn coordination of the Lewis acid to the methyl substituent.

In line with the behavior of aluminum-centered Lewis acids, deviations from the idealized conformation are observed when steric congestion is imposed on the structure. This point is illustrated in the crystal structure of the $TiCl_4$–ethyl anisate complex (Fig. 12).[27] Although at first glance
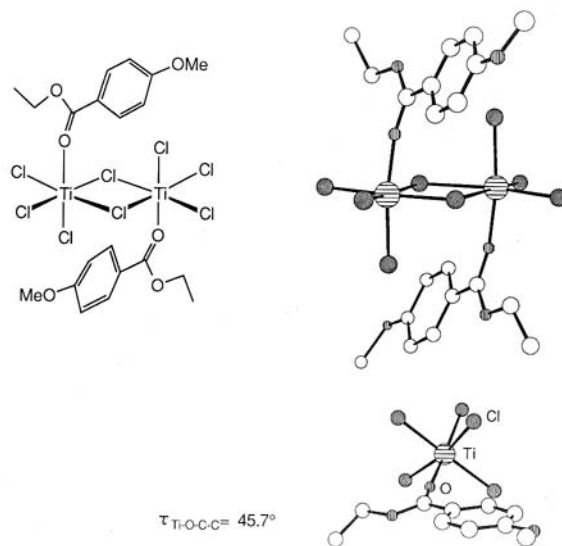

Fig. 12. Crystal structure of $TiCl_4$-ethyl anisate complex [27]. Bottom right: Side view of out-of-plane titanium coordination.

the main features of this complex (dimeric complex, octahedral titanium, etc.) are very similar to those of the $TiCl_4$–ethyl acetate structure, out-of-plane bonding to the carbonyl clearly distinguishes the two structures. The Ti–O–C–C dihedral angle is 45.7° and the Ti–O–C angle has now opened up to 168.7°. The Z conformation of the ester is still intact (τ(O-C-O-C) = 1.4°), and the Lewis acid is bound more or less syn to the phenyl substituent, which, in turn, is twisted out of conjugation and away from the Lewis acid by 13.0°. These structural features are very similar to those of the bulky aluminum Lewis acid complex (Fig. 9) and one may expect them to be quite general in similar systems. Interestingly, distortions from the idealized structures are more prominent for the titanium complex, which may suggest that, in the dimeric form, $TiCl_4$ is in fact even larger than the aryloxyaluminum reagent or that π distortion occurs more readily for Ti than for Al.

Extreme out-of-plane bonding is observed in the crystalline complex of $TiCl_4$ and acryloylmethyl lactate (Fig. 13).[28] In this structure Ti is bound by two ester car-
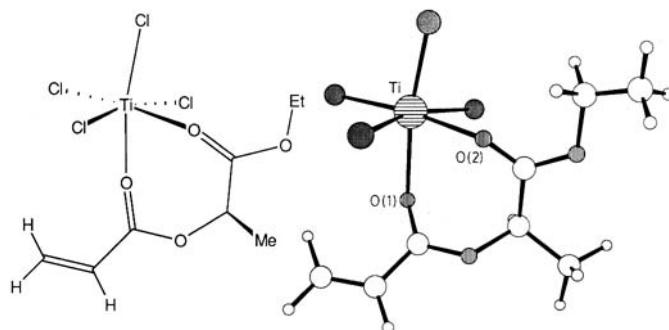

Fig. 13. Crystal structure of $TiCl_4$–acryloylmethyl lactate complex [28].

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bonyls in a seven-membered ring chelate. Both carbonyls are bound out-of-plane with $\tau(\text{Ti-O(1)-C-C}) = 63.6°$ and $\tau(\text{Ti-O(2)-C-C}) = -132.2°$. Both esters, however, remain very close to planarity ($\tau_1 = 8.8°$, $\tau_2 = 4.1°$) and in the preferred Z conformation. Furthermore, due to the presence of a chelate ring, the Lewis acid is *anti* to the acrylate double bond and the enoate adopts an s-*cis* geometry. It is difficult to rationalize out-of-plane bonding in this case since direct steric interactions appear to be unimportant. Moreover, out-of-plane bonding cannot be the result of chelation, since crystal structures of TiCl_4 chelated by acetic anhydride (Fig. 14, left)[29] or 3,3-dimethyl-2,4-pentanedione[30] show no evidence for π bonding. Even the seven-membered ring
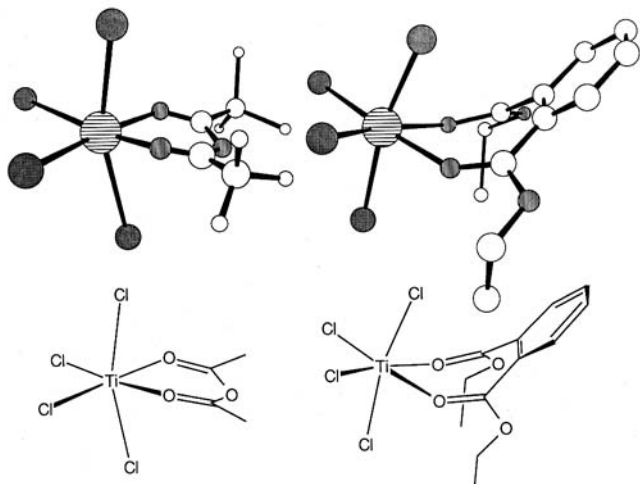
Fig. 14. Crystal structure of two TiCl_4 chelates [29, 31].

diester chelate of TiCl_4 with diethyl phthalate (Fig. 14, right) has the Lewis acid coplanar with the carbonyl ligands.[31] Another noticeable feature of the chelated structures is that they are all monomeric, probably due to the ability of the bidentate ligands to satisfy titanium's desire for hexacoordination and octahedral geometry.

The crystal structures of titanocene cations containing coordinated dimethylformamide (DMF) also support the idea of loose angle dependence of carbonyl coordination to titanium Lewis acids. For example, the $[\text{Cp}_2^*\text{TiCl}]^\oplus$–DMF complex displays a near-linear Ti–O–C angle of 167.0° and a Ti–O–C–N dihedral angle of $-140.2°$ (Fig. 15).[32] Similar semilinear η^1 bonding is also observed for the $[\text{Cp}_2^*\text{Ti}]^{2\oplus}$–$(\text{DMF})_2$ complex.[32] In this structure the two Ti–O–C an-
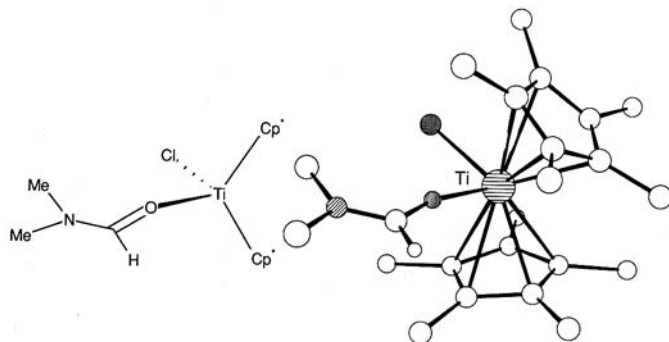

Fig. 15. Crystal structure of [Cp₂*TiCl]⊖–DMF complex [32].

gles are 148.1° and 158.2° and the respective dihedral angles 163.6° and 174.2°.

Zirconocene complexes with ketone and aldehyde ligands show yet another interesting variety of coordination chemistry. In the solid state, carbonyl-bound zirconocenes are often found η^2-coordinated and in dimeric units. The structure of the zirconocene–benzophenone complex is illustrative (Fig. 16).[33] In this structure the observed Zr–O–C geome-
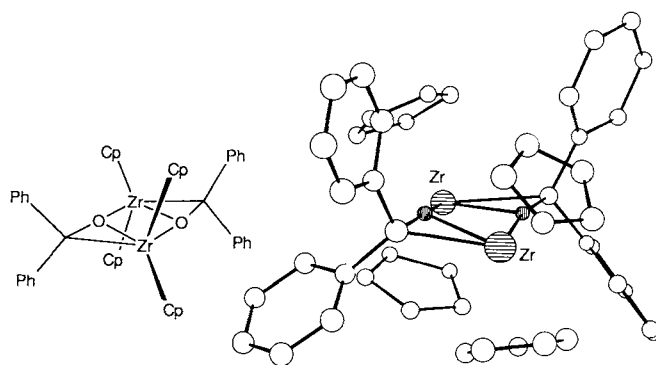

Fig. 16. Crystal structure of the Cp₂Zr–benzophenone dimer [33].

try, the benzophenone C–O bond lengths (1.425 and 1.419 Å), and the Zr–C distances (2.346 and 2.35 Å) indicate a π-bonded metallaoxirane conformation. The fundamentally different modes of coordination for the related zirconocene and titanocene structures are doubtless a result of the electronic requirements of the Lewis acid. Thus, η^2 bonding seems to be the preferred mode of coordination for the more electron-rich zirconium complexes, while η^1 complexation is observed with the more highly oxidized titanocene cations (also see Section 2.2.3).

