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A Conformational Analysis of Transition Metal η^1-Acyl Complexes: Steric Interactions and Stereoelectronic Effects

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1 Introduction

The introduction of conformational analysis revolutionized organic chemistry such that it is now routinely used to explain and, more importantly, to predict stereoselective reactions.[1] Organotransition metal complexes form a major class of compounds of interest both intrinsically and as reagents for organic synthesis.[2] Highly stereoselective reactions of these complexes are being discovered, yet surprisingly little consideration has been given to the influence of conformation on reactivity and selectivity.

The very large number of highly stereoselective reactions of acyl ligands attached to the iron chiral auxiliary $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)]$[3] can all be rationalized in terms of a very simple model based on a conformational analysis approach.[4—10] This conformational analysis, derived from models, calculations, and reactivity patterns, indicates that the preferred conformations of such complexes are governed largely by steric factors. This review first generalizes this concept to all transition metal acyl complexes, and then extends it to include stereoelectronic factors. The analysis is correlated with the extensive number of crystal structures available. Finally ligands other than acyl are considered.

2 Influence of Steric Interactions on the Preferred Conformation of Metal η^1-Acyls

A conformational analysis for a variety of metal acyl complexes of different structural types is outlined below. This analysis is based on a qualitative study of molecular models and on computer modelling performed on a series of idealized molecular structures. Consideration is given primarily to steric factors, such that

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[1] (*a*) E. L. Eliel, N. L. Allinger, J. J. Angyal, and G. A. Morrison, 'Conformational Analysis', Wiley Interscience, New York, 1965; (*b*) P. A. Bartlett, *Tetrahedron*, 1980, **36**, 3; (*c*) J. I. Seeman, *Chem. Rev.*, 1983, **83**, 83.

[2] (*a*) S. G. Davies, 'Organotransition Metal Chemistry: Applications to Organic Synthesis', Pergamon Press, Oxford. 1982; (*b*) J. P. Collman, L. S. Hegedus, J. R. Norton, and R. G. Finke, 'Principles and Applications of Organotransition Metal Chemistry', University Science Books, Mill Valley, 1987.

[3] S. G. Davies, I. M. Dordor-Hedgecock, R. J. C. Easton, S. C. Preston, K. H. Sutton, and J. C. Walker, *Bull. Chim. Soc. Fr.*, 1987, 608 and references cited therein.

[4] S. G. Davies and J. I. Seeman, *Tetrahedron Lett.*, 1984, **25**, 1845.

[5] S. G. Davies and J. I. Seeman, *J. Am. Chem. Soc.*, 1985, **107**, 6522.

[6] S. G. Davies, J. I. Seeman, and I. H. Williams, *Tetrahedron Lett.*, 1986, **27**, 619.

[7] S. L. Brown, S. G. Davies, D. F. Foster, J. I. Seeman, and P. Warner, *Tetrahedron Lett.*, 1986, **27**, 623.

[8] S. G. Davies, I. M. Dordor-Hedgecock, K. H. Sutton, and M. Whittaker, *J. Am. Chem. Soc.*, 1987, **109**, 5711.

[9] B. K. Blackburn, S. G. Davies, and M. Whittaker, *J. Chem. Soc., Chem. Commun.*, 1987, 1344.

[10] B. K. Blackburn, S. G. Davies, and M. Whittaker, in preparation.

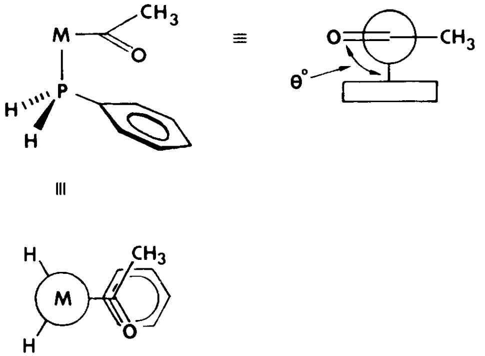

Figure 1 *Illustration of idealized model used for computer simulations*

the preferred conformation of transition metal acyl complexes is initially predicted simply by taking into account the steric interactions between the acyl and the proximate ligands. Stereoelectronic contributions to conformational preferences are also considered. This type of analysis can be most easily achieved by use of the appropriate Newman projection so as to view the molecule down the acyl carbon–metal bond. Complexes are dealt with by structural type namely square planar, octahedral, square pyramidal, trigonal bipyramidal, and pseudo-octahedral cyclopentadienyl complexes. In each case consideration is given first to complexes comprising a full complement of small carbon monoxide ligands followed by those obtained by sequential substitution of carbon monoxide ligands proximate to the acyl ligand by the large ligand triphenylphosphine.

Computer simulations (Chem-X)[11] of the conformational energy profiles were obtained using simplified models of the various parent acetyl complexes. The model complexes were all assigned idealized bond angles for the relevant structural type.[12] In order to make the calculations feasible the acetyl group was assigned an axial position with only *cis* ligands being taken into consideration. Triphenylphosphine was, unless otherwise stated, modelled by PH_2Ph, itself held in a fixed conformation such that the torsional angle C_α(carbon of the acetyl carbonyl)–M(metal)–

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[11] Chem-X, developed and designed by Chemical Design, Ltd., Oxford, England.

[12] The calculations were performed using the Chem-X molecular modelling program[11] using the default parameters which only take into account van der Waals interactions. The calculational method is an empirical force-field calculation that determines all non-bonded interactions between nuclei. The bond angles, lengths, and torsional angles for the structures on which the calculations were performed are as follows: M–P = 2.40 Å, M–CO = 1.75 Å, M–COMe = 2.15 Å, M–P–C_{ipso} = 109°, $\text{C}_\alpha\text{–M–P–C}_{ipso}$ = 0°, $\text{M–P–C}_{ipso}\text{–C}_{ortho}$ = 90°.

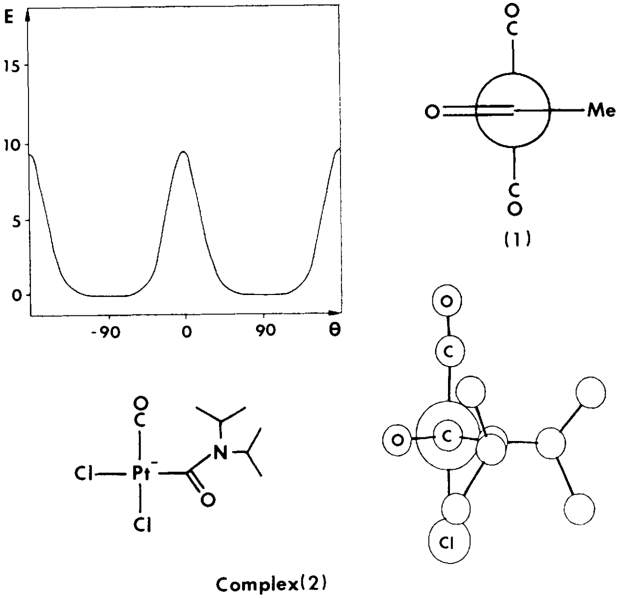
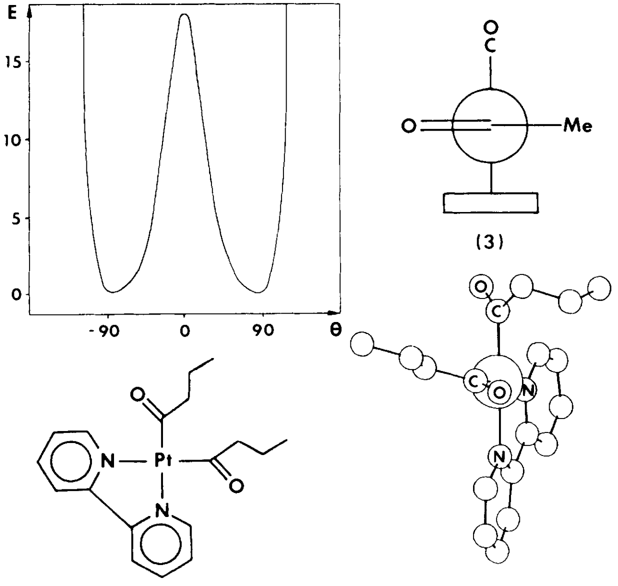


Figure 2 *Calculated energy profile for a square planar complex with two small proximate ligands* [M(CO)$_3$COMe] (1); X-*ray structure of anionic complex* (2).[13] *All the protons have been removed for clarity*

P–C_{ipso} was zero with the plane of the phenyl ring orthogonal to the plane defined by these atoms (Figure 1).[5]

For each idealized complex the acetyl group was permitted to rotate about the C_α–metal bond with the relative energies being calculated every five degrees. In each case a plot of relative energies [kcal mol^{-1} *vs* the torsional angle O–C_α–M–L (L = the largest ligand)] θ is given. Note that when the torsional angle θ is zero the acetyl oxygen is eclipsing the largest ligand and positive angles represent a counter-clockwise rotation. These calculations are not intended to predict the absolute energy of the barrier to rotation, but to provide insight into the inherent steric forces present in these complexes. In each case the computer simulation corresponds closely with the qualitative analysis obtained from inspection of molecular models. The calculated minimum energy conformation is represented alongside each energy diagram in the form of a Newman projection along C_α–M. Whenever available a crystal structure of a representative acyl complex or, on occasion, a formyl complex is shown.