NMR spectroscopic studies indicate that in solution tin-derived Lewis acids, like titanium, prefer to form 1:2 acid:carbonyl or 1:1 chelated adducts.[34] Consistent with these findings, the crystal structure of SnCl_4–4-*tert*-butylbenzaldehyde shows a 1:2 stoichiometry with two nonequivalent aromatic aldehydes *cis* to one another around the octahedrally coordinated tin atom (Fig. 17).[34]
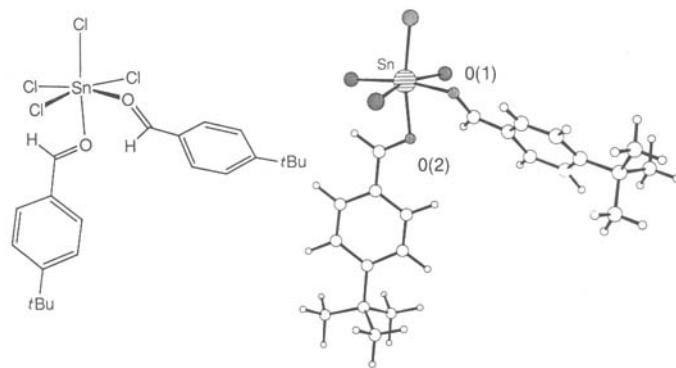

Fig. 17. Crystal structure of the SnCl₄–4-*tert*-butylbenzaldehyde complex [34].

Similar to the BF_3–benzaldehyde complex (Fig. 7), tin lies within the carbonyl plane with respect to both aldehydes ($\tau_1 = 2°$, $\tau_2 = 4°$), in the direction of sp²-hybridized lone

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pairs (Sn-O(1)-C = 128°, Sn-O(2)-C = 126.2°) and *anti* to the aromatic ring.

These measurements and the Sn–O bond lengths (2.23 Å) are close to the average values of Sn–carbonyl bond angles and bond lengths found in the CSD files (Sn-O = 2.3 ± 0.1 Å; Sn-O-C = 127 ± 10°).[12] However, the 1:2 stoichiometry and the *cis* relationship of the carbonyl ligands are not universal. Only slight alterations in the nature of the Lewis acid or its ligands are necessary to alter this arrangement. For example, an X-ray analysis of the Ph_2SnCl_2–*p*-dimethylaminobenzaldehyde complex shows a monomeric 1:1 complex with a trigonal-bipyramidally pentacoordinated tin atom (Fig. 18).[35] Although neither the Sn–O bond
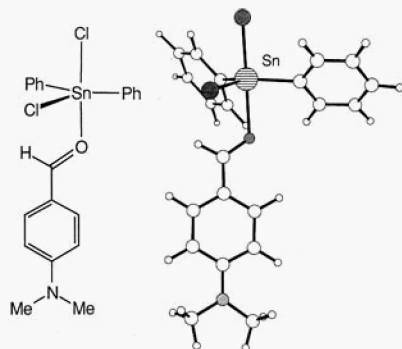
Fig. 18. Crystal structure of Ph_2SnCl_2-*p*-NMe_2-C_6H_4-CHO complex [35]

length (2.3 Å), nor the bond angles (Sn-O-C = 121°, τ(Sn-O-C-C) = 4°), nor the *anti* geometry of coordination have changed significantly, compared to the $SnCl_4$ complex (Fig. 17), the environment about the Sn atom is clearly different. It is likely that these changes are caused by the substitution of chlorines for aryl groups on the Lewis acid. Thus, crystal structures of Ph_3SnCl–TMU,[36] Me_2SnCl_2–TMU,[37] Me_3SnCl–diacetonetriphenylphosphorane,[38] and Me_2SnCl_2–salicaldehyde[39] all feature pentacoordinated, trigonal-bipyramidal 1:1 adducts, while $SnX_4 \cdot 2\,L$ (X = Cl, Br, I; L = urea or thiourea) complexes contain *cis*-octahedrally coordinated tin centers.[40] The *cis* and *trans* stereochemistry of the octahedral complexes seems to depend on the size and the basicity of the base, as well as on the nature of the Lewis acid. Me_2SnCl_2–DMU[37] and $SnCl_4$–ethyl cinnamate[41] are both *trans*-octahedral 1:2 complexes. The latter complex is particularly relevant to the discussion of the conformational preferences of α,β-unsaturated carbonyl complexes (Fig. 19). Here the ligand adopts a *Z*-s-*trans* conformation with tin coordinated *syn* to the double bond. The Sn–O–C–C dihedral angle of 21° indicates some out-of-plane bonding although not as much as in the titanium complexes.

Crystal structures of chelated tin Lewis acids have also been obtained. Recently, X-ray analysis of two five-membered chelates of $SnCl_4$ were reported by *Reetz* et al.[42] $SnCl_4$ complexes of 2-benzyloxy-3-pentanone and methoxyacetophenone are both 1:1 monomeric chelates with distorted octahedral geometry (Fig. 20). In the former complex (Fig. 20, left), tin is apparently coplanar with the carbonyl plane (10° puckering of the stannacycle) at a distance of
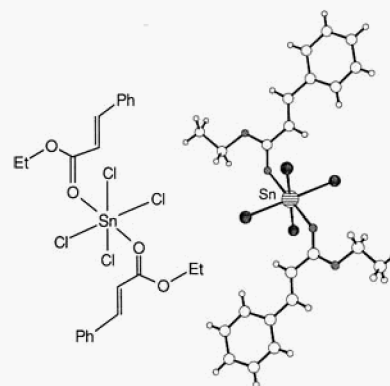
Fig. 19. Crystal structure of $SnCl_4$–ethyl cinnamate complex [41].

2.184(3) Å away from the carbonyl oxygen. More importantly, the ether group is planar and the ether oxygen seems to coordinate to the Lewis acid through an sp²-like lone pair. This observation lends credence to the proposal of *Keck* et al. for $A^{1,3}$-like interactions between the oxygen protecting group and a second β-substituent in chelation of β-alkoxy aldehydes.[43] Methoxyacetophenone chelates $SnCl_4$ in much the same way (Fig. 20, right).[42] There are, however,
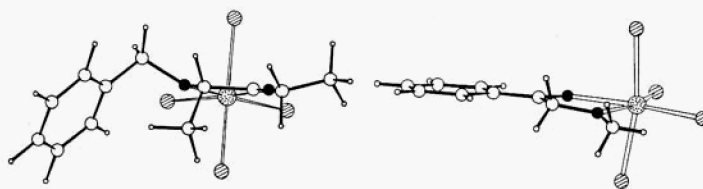
Fig. 20. Crystal structures of two $SnCl_4$ chelates [42]. Left: With 2-benzyloxy-3-pentanone. Right: With methoxyacetophenone. ⊜ = Sn, ⊘ = Cl, ● = O.

two distinct conformations about the ether oxygen in these crystals. In one conformer, the ether group is planar with sp²-like donation to the Lewis acid, while in the second conformer (not shown) the ether oxygen is better described as sp³-hybridized and pseudo-tetrahedral.

2.2.3. Late-Transition-Metal Lewis Acids

Despite the focus of the previous section on the most commonly utilized Lewis acids in organic synthesis, a much larger body of data regarding the structure of donor–acceptor complexes of late transition metals with carbonyls exists. Although a comprehensive treatment of this subject is beyond the scope of the present discussion, it is nonetheless worthwhile to consider the structural features of some of these complexes briefly, since many demonstrate novel and unusual interactions with the carbonyl group.[44]

To begin with, one can consider those high-valent transition metals that seem to behave analogously to the Lewis acids discussed thus far. The crystal structure of a cationic iridium complex, $[IrH_2(Me_2CO)_2PPh_3]BF_4$, shows *cis* coordination of two acetone ligands to an octahedrally coordinated iridium atom (Fig. 21).[45] Iridium is coordinated to the lone pairs of the acetone ligands and is coplanar with the
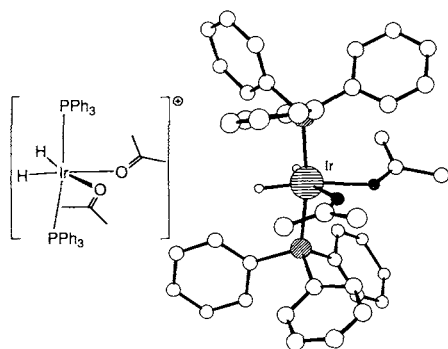
Fig. 21. Crystal structure of [IrH$_2$(Me$_2$CO)$_2$PPh$_3$]BF$_4$ [45] (anion omitted).

Fig. 23. Is there an analogy between E/Z enol ethers and *syn/anti* Lewis acid complexes with α,β-unsaturated carbonyl compounds?

carbonyl groups at an Ir–O–C angle of 133.1° for one acetone ligand and 134.9° for the other. Aside from the interest in this complex due to its role as an active dehydrogenation catalyst,[46] one can also regard it as an effective Lewis acid towards acetone, since it seems to possess all the necessary structural characteristics.

Dicarbonylcyclopentadienyliron cation, [CpFe(CO)$_2$]$^\oplus$ ({Fp}$^\oplus$), is another reactive Lewis acid. This 16-electron complex is known to coordinate ethers, nitriles, and various carbonyl-containing compounds quite effectively and with 1:1 stoichiometry. The resulting 18-electron complexes are often stable, crystalline compounds and the crystal structures of a few of them have been solved.[12, 47, 48]

X-ray analysis of [{Fp}(cyclohexenone)]PF$_6$, for instance, shows iron σ-bonded in the plane of the carbonyl ligand (τ(Fe-O-C-C) = 3.7(9)°) with an Fe–O–C angle of 132.81(4)° (Fig. 22).[12, 47] Interestingly, iron is coordinated

It is also noteworthy that the observed conformation of the Lewis acid–bound cyclohexenone is fully consistent with the transition structure **5** (Fig. 24) of *Corey, Hannon* et al. for the asymmetric 1,4-addition of alkyl cuprates to cyclohexenone (**4**).[49]

Fig. 24. The Corey–Hannon model for the asymmetric Michael reaction of alkylcopper reagents with cyclohexenone (**4**) in the presence of chiral Li salts such as **7** to give cyclohexanones (**6**). [49].
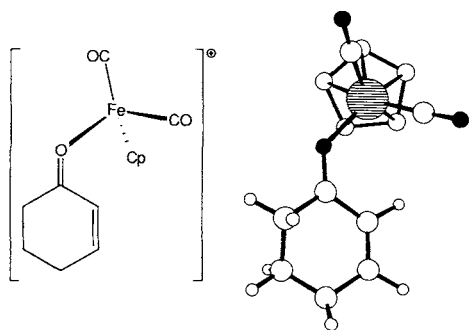

Fig. 22. Crystal structure of [{Fp}(cyclohexenone)]PF$_6$ [12, 47] (anion omitted).

syn to the C–C double bond, which could be explained by steric or electronic arguments. Sterically, coordination next to the smaller methine, as opposed to the methylene, α to the carbonyl should be favored. A similar preference may be expected if the enone moiety is envisioned in an enol ether resonance structure (cf. Fig. 23). Thus, the known preference of enol ethers to adopt a Z conformation may be extended to this case to explain the observed result. The latter, electronic argument, however, does not appear to override steric factors in an aldehyde complex. Preliminary results from a crystal structure of [{Fp}(cinnamaldehyde)]PF$_6$ indicate metal coordination *cis* to the aldehydic hydrogen and *trans* to the enal double bond.[12]
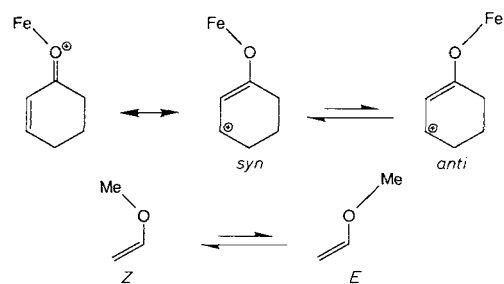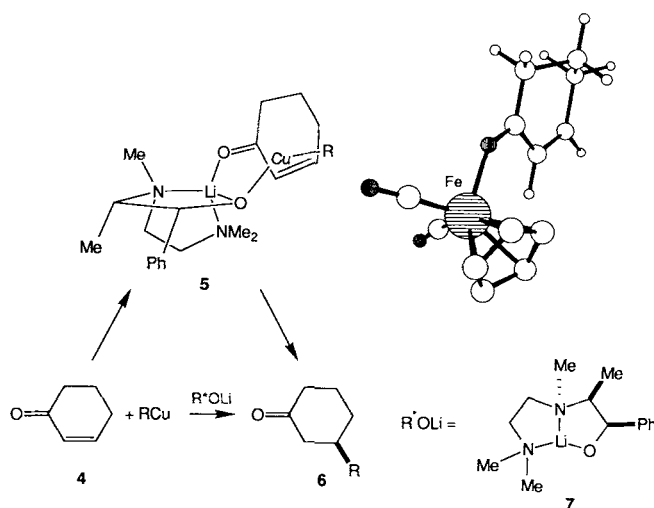
[{Fp}(4-methoxy-3-butenone)]BF$_4$ also shows coordination *syn* to the C–C double bond, s-*trans* geometry, and no evidence for π bonding (Fig. 25, τ(Fe-O-C-C) = 0(1)°).[12] [{Fp}(tropone)]BF$_4$ is yet another complex whose crystal structure has been solved.[48] In this case, the complex is particularly stable due to the high basicity of the tropone ligand and the crystal shows very similar structural features to other {Fp}$^\oplus$ complexes of carbonyl compounds.
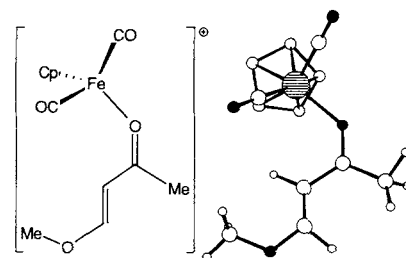

Fig. 25. Crystal structure of [{Fp}(4-methoxy-3-butenone)]BF$_4$ [12] (anion omitted).

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A tungsten Lewis acid, $[(Me_3P)(CO)_3(NO)W]SbF_6$, was recently reported to catalyze diene polymerization and Diels–Alder reactions.[50] A crystal structure of the acrolein-bound complex (Fig. 26) shows tungsten σ-coordinated
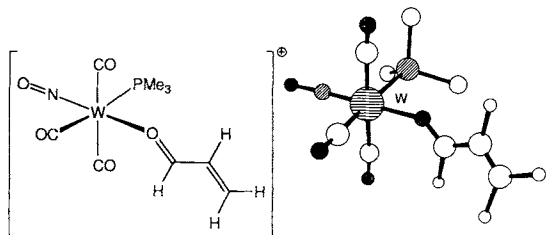

Fig. 26. Crystal structure of $[(Me_3P)(CO)_3(NO)W]SbF_6$–acrolein complex [50] (anion omitted).

(τ(W-O-C-C) = 180°), syn to hydrogen, at an angle of 137.1°. In line with ab initio predictions,[51] acrolein adopts an s-trans conformation, despite the absence of any obvious steric interactions in the s-cis conformer. It is apparent from this crystal structure that the tungsten complex behaves similarly to classical Lewis acids, and its structure can be predicted based on the same principles.