A. Square Planar Complexes.—(i) *Two Small Proximate Ligands.* The calculated energy diagram for the model square planar complex [M(CO)$_3$COMe] (1) is shown in Figure 2. There is a bias against those conformations which would eclipse the acetyl ligand with the two proximate carbon monoxide ligands; the calculated



Complex(4)

Figure 3 *Calculated energy profile for a square planar complex with one large and one small proximate ligand* [M(CO)$_2$(PH$_2$Ph)COMe] (3); *X-ray structure of complex* (4).[14a] *All the protons have been removed for clarity*

energy minimum for complex (1) places the plane defined by the acetyl group orthogonal to the line described by M(CO)$_2$. A crystal structure for the square planar anionic complex (2) shows this complex adopts the calculated minimum energy conformation in the solid state.[13]

(ii) *One Large and One Small Proximate Ligand.* The calculated energy diagram for the model complex *cis*-[M(CO)$_2$(PH$_2$Ph)COMe] (3) is shown in Figure 3. Again the minimum energy conformation has the acetyl plane orthogonal to the line P–M–(CO), that is approximately parallel to the plane of the phenyl ring. It is of note that in order to interconvert the two degenerate minimum energy conformations the path involving eclipsing the acetyl methyl with the small carbon monoxide ligand is greatly favoured over the alternative of eclipsing the methyl with the large phosphine ligand. Several crystal structures for complexes of this type are known, all of which adopt the predicted conformation in the solid state;[14] that for complex (4) is illustrated in Figure 3.[14a] For complex (4) the acyl ligand lies close to the expected conformation with the acyl oxygen slightly tilted towards the large ligand.

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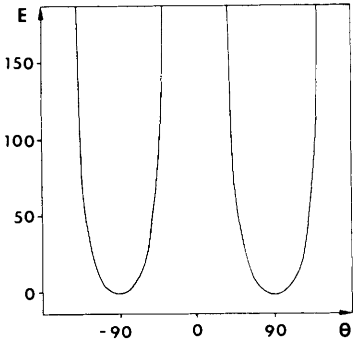
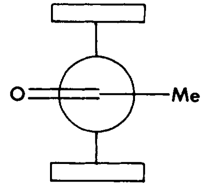
[13] D. B. Dell'Amico, F. Calderazzo, and G. Pelizzi, *Inorg. Chem.*, 1979, **18**, 1165.

[14] (*a*) R. J. Klingler, J. C. Huffman, and J. K. Kochi, *J. Am. Chem. Soc.*, 1982, **104**, 2147; (*b*) G. K. Anderson, R. J. Cross, K. W. Muir, T. Solomaun, and L. Manojlovic-Muir, *J. Organomet. Chem.*, 1979, **170**, 385; (*c*) A. Sen, J.-T. Chen, W. M. Vetter, and R. R. Whittle, *J. Am. Chem. Soc.*, 1987, **109**, 148.





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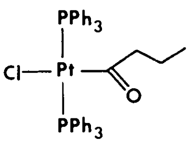

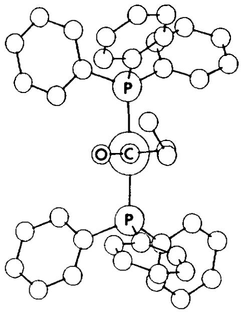

Complex(6)

Figure 4 *Calculated energy profile for a square planar complex with two large proximate ligands* [M(CO)($PH_2Ph)_2$COMe] (5); X-*ray structure of complex* (6).[15a] *All the protons have been removed for clarity*

(iii) *Two Large Proximate Ligands.* The calculated energy diagram for the model complex *trans*-[M(CO)($PH_2Ph)_2$COMe] (5) is shown in Figure 4. Two degenerate minima are again observed with the acetyl plane orthogonal to the P–M–P line. A relatively high energy barrier exists to the interconversion of these degenerate conformations which must involve eclipsing of the methyl group with one of the large phosphines. Crystal structures for many complexes of this type are available and the predicted conformation is adopted in each case.[15] The crystal structure for complex (6) is shown in Figure 4.[15a] Note that the two triphenylphosphine ligands proximate to the acyl ligand orientate their rotors such that the dihedral angles C_α–Pt–P–C_{ipso} are close to zero. Furthermore both the proximate phenyl rings are close to parallel to the acyl plane, being somewhat tilted in each case to widen the gap occupied by the large alkyl chain and consequently tighten the gap occupied by the relatively small acyl oxygen. Nonetheless this structure serves to demonstrate the validity of the model chosen for the computer simulations.

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[15] (*a*) R. Bardi, A. M. Piazzesi, G. Cavinato, P. Cavoli, and L. Toniolo, *J. Organomet. Chem.*, 1982, **224**, 407; (*b*) L. N. Zhir-Lebed,L. G. Kuzmina, Y. T. Struchkov, O. N. Temkin, and V. A. Golodov, *Koord. Khim.*, 1978, **4**, 1046; (*c*) R. Bardi, A. M. Piazzesi, A. Del Pra, G. Cavinato, and L. Toniolo, *J. Organomet. Chem.*, 1982, **234**, 107; (*d*) W. Fengsham, F. Yuguo, and C. Qiuzi, *Chem. J. Chin. Univ.*, 1984, **5**, 699; (*e*) M. A. Bennett, K.-C. Ho, J. C. Jeffrey, G. M. McLaughlin, and G. B. Robertson, *Aust. J. Chem.*, 1982, **35**, 1311; (*f*) P. Stoppioni, P. Dapporto, and L. Sacconi, *Inorg. Chem.*, 1978, **17**, 718; (*g*) E. Carmona, F. Gonzalez, M. L. Poveda, J. L. Atwood, and R. D. Rodgers, *J. Chem. Soc., Dalton Trans.*, 1980, 2108; (*h*) P. L. Bellon, M. Manassero, F. Porta, and M. Sansoni, *J. Organomet. Chem.*, 1974, **80**, 139; (*i*) G. Del Piero and M. Cesari, *Acta Crystallogr. B*, 1979, **35**, 2411.

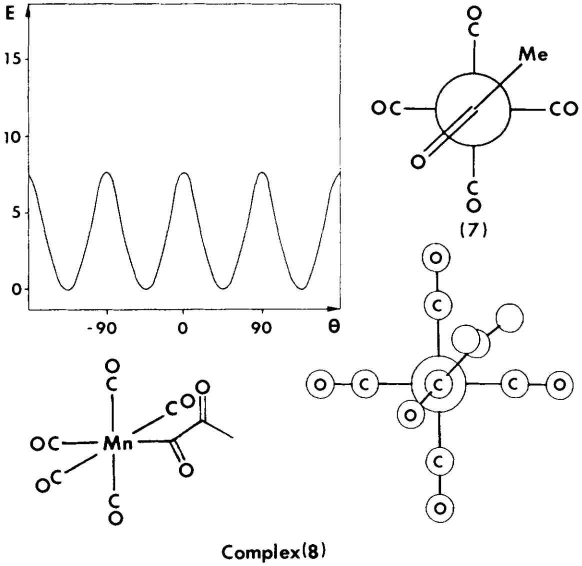

Figure 5 *Calculated energy profile for an octahedral complex with four small proximate ligands* [M(CO)$_5$COMe] (7); X-*ray structure of complex* (8).[16a] *All the protons have been removed for clarity*

B. Octahedral Complexes.—(i) *Four Small Proximate Ligands.* The calculated energy diagram for the model complex [M(CO)$_5$COMe] (7), Figure 5, suggests four degenerate minimum energy conformations with the acetyl group staggered with respect to the proximate carbon monoxide ligands. Complex (8) adopts such a staggered conformation in the solid state.[16a] Other complexes of this type also adopt the predicted conformation in the solid state.[16]

(ii) *One Large and Three Small Proximate Ligands.* The calculated energy diagram for the model complex *cis*-[M(CO)$_4$(PH$_2$Ph)COMe] (9), Figure 6, indicates two stable conformations where the acetyl ligand is staggered with respect to the four proximate ligands. The small oxygen atom is shown to reside between the carbon monoxide and phosphine ligands with the larger methyl group between two small carbon monoxide ligands. Each of the acetyl groups in the bis-acetyl anion (10)[17a] adopts the predicted minimum energy conformation in the solid state. This predicted conformation is also observed in other reported crystal structure determinations for this type of complex.[17]

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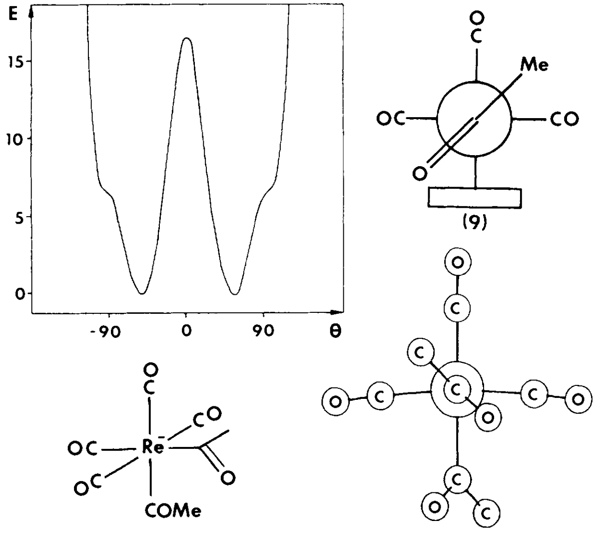
[16] (*a*) C. A. Casey, C. A. Bunnell, and J. C. Calabrese, *J. Am. Chem. Soc.*, 1976, **98**, 1166; (*b*) I. S. Astakhova, V. A. Semion, and Y. T. Struchkov, *Zh. Strukt. Khim.*, 1969, **10**, 508; (*c*) E. J. M. De Boer, J. De With, N. Meijboom, and A. G. Orpen, *Organometallics*, 1985, **4**, 259.