Gladysz's cationic complex $[(\eta^5\text{-}C_5H_5)(PPh_3)(NO)Re]^{\oplus}$ (A) is capable of binding carbonyls either η^2, through the π system, or η^1 through the lone-pair electrons.[52, 53] Crystal structures of A–phenylacetaldehyde (Fig. 27, right) and A–acetophenone (Fig. 27, left) clearly show the two different
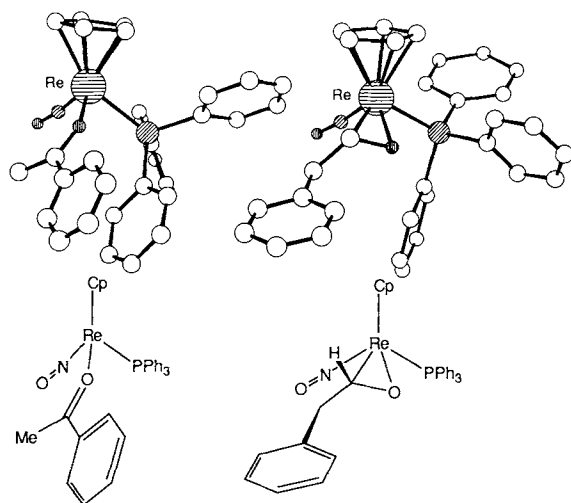

Fig. 27. η^1 (left) and η^2 (right) bonding for $[Cp(Ph_3P)(NO)Re]^{\oplus}$ (A) [52, 53].

modes of complexation. The authors attributed the difference in binding to increased steric bulk and lower π acidity of ketones as compared to aldehydes. No crystal structures of $\{Fp\}^{\oplus}$–aldehyde complexes are available in order to determine whether $\{Fp\}^{\oplus}$ has a similar "amphichelic" binding property, but $[(Ph_3P)(CO)_2Fe^0]$ binds cinnamaldehyde in an η^4 fashion.[54, 55] Additionally, it is worth noting that both of the rhenium complexes shown here are chiral and it has been shown that in the enantiomerically pure form, they undergo nucleophilic additions to the carbonyls with high enantioselectivities.[52, 53] Finally, the significance of the

phenylacetaldehyde crystal structure should not escape attention. This is the first crystal structure of a nonchelated, α-substituted complex formed between a Lewis acid and an aldehyde. Despite the unusual, η^2 bonding in this complex there may be direct implications for the conformational preferences of complexes formed between Lewis acids and α-chiral aldehydes. Remarkably, the phenyl ring lies nearly perpendicular to the plane of the carbonyl at a dihedral angle of τ(C-C-C-O) = 94°, which is reminiscent of the Felkin–Anh proposal for the reactive conformation of α-substituted carbonyl systems.[56] However, it also seems reasonable to argue that the phenyl group occupies the sterically least congested area of space, and that the observed conformation is merely an artifact of the steric requirements of this particular complex, rather than a general, electronic phenomenon.

η^2 Bonding appears to occur with electron-rich metals and electron-deficient carbonyls. This combination allows for better back-bonding from the metal to the carbonyl π^* orbital and disfavors competitive η^1 coordination by lowering the carbonyl lone-pair basicity. Hexafluoroacetone, for example, is η^2-bound to $[Ir(Ph_3P)_2(CO)Cl]^{[57]}$ (cf. also Ref. [45]), and electron-rich Ni^0 complexes show π bonding to both aldehydes[58] and ketones.[59] The crystal structure of $[(tmeda)Ni(C_2H_4)(H_2CO)]$, for example, shows formaldehyde bound in a metallaoxirane structure in which the C–O bond has lengthened to 1.311 Å (Fig. 28).[60] Similarly, a
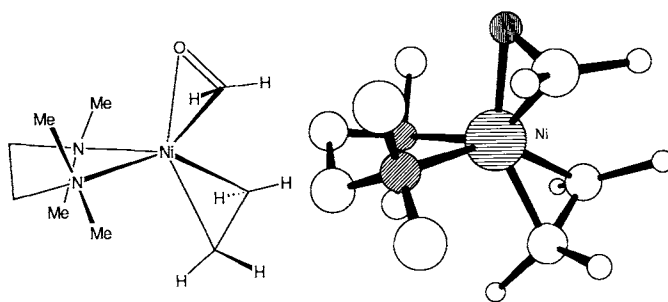

Fig. 28. Crystal structure of $[(tmeda)Ni(C_2H_4)]$–formaldehyde complex [60].

molybdenum Lewis acid bound to benzaldehyde shows η^2 bonding and a C–O bond length of 1.333 Å.[61] Acetone bound to pentaammineosmium(II) (C–O = 1.322 Å) has also been detected in the solid state, and π bonding is observed in this case as well.[62]

The structure of these η^2-bound carbonyl–Lewis acid complexes, especially those of Ni, may be relevant to the Au^I-catalyzed aldol reaction of isocyanoacetates with aldehydes to give the heterocycles 9, discovered by Ito, Sawamura, and Hayashi.[63] It is reasonable to expect that the isoelectronic Ni^0–aldehyde complexes and the presumed Au^I–aldehyde intermediate in this reaction would exhibit similar structural features. Thus, 8 can be proposed as a transition-state model (Fig. 29), although the presence of other potential ligands in the reaction mixture (i.e., isocyanates, tertiary amines) may lead to other, structurally distinct, Au^I complexes as well.

Finally, carbonyls can bind two metals at once. The crystal structure of a complex containing bridging μ-η^2-bound acetaldehyde, for example, shows the carbonyl coordinated
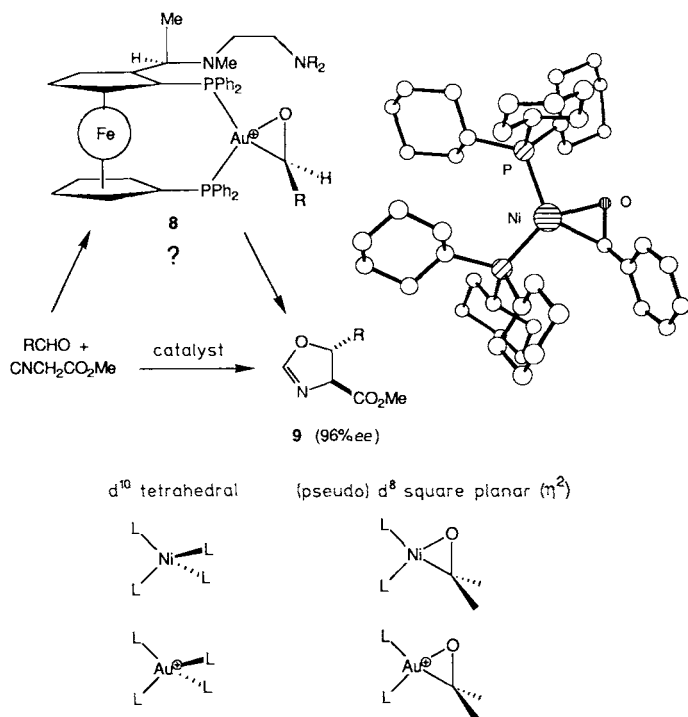
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Fig. 29. A Ni⁰-aldehyde complex as model for the transition state of Au[I]-catalyzed aldol reaction of cyanoacetoacetates and aldehydes [58, 63].

to two molybdenum atoms (Fig. 30).[64] It appears that in this structure the carbonyl utilizes its π as well as its lone-pair electrons to bond to the two metal centers. Conceptually, one can think of this molybdenum complex as a bidentate Lewis acid that chelates the carbonyl group.
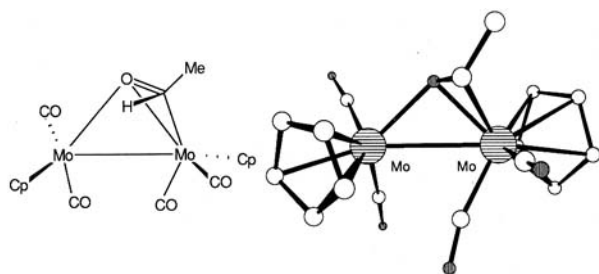

Fig. 30. Crystal structure of [(η²-μ-CH₃CHO)Cp₂(CO)₄Mo₂] [64].

2.3. Discussion

It is now appropriate to summarize a few general points that can be made, based on the structural information in Sections 2.2.1–2.2.3, regarding the complexation of the carbonyl group to various Lewis acids. It is fairly clear that alkali-metal cations do not show a strong directional preference for binding to carbonyls and, for these complexes, coordination numbers and coordination geometries vary greatly. Boron, aluminum, titanium, and tin Lewis acids all accept electron density from sp² lone pairs of a carbonyl ligand at an angle of ca. 130–140°, but, in the presence of steric interactions, they easily distort from their optimal geometry. For aluminum, titanium, and tin complexes there is fairly strong

evidence that, contrary to theoretical predictions, these distortions are invariably out of plane, toward the π cloud of the carbonyl group rather than the linear, in-plane geometry. This may also suggest a mechanism for *syn–anti* isomerization of the Lewis acid, although this point is less clear. Electron-rich metals and electron-deficient carbonyls prefer η^2 bonding. Thus, many of the late transition metals bind carbonyls through the π cloud.[65]

The stoichiometry of complexation is ordinarily 1:1 (acid:carbonyl) for boron- and aluminum-centered Lewis acids, which give pseudo-tetrahedral complexes, and 1:2 for octahedral Ti[IV] complexes. Sn[IV] Lewis acids can form either 1:2 octahedral or 1:1 trigonal-bipyramidal complexes, depending on the nature of their ligands and on the carbonyl base. For late transition metals the stoichiometry is often predicted by the 18-electron rule.

η^1-Bound Lewis acids prefer to lie *syn* to the smaller substituent of the carbonyl: for example, *syn* to H for aldehydes, *anti* to -OR for simple alkyl esters. In α,β-unsaturated systems, Lewis acid coordination *syn* to the C–C double bond favors the s-*trans* conformation, but in two crystal structures, where coordination *anti* to the olefin occurs, s-*cis* complexes are observed.[28, 66] Finally, chelation with titanium and tin occurs readily and yields stable, crystalline complexes.

Some of the difficulties encountered in obtaining structural data on Lewis acid carbonyl complexes should also be noted here. One of the most common challenges in X-ray crystallographic analyses is the task of obtaining suitable, X-ray-diffracting crystals. This task is made even more formidable for the highly reactive and often unstable Lewis acid carbonyl complexes. Most of the crystal structures discussed in Sections 2.2.1 and 2.2.2 were obtained by crystal growth and data collection at low temperatures, under inert atmospheres. Some of the late-transition-metal complexes, however, seem to be exceptional in this respect. Many of the systems discussed in Section 2.2.3 exhibit exceptional robustness, stability, and a propensity to form crystalline complexes. This would facilitate the task of crystallization and structural analysis, and one can imagine that transition-metal complexes could be used as structural probes of carbonyl–Lewis acid interactions.

3. π-Bond Hybridization in Transition-Metal Complexes[67]

Numerous theoretical[68] and structural[69] studies point to the fact that π bonding plays an important role in determining the geometry of transition-metal complexes. Conformational preferences of π-bonding ligands are often rationalized by simple consideration of the relative energies of the metal d orbitals which can overlap with the ligand in question. In d⁸ trigonal-bipyramidal complexes, for example, π-acid ligands favor equatorial positions and adopt geometries which allow π overlap with the $d_{x^2-y^2}$ or d_{xy} orbitals (metal-centered HOMOs) lying in the equatorial plane. Likewise, d⁶ octahedral and pseudo-octahedral complexes possessing a single carbonyl (or nitrosyl) ligand have a well-defined metal-centered HOMO lying in the plane perpendicular to the carbonyl (or nitrosyl) ligand (Fig. 31, left). *Gladysz* et al.

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have shown that stereoelectronic interactions involving the metal-centered HOMO in [CpRe(NO)(PPh$_3$)R] complexes dramatically influence the structure and reactivity in a wide variety of these chiral molecules (Fig. 31, middle and right).[70] Thus, electronic interactions involving ligand π
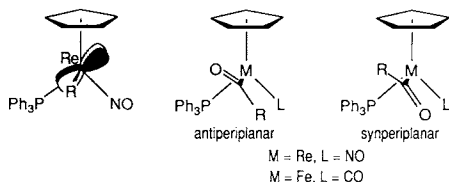

Fig. 31. Alternative acyl ligand conformations that maximize primary stereoelectronic interactions in d^6 complexes containing a single carbonyl (or nitrosyl) ligand. Left: Metal-centered HOMO.

orbitals and metal-centered HOMOs and LUMOs, which we will term primary stereoelectronic interactions, are often reliable predictors of ligand conformation.[71]

Ordinarily, assessment of primary stereoelectronic interactions plays a key role in the conformational analysis of transition-metal complexes. Nevertheless, ligand alignment is seldom uniquely determined by primary stereoelectronic interactions since there are often two ligand alignments that maximize π bonding or primary stereoelectronic interaction (see Fig. 31). Considering the chiral metal acyl complexes studied by Gladysz et al.,[72] Davies et al.[73] and Liebeskind et al.,[74] we note that the observed alignment of the acyl carbonyl antiperiplanar to the π-bonding CO (or NO) ligand maximizes π back-bonding to the acyl ligand from the metal-centered HOMO. However, alignment of this acyl carbonyl syn to the CO (or NO) ligand also maximizes π back-bonding. This raises the question: What forces govern the preferred antiperiplanar orientation of the acyl carbonyl?

The influence of steric interactions on the syn–anti isomerism of acyl ligands in [CpFe(CO)(PPh$_3$)(RC=O)] and [CpRe(NO)(PPh$_3$)(RC=O)] complexes (see Fig. 31) has been argued persuasively by Davies.[75] While steric interactions are certainly important in these systems, there are some trends which indicate that syn–anti isomerism in these complexes is not adequately rationalized by consideration of steric interactions alone. Notably, formyl complexes (R = H) show the same antiperiplanar conformational preference as acyl complexes possessing bulky alkyl (e.g., R = sec-butyl) substituents (see Section 3.1.2).

Since a number of metal acyl complexes with cis π-bonding ligands show a preference for alignment of the acyl oxygen antiperiplanar to the π-bonding ligand, and since evaluation of steric interactions does not adequately explain this alignment in all of the cases, we sought another explanation for the phenomenon. In Section 3.1 we discuss how examination of crystallographic data led to the proposal that syn–anti isomerism in transition-metal acyl complexes possessing cis π-bonding ligands is influenced by secondary stereoelectronic interactions. Secondary stereoelectronic interactions result from the mixing of metal-centered d and p orbitals, which occurs during π bonding. This dp mixing leads to hybridization of π-bonding molecular orbitals toward the π-bonding ligand. Interaction of the C–O σ^* orbital of the acyl ligand with the π-bonding orbitals of the cis CO (or NO) ligand

leads to a stereoelectronically preferred antiperiplanar orientation of the acyl ligand.

Secondary stereoelectronic interactions may also influence the alignment of cis π-bonding ligands in systems other than the acyl complexes mentioned above. Based on the presence of orbital interactions similar to those found for acyl complexes, we also propose that ligand orientations that place a ligand acceptor orbital (e.g., σ^*) syn or a ligand donor orbital (e.g., heteroatom lone pair) anti to a cis π-bonding ligand are stereoelectronically favored (Fig. 32).
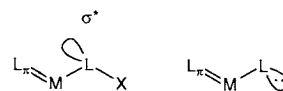

Fig. 32. Ligand conformation favored by secondary stereoelectronic interactions in complexes containing a cis π-bonding ligand. Left: Ligand acceptor orbital (σ^*) syn to L$_\pi$. Right: Lone-pair donor orbital anti to L$_\pi$. See sections 3.2.1–3.2.3.

The theoretical basis for the conformational model depicted in Figure 32 has been presented elsewhere.[67] Here, we consider the structural data which lend credence to this model.

3.1. Syn–Anti Isomerism in Metal Acyl Complexes

3.1.1. Steric Interactions in Metal Acyl Complexes: The Seeman–Davies Model

Certain reactions of organic ligands attached to stereogenic transition-metal centers in complexes of the type CpML$_3$ have been shown to proceed with a remarkable degree of asymmetric induction. Prompted by this observation, Seeman and Davies recently published conformational models for alkyl and acyl complexes containing the organometallic fragment [CpFe(CO)(PPh$_3$)].[76] Their models were based on the results of extended Hückel and ab initio calculations on model systems where PPh$_3$ was replaced with simpler ligands. Their principal conclusions were that iron serves primarily as a template for the ligands and that alkyl or acyl ligand conformation is governed by steric interactions with the PPh$_3$ ligand.