[17] (*a*) P. G. Lenhert, C. M. Lukehart, P. D. Sotiropoulos, and K. Srinivasan, *Inorg. Chem.*, 1984, **23**, 1807; (*b*) C. P. Casey and C. A. Bunnell, *J. Am. Chem. Soc.*, 1976, **98**, 436; (*c*) A. Mayanza, J.-J. Bonnet, J. Galy, P. Kalck, and R. Poilblanc, *J. Chem. Res.* (*S*), 1980, **146**, 2101; (*d*) C.-H. Cheng, B. D. Spivack, and R. Eisenberg, *J. Am. Chem. Soc.*, 1977, **99**, 3003.



Complex (10)

Figure 6 *Calculated energy profile for an octahedral complex with one large and three small proximate ligands* [M(CO)$_4$(PH$_2$Ph)COMe] (9); X-*ray structure of anionic complex* (10).[17a] *All the protons have been removed for clarity*

(iii) *Two Large and Two Small Proximate Ligands.* The calculated energy profiles for the model complexes *fac*-[M(CO)$_3$(PH$_2$Ph)$_2$COMe] (11) and *mer*-[M(CO)$_3$(PH$_2$Ph)$_2$COMe] (13) are shown in Figures 7 and 8 respectively. When the two large phosphine ligands are *cis* a single minimum energy conformation is predicted with the acetyl oxygen lying staggered between the two phosphines. The crystal structure for the complex (12) illustrates this feature,[18a] which is common to all other reported structures for this type of complex.[18]

When the two phosphine ligands are *trans*, however, two degenerate conformations are expected where the acetyl group eclipses the small carbon monoxide ligands. The one known example, for which the *X*-ray crystal structure data are available, of this type of complex, {[(PhO)$_3$P]$_3$(CO)$_2$MnCHO} (14), adopts the expected conformation in the solid state.[19]

(iv) *Three Large and One Small Proximate Ligands.* In the calculated minimum energy conformation for the model complex *mer*-[M(CO)$_2$(PH$_2$Ph)$_3$COMe] (15), Figure 9, the small acetyl oxygen is close to eclipsing the central phosphine and the methyl close to eclipsing the small carbon monoxide ligand. Once again the dominant interactions are those between the methyl hydrogens and the phosphine

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[18] (*a*) J. R. Anglin, H. P. Calhoun, and W. A. G. Graham, *Inorg. Chem.*, 1977, **16**, 2281; (*b*) M. F. McGuiggan, D. H. Doughty, and L. H. Pignolet, *J. Organomet. Chem.*, 1980, **185**, 241.

[19] (*a*) H. Berke, G. Huttner, O. Scheidster, and G. Weiler, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 735; (*b*) H. Berke, G. Weiler, G. Huttner, and O. Orama, *Chem. Ber.*, 1987, **120**, 297.

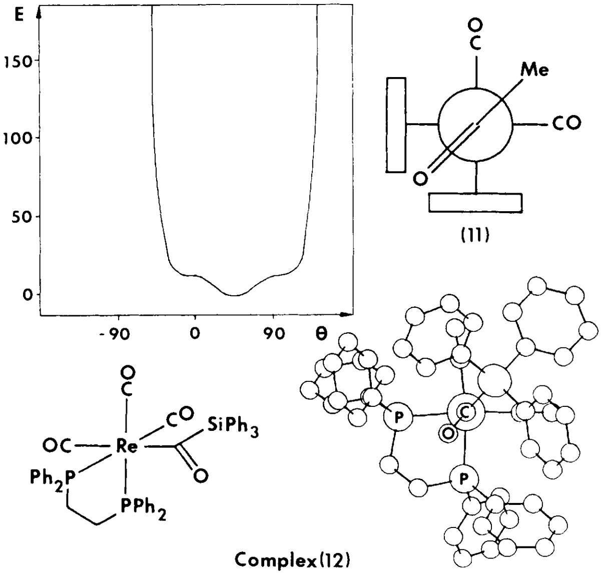

Figure 7 *Calculated energy profile for an octahedral complex with two large* cis *and two small proximate ligands* fac-[M(CO)$_3$(PH$_2$Ph)$_2$COMe] (11); X*-ray structure of complex* (12).[18a] *All the protons have been removed for clarity*

phenyls. The acyl complex (16)[20a] adopts the predicted conformation in the solid state, as do other complexes of this type.[20]

(v) *Four Large Proximate Ligands*. This case parallels that for the four small proximate ligands except that the energy barriers for the interconversion of the four degenerate staggered conformations are very much larger. Figure 10 shows the calculated energy profile for the model complex *trans*-[M(CO)(PH$_2$Ph)$_4$COMe] (17). All known structures of this class of compounds[21] adopt the predicted conformation, which is illustrated by the cationic formyl complex (18).[21a]

C. Square Pyramidal Complexes.—The conformational analysis for square pyramidal complexes where the acyl ligand is axial exactly parallels that for the corresponding octahedral complexes, as illustrated by the Newman projection (19). However because of the increased bond angles between C_α and any of the other ligands the energy barriers can be expected to be lower for the square pyramidal

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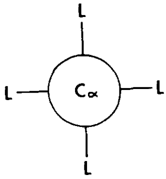
[20] S. A. Chawdhury, Z. Dauter, J. Mawby, C. D. Reynolds, D. R. Saunders, and M. Stephenson, *Acta Crystallogr., C (Cryst. Struct. Commun.)*, 1983, **39**, 985; (*b*) D. Milstein, W. C. Fultz, and J. C. Calabrese, *J. Am. Chem. Soc.*, 1986, **108**, 1336; (*c*) G. W. Adamson, J. J. Daly, and D. Forster, *J. Organomet. Chem.*, 1974, **71**, C17.

[21] (*a*) G. Smith, D. J. Cole-Hamilton, M. Thorton-Pett, and M. B. Hursthouse, *Polyhedron*, 1983, **2**, 1241; (*b*) R. L. Harlow, J. B. Kinney, and T. Herskovitz *J. Chem. Soc., Chem. Commun.*, 1980, 813; (*c*) G. Smith, D. J. Cole-Hamilton, M. Thorton-Pett, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1983, 2501.



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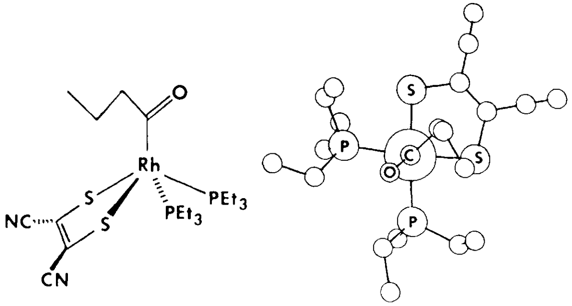
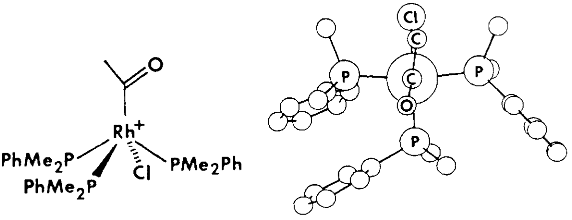
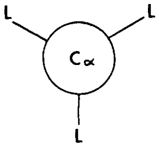


Complex(20)



Complex(21)



(22)

structures than for the corresponding octahedral complexes. Known examples of this type of complex adopt the structure in the solid state which is predicted for the corresponding octahedral complexes.[22–25] Complexes (20),[22a] with two large *cis* ligands, and the cation (21),[23] with three large ligands, illustrate the applicability of the analysis.

For square pyramidal complexes where the acyl is basal, Newman projection (22), the conformational analysis will parallel that for the trigonal bipyramid structures outlined below. However to date there are no representative crystal structure determinations available to test this hypothesis.

D. Trigonal Bipyramidal.—If the acyl ligand is equatorial the analysis parallels that described for the square planar complexes above. The analysis for axial acyl complexes is outlined below.

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[22] (*a*) C.-H. Cheng, and R. Eisenberg, *Inorg. Chem.*, 1979, **18**, 1418; (*b*) C.-H. Cheng, D. E. Hendriksen, and R. Eisenberg, *J. Organomet. Chem.*, 1977, **142**, C65.

[23] M. A. Bennett, J. C. Jeffrey, and G. B. Robertson, *Inorg. Chem.*, 1981, **20**, 323.

[24] D. L. Egglestone, M. C. Baird, C. J. L. Lock, and G. Turner, *J. Chem. Soc., Dalton Trans.*, 1977, 1576. The *X*-ray crystal structure reported in this article has come under close scrutiny and is deemed unreliable.[22]

[25] B. B. Wayland, B. A. Woods, and R. J. Pierce, *J. Am. Chem. Soc.*, 1982, **104**, 302.