3.1.2. Acyl Ligand Conformations Not Explained by the Seeman–Davies Model

If Seeman–Davies-type steric interactions are the only forces responsible for the observed conformational preferences for metal acyl complexes, then formyl complexes should—due to the smaller size of H versus O on the formyl ligand—show a preference for alignment of the acyl oxygen syn to the M–CO bond. This is not the case.

The solid-state structure of [CpRe(NO)(PPh$_3$)(CHO)] (10) has been determined by Gladysz et al.[77] and this formyl complex has the formyl oxygen oriented antiperiplanar (N–Re–C$_{acyl}$–O$_{acyl}$ torsional angle = 176°) to the M–NO bond (Fig. 33). This conformation is not predicted by the Seeman–Davies model. Gladysz has noted that the observed conformation allows for a stabilizing electronic interaction between the highest occupied d orbital on the rhenium and the π^*_{CO} orbital on the acyl ligand. Complex 10 also shows a very short Re–C$_{formyl}$ bond (2.06 Å) and a low formyl car-
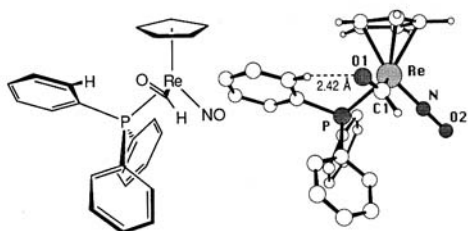
Fig. 33. Structure of **10** [77].

bonyl stretching frequency ($\nu_{CO} = 1558$ cm^{-1}); both of these observations are in accord with a substantial amount of Re-to-formyl electron donation. However, synperiplanar orientation of the formyl ligand would allow for the same electronic stabilization. There are no obvious intramolecular steric interactions between the other ligands and the formyl ligand; in fact, the triphenylphosphane conformation is as observed by *Davies* and *Seeman* in iron acyl complexes. Intermolecular steric interactions (crystal packing forces) are unlikely to play a major role in determining the formyl ligand conformation due to the smallness of this ligand relative to other ligands on the complex. Clearly, some other force must be acting to align the formyl ligand in the observed antiperiplanar orientation.

Based on the examination of some other metal acyl complexes with *cis* CO ligands that do not possess Seeman–Davies-type steric interactions (Figs. 34–36), it is tempting to speculate that there is an intrinsic electronic preference for alignment of the acyl oxygen *anti* to the CO ligand. In *Herndon*'s iron acetyl complex **11** (Fig. 34)[78] the bulky
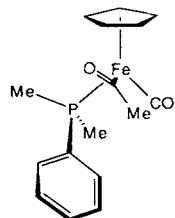

Fig. 34. Solid-state geometry of [CpFe(CO)(PMe$_2$Ph)COMe] (**11**) [78].

triphenylphosphane ligand central to the Seeman–Davies model is replaced by the smaller dimethylphenylphosphane ligand. Although there is no steric interaction between the acyl ligand and the *ortho* C–H bond of a phenyl group, the acetyl ligand adopts an antiperiplanar alignment (C_{CO}–Fe–C_{acyl}–O_{acyl} torsional angle $= -163°$). The methoxycarbonyl ligand in *Albano*'s octahedral iridium complex **12** (Fig. 35)[79] certainly is in a very different steric environment
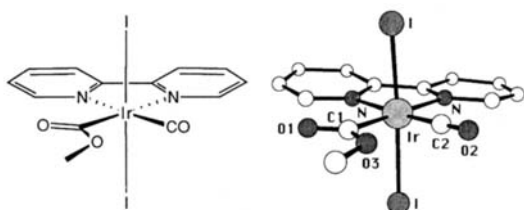

Fig. 35. Structure of [Ir(bpy)I$_2$(CO)CO$_2$Me] (**12**) [74].

than that found in pseudo-octahedral complexes of the type [CpFe(CO)(PPh$_3$)(COR)], yet the carbonyl oxygen is aligned antiperiplanar to the CO ligands (C_{CO}–Ir–C_{acyl}–O_{acyl} torsional angle $= 176°$).

Berke's octahedral rhenium complex **13**[80] (Fig. 36) is another example of a rhenium formyl complex where the formyl oxygen is aligned *anti* to the *cis* π-bonding ligand (cf. *Gladysz*'s complex, Fig. 33) despite steric interactions which should favor the *syn* alignment.
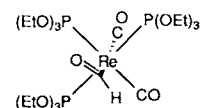

Fig. 36. Solid-state geometry of [Re(CO)$_2$\{P(OEt)$_3$\}$_3$CHO] (**13**) [80].

Electronic interactions that lead to preferential stabilization of the antiperiplanar rotational isomer of the metal acyl complexes discussed above are depicted in Figure 37. Primary stereoelectronic interaction is optimized when the acyl ligand is coplanar with the M–CO bond, since this allows for maximum overlap of the π_{CO}^* orbital of the acyl ligand with the metal-centered HOMO (cf. Fig. 31). Secondary stereoelectronic interactions are optimized when the acyl ligand is antiperiplanar to the M–CO bond, since this allows for max-
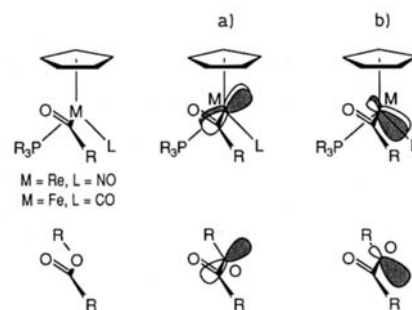

Fig. 37. Stereoelectronic interactions in metal acyl complexes and carboxylic esters. a) Primary stereoelectronic effect; b) secondary stereoelectronic effect.

imum overlap of the σ_{CO}^* orbital of the acyl ligand with the M–CO π-bonding orbital, which is metal-centered *and hybridized toward the CO ligand*. Similar electronic effects have been invoked to explain the stability of the Z conformation of carboxylic esters (Fig. 37, bottom).[81, 82] In this description of π bonding, the polarized metal-centered d orbitals are similar to the lone pair of the oxygen heteroatom.

Despite the plausibility of these arguments in a qualitative sense, it is extremely difficult to assess the exact energetic worth of secondary stereoelectronic interactions. However, a general sense of the energetic contributions of secondary stereoelectronic effects may be derived from the consideration of factors that can override these preferences. We close this section with a discussion of some metal acyl complexes with *cis* CO ligands where the acyl ligands are not oriented antiperiplanar to CO ligands.

Ruthenium formyl complex **14** (Fig. 38), prepared by *Nelson* et al.,[83] has a C_{CO}–Ru–C_{formyl}–O_{formyl} torsional angle of $-28°$. However, this complex possesses several unusual structural features, including an exceptionally short C–O
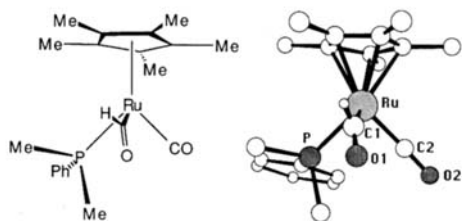
Fig. 38. Structure of [Cp*Ru(CO)(PMe₂Ph)CHO] (14) [83].

Fig. 40. Structure of [Ir(PPh₃)₂(CO)(NO)Cl]BF₄ (17) (anion omitted). The C–Ir–N–O torsional angle is − 5° [86].

Fig. 41. Structure of [Ru(PPh₃)₂(NO)₂Cl]PF₆ (18) (anion omitted). The N_linear–Ir–N_bent–O torsional angle is 2° [87].

Scheme 1. Conformations of the nitrosyl ligand (cf. Fig. 32).

bond length (1.106 Å) and a large Ru–C–O bond angle (140°) for the formyl ligand—the C–O bond of the formyl ligand is shorter than that of the carbonyl ligand present in the same complex (C-O = 1.134 Å for the carbonyl ligand). The reasons for the unusual structural features present in 14 are unclear. However, a comparison between *Nelson*'s ruthenium formyl complex 14 (C-O$_{formyl}$ = 1.11 Å, $\tilde{v}_{CO}$ = 1601 cm^{-1}) and *Gladysz*'s rhenium formyl complex 10 (C-O$_{formyl}$ = 1.22 Å, $\tilde{v}_{CO}$ = 1554 cm^{-1}) indicates that there is substantially less back-bonding to and hence less electronic stabilization of the formyl ligand in the ruthenium complex 14. In *Nelson*'s complex, the stereoelectronic preference for antiperiplanar alignment of the formyl ligand is presumably overridden by the steric demand of the bulky pentamethyl-cyclopentadienyl ligand.