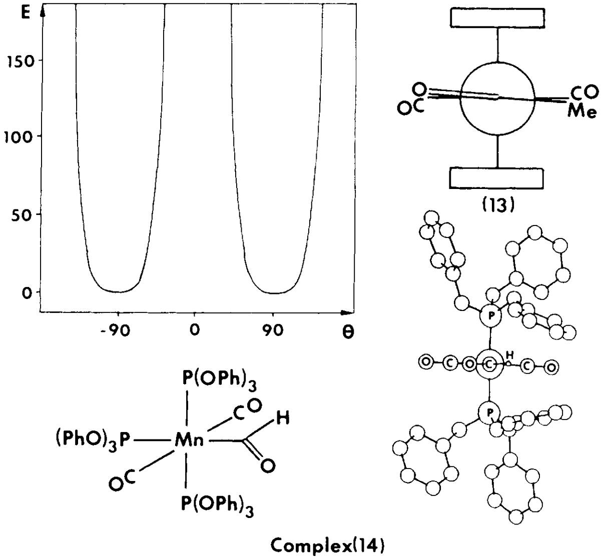


Figure 8 *Calculated energy profile for an octahedral complex with two large* trans *and two small proximate ligands* mer-[M(CO)$_2$(PH$_2$Ph)$_3$COMe] (13); X-*ray structure of complex* (14).[19b] *All the protons and the* P(OPh)$_3$ *ligand* trans *to the formyl ligand have been removed for clarity*

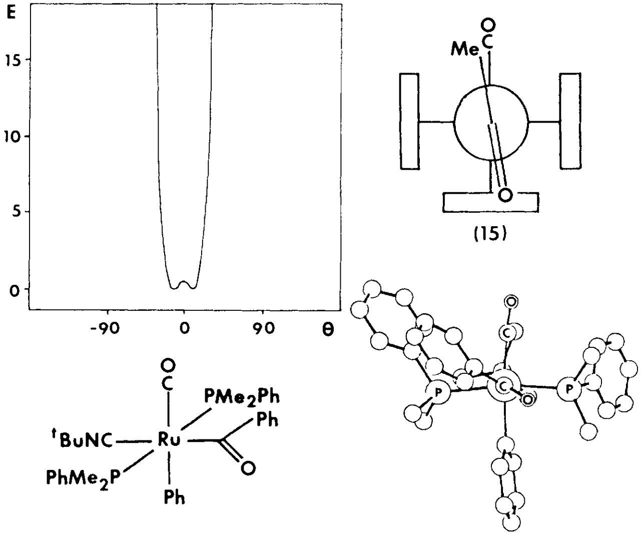


Figure 9 *Calculated energy profile for an octahedral complex with three large and one small proximate ligands* mer-[M(CO)$_2$(PH$_2$Ph)$_3$COMe] (15); X-*ray structure of complex* (16).[20a] *All the protons have been removed for clarity*

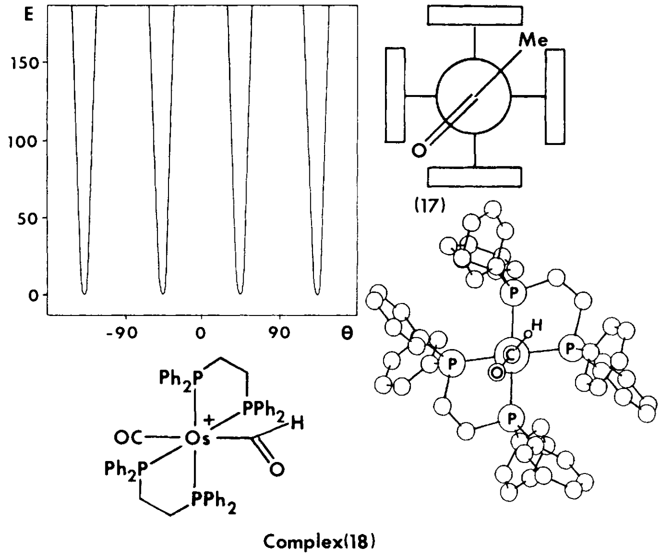


Figure 10 *Calculated energy profile for an octahedral complex with four large proximate ligands* trans-[M(CO)($PH_2Ph)_4$COMe] (17); *X-ray structure of cationic complex* (18).[21a] *All the protons have been removed for clarity*

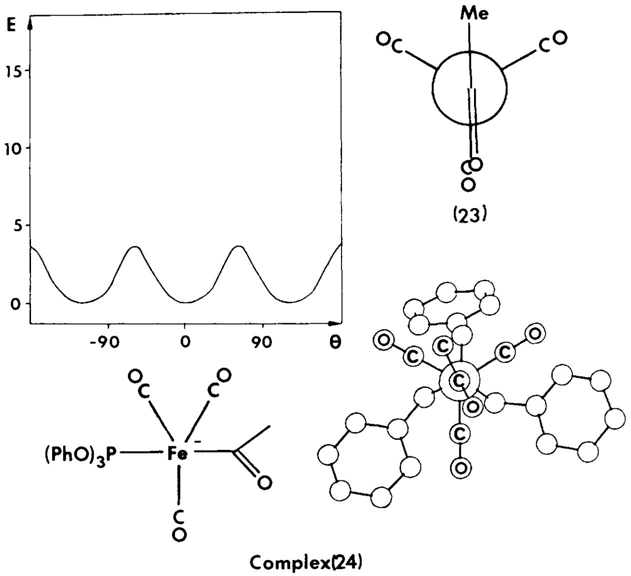
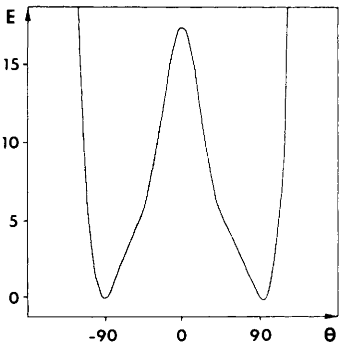


Figure 11 *Calculated energy profile for a trigonal bipyramidal complex with three small proximate ligands* [M(CO)$_4$COMe] (23); *X-ray structure of anionic complex* (24).[26a] *All the protons have been removed for clarity*



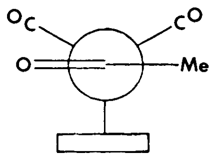


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Figure 12 *Calculated energy profile for a trigonal bipyramidal complex with one large and two small proximate ligands* cis-[$M(CO)_3(PH_2Ph)COMe$] (25)

(i) *Three Small Proximate Ligands.* The calculated energy profile for the model complex [$M(CO)_4COMe$] (23) is shown in Figure 11. The minimum energy conformation staggers the large methyl group between two carbon monoxide ligands, and consequently eclipses the acetyl oxygen with a carbon monoxide ligand. There are therefore three degenerate minimum energy conformations. The structure of anion (24) shows it to adopt a conformation close to the expected one in the solid state.[26a] It is noteworthy that the triphenylphosphite ligand *trans* to the acyl staggers itself relative to the three proximate carbon monoxide ligands. Other complexes of this type adopt the predicted conformation in the solid state.[26]

(ii) *One Large and Two Small Proximate Ligands.* The calculated conformational energy profile for the model complex *cis*-[$M(CO)_3(PH_2Ph)COMe$] (25) is shown in Figure 12. In the minimum energy conformation the acetyl ligand is orthogonal to the metal–phosphorus bond, thus minimizing the steric interactions between the methyl and acetyl oxygen with the large phosphine ligand. There are currently no examples of structures in this class of complex.

CAVEAT: The latter analysis assumes that the phosphine orientates itself to eclipse the C_α–M and P–C_{ipso} bonds, as in structure (25). If however these bonds are staggered then the conformational analysis applicable to structure (11) (octahedral with two large *cis* proximate ligands) pertains, *i.e.* the acyl oxygen will eclipse the phosphorus atom, that is staggered between the two large phenyl rings. This situation exists in complex (26)[27] where the bridge between the phosphines imposes such a conformation on the diphenylphosphine residue proximate to the acyl ligand. Figure 13 shows the calculated conformational energy profile for the related bis-(diphenylphosphino)ethane-substituted trigonal bipyramidal acetyl

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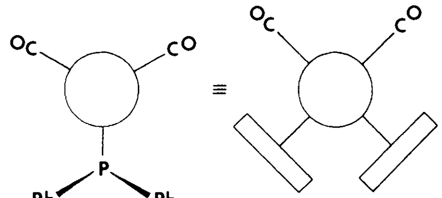
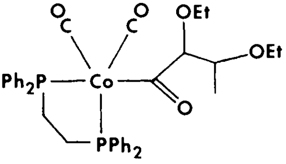
[26] (*a*) C. P. Casey, M. W. Meszaros, S. M. Neumann, I. G. Cesa, and K. J. Haller, *Organometallics*, 1985, **4**, 143; (*b*) D. Milstein and J. L. Huckaby, *J. Am. Chem. Soc.*, 1982, **104**, 6150; (*c*) K. H. Dötz, U. Wenicker, G. Muller, H. Alt, and D. Seyferth, *Organometallics*, 1986, **5**, 2570; (*d*) V. Galamb, G. Palyi, F. Unguary, L. Marko, R. Boese, and G. Schmid, *J. Am. Chem. Soc.*, 1986, **108**, 3344; (*e*) J. B. Wilford and H. M. Powell, *J. Chem. Soc. A*, 1967, 2092; (*f*) M. Roper and C. Kruger, *J. Organomet. Chem.*, 1988, **339**, 159.

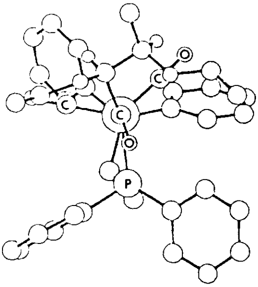
[27] A. R. Cutler, C. C. Tso, and R. K. Kullnig, *J. Am. Chem. Soc.*, 1987, **109**, 5844.



(11)



Complex(26)



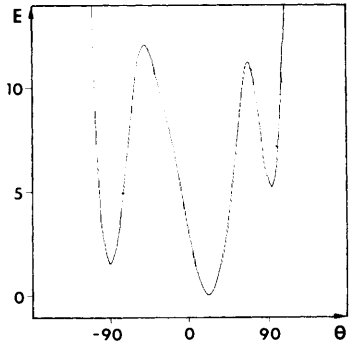


Figure 13 X-*Ray structure of complex* (26)[27] (*all the protons have been removed for clarity*); *energy profile calculated from* X-*ray structure of complex* (26)[28]

complex.[28] The preferred conformation predicted for the acetyl complex is that where the acetyl oxygen nearly eclipses the metal–phosphorus bond, which is similar to that found in the *X*-ray crystal structure of complex (26).[27]

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[28] This calculation was performed using CHEM-X molecular modelling program[11] on the basis of the reported *X*-ray crystal structure determination[27] using the default parameters that only take into account van der Waals interactions.

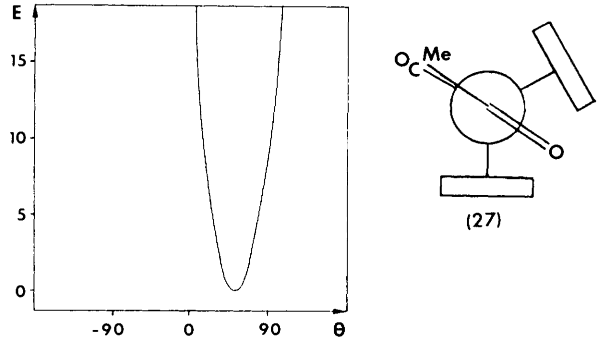


Figure 14 *Calculated energy profile for a trigonal bipyramidal complex with two large and one small proximate ligands* [$M(CO)_2(PH_2Ph)_2COMe$] (27)

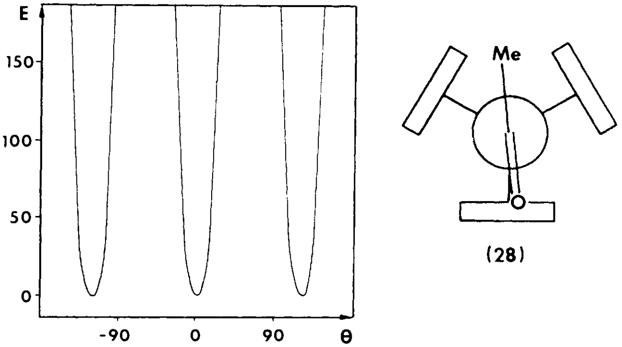
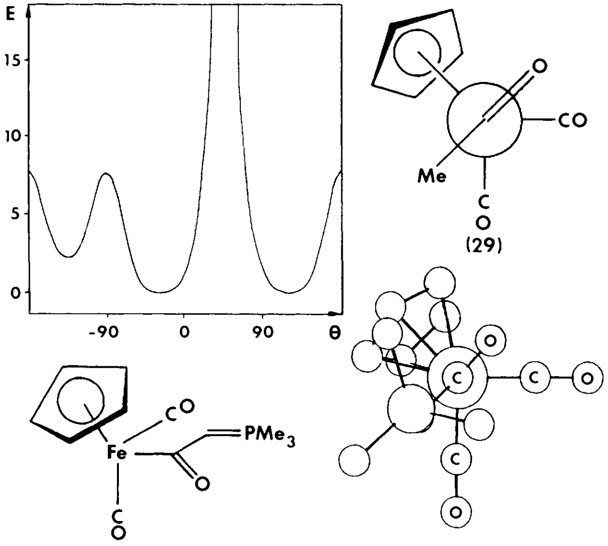


Figure 15 *Calculated energy profile for a trigonal bipyramidal complex with three large proximate ligands* trans-[$M(CO)(PH_2Ph)_3COMe$] (28)

(iii) *Two Large and One Small Ligands.* The calculated conformational energy profile for the model complex *cis*-[$M(CO)_2(PH_2Ph)_2COMe$] (27) is shown in Figure 14. The minimum energy conformation staggers the small acetyl oxygen between the two large phosphines and consequently eclipses the methyl with the proximate carbon monoxide ligand. There are no known examples of this type of complex.

(iv) *Three Large Ligands.* The calculated conformational energy profile for the model complex *trans*-[$M(CO)(PH_2Ph)_3COMe$] (28) is shown in Figure 15. It parallels that for the three small ligand case (Figure 11) except that the energy barriers for interconversion of the three degenerate minimum energy conformations will be much larger. Again, there are no known *X*-ray crystal structure determinations of a complex of this type.

E. Tetrahedral Complexes.—The conformational analysis for the tetrahedral complexes parallels that for the corresponding trigonal bipyramid complexes described



Complex(30)

Figure 16 *Calculated energy profile for a pseudo-octahedral cyclopentadienyl complex with two small ligands* [η^5-C_5H_5)M(CO)$_2$COMe] (29); X-*ray structure of complex* (30).[29a] *All the protons have been removed for clarity*

above. However, rotational energy barriers will be lower for tetrahedral acyl complexes than for the analogous trigonal bipyramid complexes, because of the increased bond angles between C_α and any of the proximate ligands.

F. Pseudo-octahedral Cyclopentadienyl Complexes.—By examination of the available *X*-ray crystallographic data the cyclopentadienyl complexes [(η^5-C_5H_5)ML_3] are best described as pseudo-octahedral, where each of the three ligands L are orthogonal to each other.[5] Thus, the three ligands L occupy adjacent coordination sites of an octahedron with the cyclopentadienyl ligand occupying the three remaining coordination sites.

(i) *Two Small Ligands.* The calculated conformational energy profile for the model complex [(η^5-C_5H_5)M(CO)$_2$COMe] (29) is shown in Figure 16. The two degenerate minimum energy conformations place the acetyl orthogonal to the metal–cyclopentadienyl centroid line. Complex (30) adopts this conformation in the solid state,[29a] as do other examples.[29]

(ii) *One Large and One Small Ligand.* The calculated conformational energy diagram for the model complex [(η^5-C_5H_5)M(CO)(PH_2Ph)COMe] (31) is shown in Figure 17. The minimum energy conformation places the small acetyl oxygen

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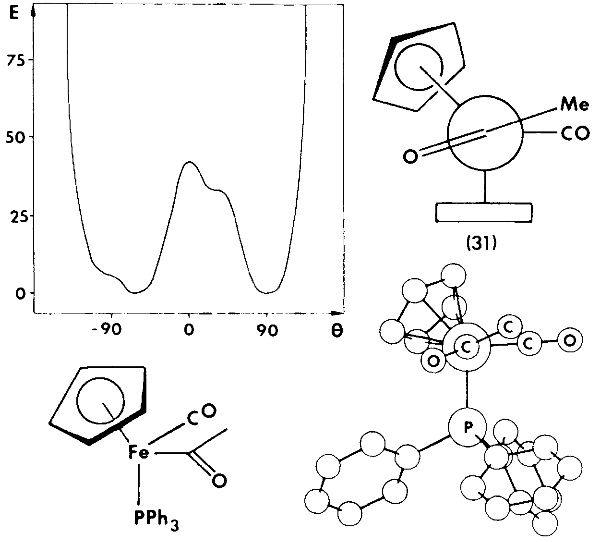
[29] (*a*) H. Blau, W. Malisch, S. Voran, K. Blank, and C. Kruger, *J. Organomet. Chem.*, 1980, **202**, C33; (*b*) A. Eisenstadt, F. Frolow, and A. Efraty, *J. Chem. Soc.. Dalton Trans.*, 1982, 1013; (*c*) J. B. Sheridan and G. L. Geoffroy, *J. Am. Chem. Soc.*, 1987, **109**, 1584.



Complex(32)

Figure 17 *Calculated energy profile for a pseudo-octahedral cyclopentadienyl complex with one large and one small ligand* [(η^5-C_5H_5)M(CO)(PH_2Ph)COMe] (31); *X-ray structure of complex* (32).[30a] *All the protons have been removed for clarity*

between the cyclopentadienyl and the largest ligand, the phosphine. The iron acetyl complex (32)[30a] conforms to this prediction and further consideration to its conformational properties is given below. Similarly, the predicted conformation is adopted by the other known examples.[30]

(iii) *Two Large Ligands.* The calculated conformational energy profile for the model complex [(η^5-C_5H_5)M($PH_2Ph)_2$COMe] (33), which possesses idealized bond angles ($\theta = 90°$) between the two large ligands, is shown in Figure 18a. The two degenerate minimum energy conformations place the acyl oxygen between the cyclopentadienyl ligand and one of the phosphine ligands. This conformation is adopted in the solid state by most known examples,[31a,b] however, it is not observed in the solid state for complex (34)[31c] where the acyl oxygen resides between the two