Polar groups such as the CO group in metal acyl complexes are often involved in electrostatic interactions. Figure 39
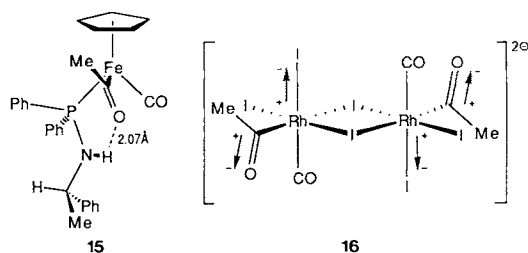

Fig. 39. Structures of [CpFe(CO)(PPh₂NHCHMePh)COMe] (15) [84] and [RhI₃(CO)COMe]₂$^{\ominus}$ (16) [85], where electrostatic interactions determine acyl ligand conformation.

shows two acyl complexes whose solid-state structures may be influenced by electrostatic interactions. The orientation of the acetyl ligand in iron complex 15 is controlled by a strong hydrogen bond to the NH group attached to the phosphane ligand.[84] The orientation of acetyl ligands in the binuclear rhodium complex 16[85] may be determined by dipole–dipole interactions, since the observed conformation leads to the most favorable alignment of Rh$^{\delta\oplus}$–I$^{\delta\ominus}$ and (C$^{\delta\oplus}$–O$^{\delta\ominus}$)$_{acyl}$ dipoles.

3.2. *Syn–Anti* Isomerism of Ligands other than η¹-Acyl

3.2.1. Bent Nitrosyl Ligands

X-ray crystal structures of the bent nitrosyl complexes 17[86] and 18[87] are shown in Figures 40 and 41. In both cases the bent nitrosyl ligand adopts the stereoelectronically preferred conformation (Scheme 1) that places its lone pair antiperiplanar to the *cis* π-bonding ligand.
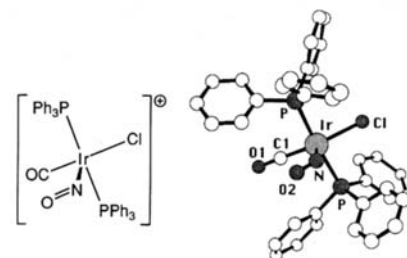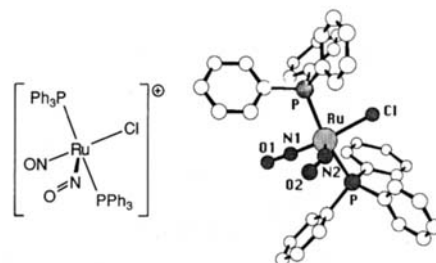
Bent nitrosyl complexes are related to acyl complexes by the isoelectronic substitution of N for CR. As this substitution replaces the C–R bond with a nitrogen lone pair, the stereoelectronically preferred alignment of the nitrosyl N=O bond is different from that of the acyl C=O bond [Eq. (a)]. Since the metal-centered M–CO π cloud ("lone

(a)
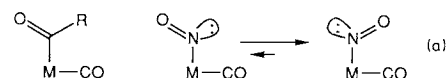
pair") is concentrated along the M–C bond, the lone pair of the bent nitrosyl can minimize "lone pair–lone pair" repulsion in the *syn* conformation.

It is interesting to compare bent nitrosyl and acyl complexes to their organic analogues: nitrite and carboxylic esters. Since nitrite esters are related to carboxylic esters by the same isoelectronic substitution (N for CR), the stereoelectronically preferred alignment of the nitrite N=O bond should be different from that of the carboxylic C=O bond. In fact, this appears to be the case: In both methyl nitrite[88] and methyl formate[89] the Z conformer is preferred, but to a very different extent [Eqs. (b) and (c)].

ΔG = 0.8 kcal mol^{-1} (b)

ΔG = 6-8 kcal mol^{-1} (c)
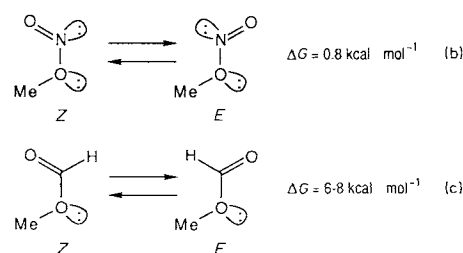
This difference is understood if the forces governing these conformational preferences are viewed as a superposition of electrostatic (dipolar) and stereoelectronic interactions (Fig. 42). Electrostatic forces favor the *Z* conformation for
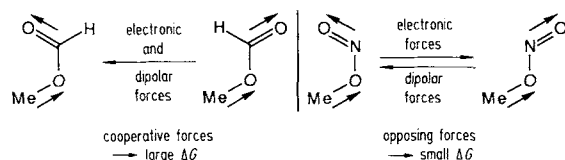

Fig. 42. The influence of electronic and dipolar forces on the preferred conformations of carboxylic esters (left) and nitrite esters (right).

both nitrite and carboxylic esters. Stereoelectronic forces, however, favor the *Z* conformation for carboxylic esters and the *E* conformation for nitrite esters. In the case of methyl formate stereoelectronic and electrostatic forces act in unison to produce an energetically substantial conformational preference, whereas in the case of methyl nitrite these forces largely cancel out to produce a small conformational preference.

3.2.2. Acetylene Ligands

Figures 43–45 show some ynolate and ynol ether complexes of tungsten (**19–21**) which are derived from carbyne–
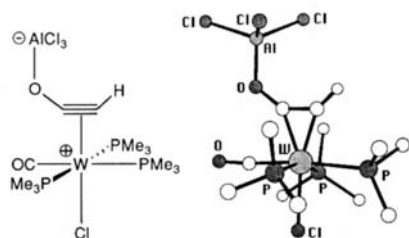

Fig. 43. Structure of [W(HC≡COAlCl₃)(CO)(PMe₃)₃Cl] (**19**) [90a].

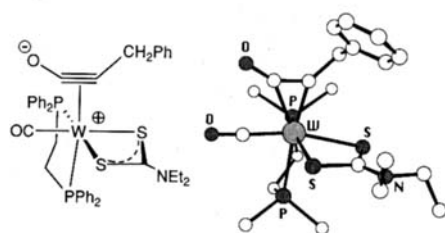Fig. 44. Structure of [W(PhCH₂C≡CO)(CO)(Ph₂PCH₂CH₂PPh₂)(S₂CNEt₂)] (**20**) [90b].
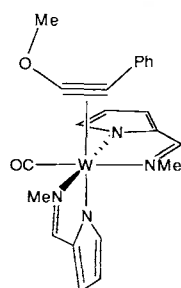

Fig. 45. Solid-state structure of [W(PhC≡COMe)(CO)(2-MeNCH-pyrrole)₂] (**21**) [90c].

CO coupling reactions.[90] In each case the alkyne is aligned parallel to the M–CO bond axis and its oxygen substituent is oriented *syn* to the carbonyl ligand (Scheme 2). The electron-

Scheme 2. Conformations of alkyne ligands (see also Fig. 46).

ic interactions that cause the alkyne ligands to be parallel to the carbonyl ligand have been discussed at length by *Templeton* et al.[91] The alkyne is thus aligned so that it may receive electron density from a filled tungsten-centered orbital and donate electron density to an empty one. The *syn* orientation of the oxygen substituent, however, is not explained by these interactions. The π^*_{CC} orbital of an ynolate or ynol ether is hybridized toward the carbon bearing the oxygen substituent and the filled metal-centered orbital with which it interacts is polarized toward the carbonyl ligand (Fig. 46).[92] Thus, the observed conformation of the alkynes is that which maximizes the overlap between these two orbitals.
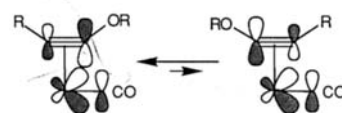
Fig. 46. Preferred alkyne alignment for maximum π back-bonding in complexes **19–21**.