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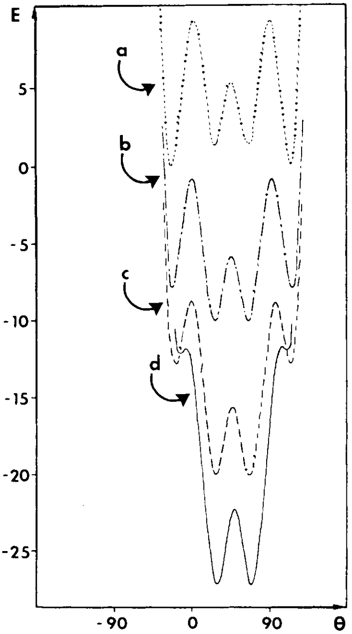
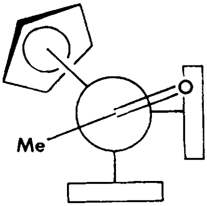
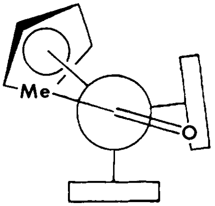
[30] (*a*) I. Bernal, H. Brunner, and M. Muschiol, *Inorg. Chim. Acta*, 1988, **142**, 235; (*b*) G. J. Baird, J. A. Bandy, S. G. Davies, and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1983, 1202; (*c*) V. A. Semion and Y. T. Struchkov, *Zh. Strukt. Khim.*, 1969, **10**, 664; (*d*) G. M. Reisner, I. Bernal, H. Brunner, and L. Muschliol, *Inorg. Chem.*, 1978, **17**, 783; (*e*) S. G. Davies, I. M. H. Dordor-Hedgecock, K. H. Sutton, and J. C. Walker, *Tetrahedron*, 1986, **42**, 5123; (*f*) S. G. Davies, I. M. H. Dordor-Hedgecock, K. H. Sutton, J. C. Walker, C. Bourne, R. H. Jones, and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1986, 607; (*g*) P. Helquist and E. J. O'Connor, *J. Am. Chem. Soc.*, 1982, **104**, 1869; (*h*) G. J. Baird, S. G. Davies, R. H. Jones, K. Prout, and P. Warner, *J. Chem. Soc., Chem. Commun.*, 1984, 745; (*i*) G. O. Nelson and C. E. Sumner, *Organometallics*, 1986, **5**, 1983; (*j*) K. H. Pannell, R. N. Kapoor, M. Wells, and T. Giasolli, *Organometallics*, 1987, **6**, 663.

[31] (*a*) H. Felkin, B. Meunier, C. Pascard, and T. Prange, *J. Organomet. Chem.*, 1977, **135**, 361; (*b*) H. Werner, L. Hofmann, and R. Zolk, *Chem. Ber.*, 1987, **120**, 379; (*c*) H. G. Alt, M. E. Eichner, B. M. Jansen, and U. Thewalt, *Z. Naturforsch., Teil B*, 1982, **37**, 1109.

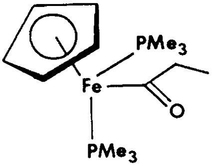


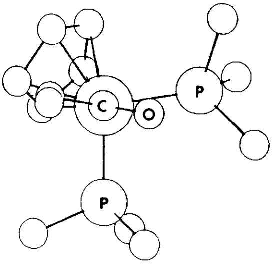


(33)



(35)





Complex (34)

Figure 18 *Calculated energy profile for a pseudo-octahedral cyclopentadienyl complex with two large ligands* $[(\eta^5\text{-}C_5H_5)M(PH_2Ph)_2COMe]$ (33) {θ(< P–M–P) = (*a*) 90° [· · ·]; (*b*) 92° [- - · - -]; (*c*) 95° [- - -]; (*d*) 100° [———]}; *X-ray structure of complex* (34).[31c] *All the protons have been removed for clarity*

large phosphines. The angle between the two PMe_3 ligands in (34), however, is larger (θ = 99.1°) than in the model complex (33). Revision of the model by widening the bond angle between the two phosphorus atoms results in new calculated energy diagrams (Figure 17b—d). It was calculated that even a small change of only two degrees results in a new energetically favoured conformation, (35), which is similar to that observed for complex (34) in the solid state.

The predicted conformations for the types of pseudo-octahedral cyclopentadienyl complexes described above are related by isolobal analogy[32] to the predictions made for the octahedral complexes (Sections B i—iii). Figure 19 shows

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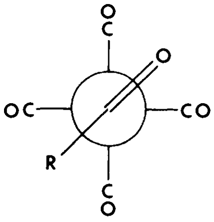
[32] (*a*) A. R. Pinhas, T. A. Albright, P. Hofmann, and R. Hoffmann, *Helv. Chem. Acta*, 1980, **63**, 29; (*b*) R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 711.



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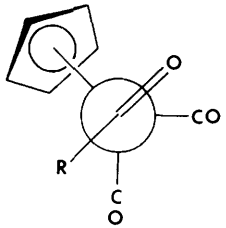
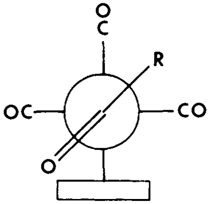


(7) (29)



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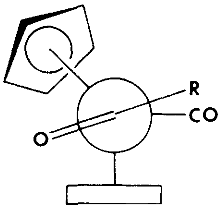
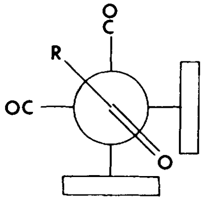


(9) (31)



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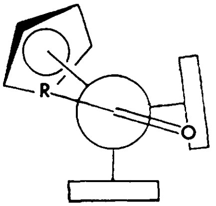

(11) (35)

Figure 19 *Illustration of isolobal analogies between octahedral and the corresponding pseudo-octahedral complexes*

this relationship between the preferred conformation for an acetyl ligand attached to octahedral and the corresponding pseudo-octahedral types of complexes. This relationship results from substituting three coordination sites in the octahedral complexes, each occupied by a small carbon monoxide ligand, by a cyclopentadienyl ligand, which is representative of a medium sized ligand, in the pseudo-octahedral complexes. Thus the preferred conformations for the octahedral complexes are directly analogous to those predicted for the corresponding cyclopentadienyl complexes, after adjustments to take into account the medium size of the cyclopentadienyl ligand. The influence of steric interactions on acyl con-

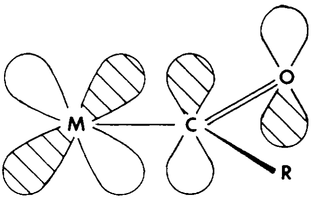

Figure 20 *Graphical representation of* d_π–p_{π^*} *orbital overlap*

formation by other types of ligands not covered here can, therefore, be accomplished through consideration of their relative steric size and isolobal analogy.

3 Electronic and Electrostatic Contributions to the Preferred Conformation

A. Stereoelectronic Effects.—The above analysis correctly correlates prediction of acyl geometry based on steric interactions to the wealth of *X*-ray crystallographic data available, thus providing a working hypothesis whereby the preferred conformation of an η^1-acyl complex may be confidently predicted; acyl geometry is predominately dictated by steric interactions. However, this simple rule does not allow for stereoelectronic contributions arising from electron delocalization of a lone pair of electrons on the metal into the π^* orbital of the acyl ligand. Resonance stabilization of this type, through d_π–p_{π^*} orbital overlap,[33–35] is maximized when the acyl ligand lies perpendicular to a filled molecular orbital, of the correct symmetry and energy, on the metal fragment (Figure 20). Only when such a stereoelectronic contribution outweighs the steric effects will it take precedence in defining acyl geometry.

Three situations may be envisioned for organotransition metal complexes, namely when there are zero, one, or two lone pairs of electrons in high lying molecular orbitals on the metal that are of the appropriate symmetry to participate in d_π–p_{π^*} orbital overlap. For metal fragments with zero lone pairs no stereoelectronic effect can exist. Metal fragments with two lone pairs, which lie orthogonal to each other, will exert a stereoelectronic influence on the acyl ligand but it will not be directional. For metal fragments with one lone pair of electrons, however, a directional stereoelectronic effect on acyl conformation may exist. Figure 21 illustrates the stereochemical influence of zero (a), one (b), and two (c) pairs of electrons on the metal fragment in relation to the preferred acyl conformation. For zero lone pairs of electrons there is no significant d_π–p_{π^*} orbital overlap and thus no stereoelectronic effect. Evidence in support of this is the commonly observed shortening of the M–C_α bond of approximately 0.2 Å when going from zero to one (or more) lone pairs of electrons on the metal. For example, the rhenium complex [$(CO)_5ReCOC_6H_4Cl$], having zero lone pairs (*vide infra*),

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[33] (*a*) P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, *Inorg. Chem.*, 1966, **5**, 177; (*b*) M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, 1968, **7**, 953.

[34] E. Hadicke and W. Hoppe, *Acta Crystallogr.*, *B*, 1971, **27**, 760.

has a M–C_α bond length of 2.22 Å[16b] whereas the rhenium acyl complex *RS*,*SR*-[(η^5-C_5H_5)Re(NO)(PPh_3)COCH(Me)CH_2Ph], which has one lone pair of electrons (*vide infra*), is observed to have a M–C_α bond length of 2.08 Å.[35b,c] Two orthogonal, energetically similar lone pairs of electrons (Figure 21c) are able to participate equally in orbital overlap and in consequence do not exert a conformational preference on the acyl ligand. Therefore, when there is zero, two, or more lone pairs of electrons centred at the metal, steric interactions will dominate conformational preferences. Only in the case where there is a single, energetically distinct lone pair of electrons (or HOMO) on the metal fragment can there be a significant stereoelectronic influence on acyl conformation.