3.2.3. Bent Imido Ligands

X-ray crystal structures of the bis-imido complexes **22**[93] and **23**[94] are shown in Figures 47 and 48. In both cases the bent imido ligand adopts the stereoelectronically preferred conformation that places its lone pair antiperiplanar to the
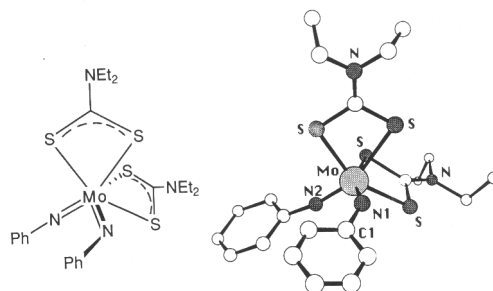
Fig. 47. Structure of [Mo(S₂CNEt₂)₂(NPh)₂] (**22**). The N$_{linear}$–Mo–N$_{bent}$–C torsional angle is − 5° [93].

Fig. 48. Structure of [OsO₂(N-*t*Bu)₂] (**23**). The N$_{linear}$–Os–N$_{bent}$–C torsional angle is 0° [94].

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metal–nitrogen triple bond of the linear imido ligand (Scheme 3). Here, the stereoelectronic preference is probably governed by donation of the lone pair of the bent amido

Scheme 3. Conformations of imido ligands (cf. Fig. 32).

ligand into a metal-centered non-bonding orbital.[82c] Of course, avoidance of "lone-pair"–π interactions in the antiperiplanar arrangement may also contribute to a bias for the observed conformation.
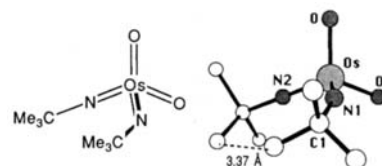
Interestingly, both 22 and 23 adopt conformations which place the imido substituent in a sterically more hindered environment. Thus, in these cases secondary stereoelectronic effects seem to override steric preferences.

4. Summary and Outlook

The examples presented in this article demonstrate a few of the many ways that useful conformational conjectures can be made using the Cambridge Structural Database. Synthetic and design applications aside, the development of further mechanistic studies that would verify the validity of these conjectures should be emphasized. In particular, systematic structural analyses of a family of related complexes—where only a few parameters change in going from one complex to another—would be highly informative. In the absence of systematic studies, care should be taken to avoid overinterpretation of single structures and invalid generalizations. Generally, statistical analyses of a larger number of crystal structures can be used to distinguish the ordinary from the unusual. In unusual systems, crystal packing forces may be the cause of deviations from the norm, and it is always important to take this factor into consideration.

In the complexation of Lewis acids to carbonyls—a process of great interest in organic synthesis—definite structural trends were observed. The more unexpected observations included the widespread occurrence of out-of-plane bonding and the diversity of coordination geometries for very similar Lewis acids (e.g., $L_nX_{4-n}Sn$ Lewis acids). Of the unanswered questions, the conformational preferences of Lewis acid-bound, α-chiral carbonyls seem to attract the most immediate attention.

In organometal complexes with π-bonding ligands, the presence of secondary stereoelectronic interactions is strongly implicated by the structural data. Considerations of molecular orbital theory also support this notion. Notably, the cases where stereoelectronic syn–anti preferences override clear steric preferences (complexes 10, 13, 22, and 23) occur for metals (Re, Mo, and Os) that have been noted to show a predilection for forming metal–ligand multiple bonds. It may be that stereoelectronic interactions (primary and secondary) are more important for these metals than for metals, such as Fe, which do not show a tendency to form multiple bonds. A more definitive answer, however, is likely to come from future X-ray analyses and the test of our ability to predict the conformation of these complexes.

Another way to gain insights from the structure of molecules is through the structure–reactivity correlation method.[1, 3, 4] Recently, for example, the question of the structure and basicity of silyl ethers was probed using the CSD.[95] A search for the $Si-O-C_{sp^3}$ fragment revealed an unusually wide average Si–O–C angle (134.2°) and a negative correlation between the Si–O bond length and the Si–O–C bond angle (Fig. 49; correlation factor − 0.68). The latter observation contradicts the steric arguments previously presented for the occurrence of wide Si–O–C angles.
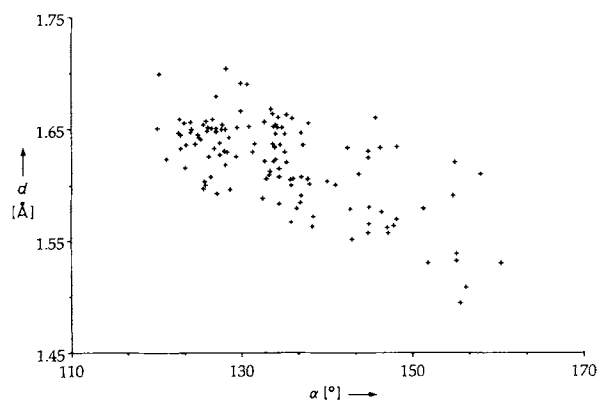

Fig. 49. Correlation of the Si–O bond length and the Si–O–C angle in acyclic silyl ethers [95].

An alternative explanation, based on Si–O π interactions, on the other hand, is consistent with the observed results.[96] Subsequently, calculations of Jorgensen et al.[95] at the 6-31G* level reproduced the same contrasteric trend and presented a theoretical basis for these observations. Although these findings do not yield any direct information on the features of a transition structure, they can account for the relatively low basicity of silyl ethers and also for the inability of α- and β-siloxy carbonyls to chelate Lewis acids.[96]

Finally, it should be recalled that "chemical reactivity depends on many factors besides purely conformational ones; an exclusive preoccupation with the geometric aspects of molecular structure can sometimes prevent us from recognizing other factors that might be important or even decisive in influencing the rate of a reaction."[97] Future work in this area will focus not only on the refinement of the conformational models, but also on the uncovering of the "other factors" that influence the reactivity of organometal complexes.

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[82] Evaluation of the orbital mixing that occurs when a π-bonding ligand interacts with a transition-metal center requires the assessment of second-order mixing which takes place when two or more orbitals on the same fragment (i.e., metal d and p orbitals) overlap with the same orbital of an interacting ligand (i.e., ligand p orbital). The result of this second-order mixing is that bonding and antibonding orbitals are hybridized toward the ligand involved in the bonding interaction, and nonbonding orbitals are hybridized away from the ligand. This is illustrated in Scheme 4 for the
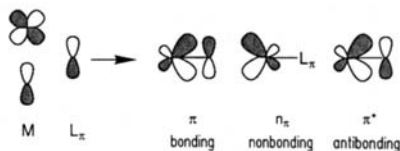
Scheme 4. Orbital mixing leading to π-bond hybridization.
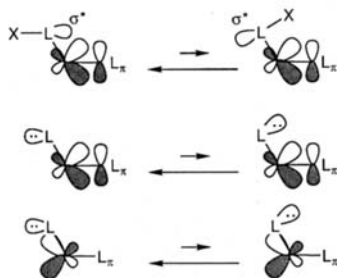
Scheme 5. Possible stereoelectronic interactions in complexes consisting of a σ-bound ligand L and a complex fragment M-L_π, where L and L_π are cis. The X–L–M–L_π dihedral angle is 180° on the left and 0° on the right.

interaction of a π-bonding ligand with a transition-metal center. There are three types of stereoelectronic interactions that could influence the syn–anti isomerism of a ligand bound cis to a π-bonding ligand: (1) $\pi \leftrightarrow$ acceptor (e.g., σ^*)—a stabilizing two-center two-electron interaction (Scheme 5,

top); (2) $\pi \leftrightarrow \pi'$ donor (e.g., lone pair)—a destabilizing two-center four-electron interaction (Scheme 5, middle); (3) $n_\pi \leftrightarrow$ donor (e.g., lone pair)—a stabilizing two-center two-electron interaction (Scheme 5, bottom). The relative importance of the three types of stereoelectronic interactions depicted above will, of course, depend on the nature of the metal–L_π bonding interaction [70]. In all cases, however, ligand conformations that place a ligand acceptor orbital syn or a donor obital anti to a metal ligand π bond are stereoelectronically favored. For a complete discussion of the theoretical basis of second-order mixing see ref. [67].

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