Clearly, therefore, only for complexes where a single lone pair of electrons is centred at the metal is it necessary to consider the influence of stereoelectronic preferences. The number of lone pairs of electrons on the metal can be readily determined by the following method, which is in accordance with previously reported theoretical analyses of the frontier orbitals of ML_n fragments.[36–40]

(i) Considering the complex of interest determine the number of valence *d*-electrons of the metal (Group Number)[41] and subtract (for positively charged complexes) or add (for negatively charged complexes) the total charge of the complex. Subtract from this number the number of hydrocarbon ligands with odd *hapto* (η) numbers and the number of other odd electron ligands (*e.g.* hydride, halide, nitrosyl, *etc.*). Finally, divide by two to give the total number of electron pairs potentially available for backbonding. (When the result is a count of four reduce by one, since the fourth lone pair is in an orbital inappropriate for backbonding according to the rules of symmetry.[42])

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[35] (*a*) W. K. Wong, W. Tam, C. E. Strouse, and J. A. Gladysz, *J. Chem. Soc., Chem. Commun.*, 1979, 530; (*b*) D. E. Smith and J. A. Gladysz, *Organometallics*, 1985, **4**, 1480; (*c*) G. S. Bodner, A. J. Patton, D. E. Smith, S. Georgiou, W. Tam, W.-K. Wong, C. E. Strouse, and J. A. Gladysz, *Organometallics*, 1987, **6**, 1954.

[36] T. A. Albright, J. K. Burdett, M.-H. Whangbo, 'Orbital Interactions in Chemistry', Wiley Interscience: New York, 1985 and references cited therein.

[37] (*a*) M. Elian and R. Hoffmann, *Inorg. Chem.*, 1975, **14**, 1059; (*b*) R. Hoffmann, *Science*, 1981, **211**, 995; (*c*) T. A. Albright, *Tetrahedron*, 1982, **38**, 1339; (*c*) D. E. Sherwood and M. B. Hall, *Inorg. Chem.*, 1983, **22**, 93; (*d*) D. E. Sherwood and M. B. Hall, *Inorg. Chem.*, 1980, **19**, 1805; (*e*) R. Hoffmann and P. Hofmann, *J. Am. Chem. Soc.*, 1981, **103**, 4320; (*f*) P. Kubacek and R. Hoffmann, *J. Am. Chem. Soc.*, 1981, **103**, 4320; (*g*) T. Ziegler and A. Rauk, *Inorg. Chem.*, 1979, **18**, 1755; (*h*) J. L. Templeton, P. B. Winston, and B. C. Ward, *J. Am. Chem. Soc.*, **1981**, **103**, 7713; (*i*) R. Hoffmann and H. Berke, *J. Am. Chem. Soc.*, 1978, **100**, 7224; (*j*) R. Hoffmann and A. R. Rossi, *Inorg. Chem.*, 1975, **14**, 365; (*k*) J. K. Burdett, *Inorg. Chem.*, 1975, **14**, 375; (*l*) *idem*, *J. Chem. Soc., Faraday Trans. 2*, 1971, **70**, 1599; (*m*) D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1977, 602; (*n*) P. Hofmann, *Angew. Chem.*, 1977, **15**, 1.

[38] (*a*) R. Hoffman, B. E. R. Schilling, and D. L. Lichtenberger, *J. Am. Chem. Soc.*, 1979, **101**, 585; (*b*) B. E. R. Schilling, R. Hoffmann, and J. W. Faller, *J. Am. Chem. Soc.*, 1979, **101**, 592.

[39] (*a*) R. F. Fenske, M. C. Milletti, and M. Arndt, *Organometallics*, 1986, **5**, 2316; (*b*) W. A. Kiel, G.-Y. Lin, A. G. Constable, F. B. McCormick, C. E. Strouse, O. Eisenstein, and J. A. Gladysz, *J. Am. Chem. Soc.*, 1982, **104**, 4865; (*c*) S. Georgiou and J. A. Gladysz, *Tetrahedron*, 1986, **42**, 1109.

[40] (*a*) D. M. P. Mingos, *Adv. Organomet. Chem.*, 1977, **15**, 1; (*b*) D. M. P. Mingos, 'Bonding of Unsaturated Organic Molecules to Transition Metals' in *Comprehensive Organometallic Chemistry*; ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon Press: New York, 1982, Vol. 3, 1; (*c*) T. A. Albright, R. Hoffmann, J. C. Thibeault, and D. L. Thorn, *J. Am. Chem. Soc.*, 1979, **101**, 3801; (*d*) O. Eisenstein and R. Hoffmann, *J. Am. Chem. Soc.*, 1981, **103**, 4308.

[41] The Group Number refers to the new periodic group notation recently adopted by the IUPAC and ACS nomenclature committees. Ligands are classified according to ref. 2*a* page 2.

[42] By definition, only up to three orbitals may have the appropriate symmetry to participate in orbital mixing with a ligand p_{π^*} orbital.

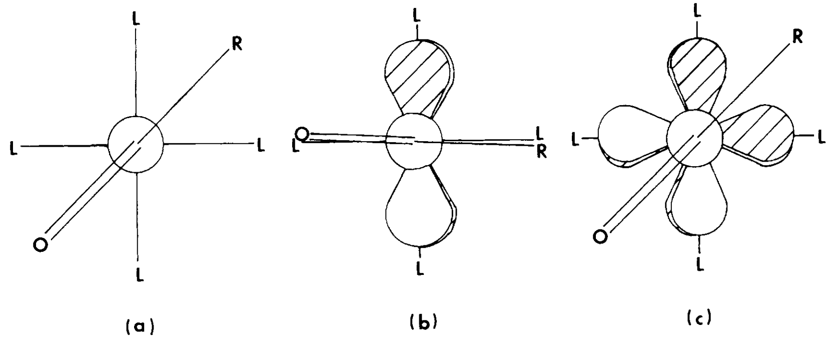

Figure 21 *Implications for acyl ligand conformation on metal fragments with (a) zero, (b) one, and (c) two lone pairs of electrons*

(ii) Now, only considering the ligands on the ML_n fragment, reduce the number of electron pairs (0—3) by one (1) for every pair of *trans* π acidic ligands (*e.g.* carbon monoxide, linear nitrosyl, isonitrile ligands, *etc.*) and one for all other strongly π acidic ligands.*

A calculation of this sort will yield a count of zero to three lone pairs of electrons where a result of one lone pair is of particular interest.

In order to predict acyl conformation, it is necessary to determine the orientation of the HOMO containing the single lone pair of electrons, since the acyl ligand will prefer to lie orthogonal to this orbital to achieve maximum orbital overlap. The orientation of the HOMO can be predicted to lie along the line defined by the bond between the poorest d_π acceptor ligand and metal atom.[36–40] In general, the poorest d_π acceptor ligand is a phosphine ligand, which commonly is also the sterically most demanding ligand. Therefore, in these types of acyl complexes stereoelectronic and steric interactions are complementary. Figure 22 shows the orientation of the HOMO for the types of metal fragments which possess a single lone pair of electrons. Again, as in Section 2, the metal fragments are dealt with by structural type with a sequential substitution of the proximate ligands, initially carbon monoxide, with a tertiary phosphine.

The description of the HOMO on the metal fragments, as outlined above and depicted in Figure 22, is based principally on previously reported molecular orbital calculations.[36–40]

When considering the preferred conformation of an organotransition metal acyl complex it is important to weigh the effects of both steric and stereoelectronic interactions and determine which predominates. Several examples are shown in Table 1 of known complexes that are categorized by the number of pairs of electrons centred at the metal. The metal fragments that are determined to have zero, two, or more pairs of electrons have the acyl geometry predicted on steric arguments. For the metal fragments calculated to have one lone pair, the stereo-

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* Generally, even-hydrocarbon, phosphine, and phosphite ligands are not strong π acidic ligands whereas η^2-carbene, η^2-vinylidene, carbon monoxide, linear nitrosyl, and isonitrile ligands are strongly π acidic ligands.

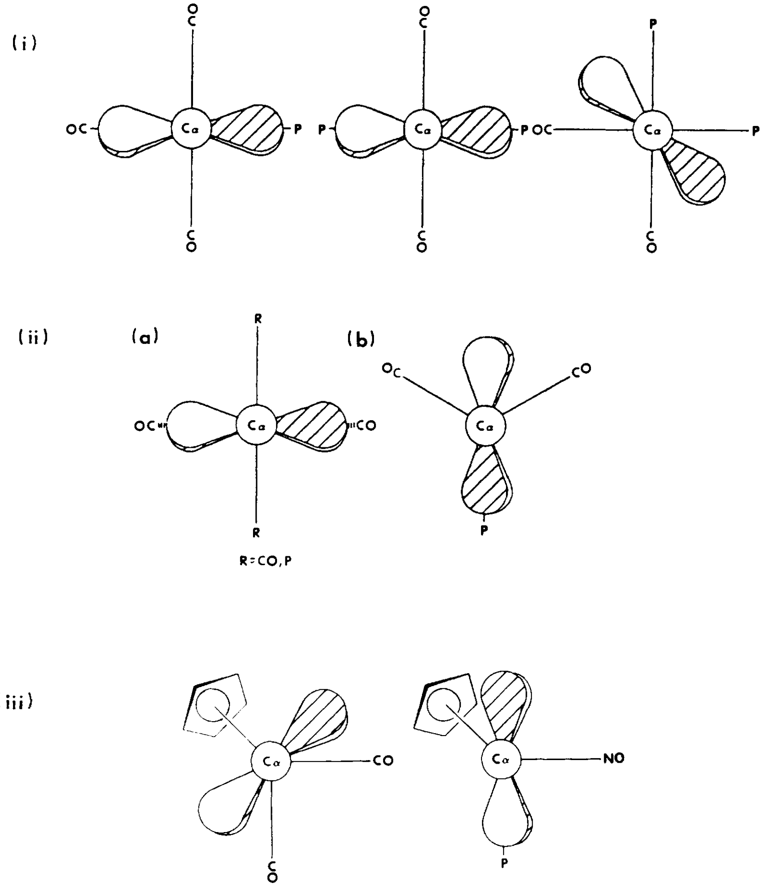


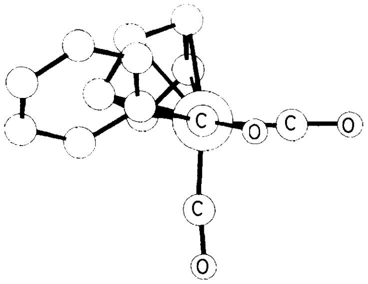
Figure 22 *Postulated orientation of a single lone-pair of electrons on metal fragments of the complex types:* (i) *octahedral;* (ii*a*) *trigonal bipyramid equatorially substituted;* (ii*b*) *trigonal bipyramid axially substituted;* (iii) *pseudo-octahedral*

electronic effect, depending on its magnitude relative to steric effects, is shown to dictate the acyl orientation, reinforce with the steric restrictions present in the complex, or in certain cases be completely outweighed by the steric interactions.

The pseudo-octahedral cyclopentadienyl manganese anion $[(\eta^5\text{-}C_5H_5)Mn(CO)_2COPh]^-$ (36)[34] is determined to have three pairs of electrons available for backbonding, by adding one for a negative charge then subtracting the total number of odd hapto (η) ligands from the seven valence *d*-electrons and finally dividing by two. Reducing by two to allow for backbonding into the carbon monoxide ligands yields one lone pair of electrons (or HOMO) which, upon inspection of Figure 22, lies parallel to the cyclopentadienyl ring. The *X*-ray crystal

Table 1 *Selected complexes categorized by the number of pairs of electrons available for d_π–$p_{\pi*}$ orbital overlap*

	Number of lone pairs	0	1	2	3
COMPLEX	square planar			*cis*-$[COPt(Cl)_2CON(Pr^i)_2]$[13] (2)	$Cl(PPh_3)_2PtCOPr$[15a] (6)
	octahedral	$(CO)_5MnCOCOMe$[16a] (8)		$[P(OEt)_3]_3Mn(CO)_2CHO$[19] (14)	
	trigonal bipyramidal	$[(MeO)_3P]Fe(CO)_3COMe$[26a] (24)	$(dppe)Co(CO)_2COR$[27] (26)		
	η^5-cyclopentadienyl pseudo-octahedral	$(C_5H_5)Re(NO)(CO)COR$	$(C_5H_5)Re(NO)(PPh_3)COPh$[29a] (30) $(C_5H_5)Fe(CO)_2COR$ $[C_5H_5)Fe(NO)(PPh_3)COR]^+$	$(C_5H_5)Fe(CO)(PPh_3)COMe$[30a] (32)	$(C_5H_5)Fe(PMe_3)_2COEt$[31a] (34)



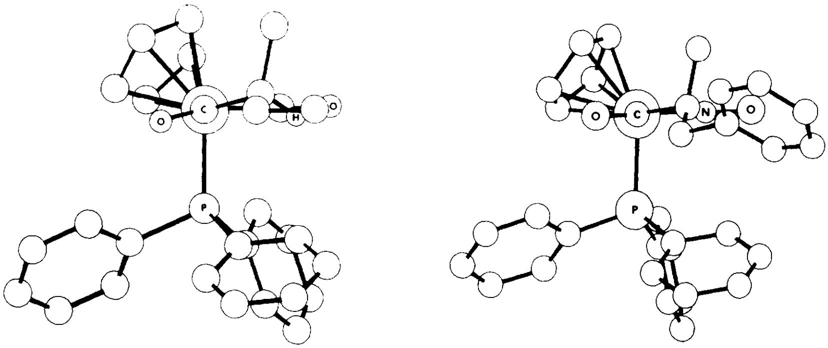
(36)

Figure 23 X-*Ray crystal structure of the anionic complex* [(η^5-C_5H_5)Mn(CO)$_2$COPh]$^-$ (36).[34] *The diagram shows the Newman projection along the* alpha *carbon to manganese bond. The protons have been removed for clarity*

structure determination for complex (36) shows that the stereoelectronically preferred conformation is adopted in the solid state (Figure 23), where maximum d_π–p_{π^*} orbital overlap can be achieved. If the preferred conformation of the acyl function in (36) was controlled by steric effects then the benzoyl moiety would tend to lie parallel to the cyclopentadienyl ligand (see Section 2E, i). In this case the stereoelectronic effect is greater than the steric effect.

Another example of the use of the guidelines discussed above is the comparison of the chiral iron acetyl [(η^5-C_5H_5)Fe(CO)(PPh$_3$)COMe] (32) and its rhenium analogue [(η^5-C_5H_5)Re(NO)(PPh$_3$)COMe] (37). Iron has a total of three pairs of electrons available for backbonding as determined by having eight valence *d*-electrons, subtracting the number of odd η ligands, and dividing by two. Backbonding into the carbon monoxide ligand leaves two lone pairs of electrons that are of similar energy and which are potentially available for resonance interaction with the acyl ligand. It is concluded then that the preferred conformation of the iron acyl complex will be dictated by steric interactions. Note that an electronic contribution from the metal to acyl ligand is operating in the chiral auxiliary [(η^5-C_5H_5)-Fe(CO)(PPh$_3$)] but does not exert any significant directional influence on attached acyl ligands. In a similar calculation for complex (37), rhenium having seven valence *d*-electrons results in a total of two electron pairs. Subtraction of one pair for backbonding to the strongly π-acidic nitrosyl ligand leaves only one lone pair of electrons on the rhenium metal. An electronic interaction with the HOMO of the rhenium fragment, which lies in the plane containing the phosphorus, rhenium, and carbonyl carbon atoms (Figure 22), and the acyl ligand will result in a strong stereoelectronic conformational preference for the acetyl ligand on the rhenium complex (37) to lie orthogonal to the rhenium–phosphorus bond.

Direct comparison of the *X*-ray crystal structures of [(η^5-C_5H_5)Fe(CO)(PPh$_3$)-COMe] (32)[30a] and *RS,SR*-[(η^5-C_5H_5)Fe(CO)(PPh$_3$)COCH(Me)Et] (38)[30k] with *RS,SR*-[(η^5-C_5H_5)Re(NO)(PPh$_3$)COCH(Me)CH$_2$Ph] (39)[35b,c] shows that the methyl and iso-butyl groups for the two iron acyl complexes (32) and (38), respectively, occupy the space between the cyclopentadienyl and carbon monoxide



(38) **(39)**

Figure 24 X-*Ray crystal structures of RS,SR*-[(η^5-C_5H_5)Fe(CO)(PPh_3)COCH(Me)Et] (38)[30k] *and RS,SR*-[(η^5-C_5H_5)Re(NO)(PPh_3)COCH(Me)CH_2Ph] (39).[35b,c] *The diagram shows the Newman projections along the* alpha *carbon to metal bond. Selected protons have been removed for clarity*

ligands (Figure 24), which is the expected result based on a simple analysis derived solely on steric interactions (see Section 2E, ii).[4–10,43] For the rhenium acyl complex (39), however, the CH(Me)CH_2Ph group, a sterically more demanding moiety than methyl, nearly eclipses the nitrosyl ligand. Figure 17 indicates that the energy due to eclipsing interactions ($\theta = -90°$) is not significant, as compared to the preferred conformation ($\theta = -60°$), and can be overcome by electronic forces. Thus, the stereoelectronic requirement present in the rhenium complex outweighs the steric forces that result from eclipsing interactions.

It is of interest to note that calculations on both the iron and rhenium complexes have been reported and have shown the HOMO in each complex to lie in the plane defined by the phosphorus, metal, and C_α carbon atoms with the second highest occupied molecular orbital (SHOMO) orthogonal to this plane.[39,40] The energy difference between the HOMO and SHOMO for the iron auxiliary is calculated[44] to be *ca.* 11 kcal mol^{-1} whereas for the rhenium auxiliary this difference is *ca.* 48 kcal mol^{-1}.[45] Based on PMO theory[46] the preferred conformation of these metal acyl

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[43] B. K. Blackburn, S. G. Davies, and M. Whittaker, in 'Stereochemistry of Organometallic and Inorganic Compounds', ed. I. Bernal, Elsevier Science: Amsterdam, 1988, Vol. 3.

[44] This value is taken from the EHMO calculations performed by Hoffmann and co-workers for the unsubstituted analogue [(η^5-C_5H_5)Mo(CO)(PH_3)]$^+$ and is the energy difference between the *a″* (HOMO) and 2*a′* (SHOMO) molecular orbitals for [(η^5-C_5H_5)Fe(CO)(PPh_3)]$^+$.[35b]

[45] This value is the calculated energy difference between the HOMO and SHOMO on [(η^5-C_5H_5)Re(NO)(PH_3)Me][36a] where there is expected to be no substantial orbital interactions from the metal to alkyl ligand and should, therefore, act as a satisfactory model for the fragment [(η^5-C_5H_5)Re(NO)(PH_3)]$^+$.

[46] (*a*) K. Fukui, *Bull. Chem. Soc. Jpn.*, 1966, **39**, 498; (*b*) K. Fukui and H. Fujimoto, *ibid.*, 1968, **41**, 1989; (*c*) *idem, ibid.*, 1969, **42**, 3399; (*d*) K. Fukui, *Acc. Chem. Res.*, 1971, **4**, 57; (*e*) *idem, Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 801; (*f*) *idem*, 'Theory of Orientation and Stereoselection', Springer-Verlag: West Berlin, 1975

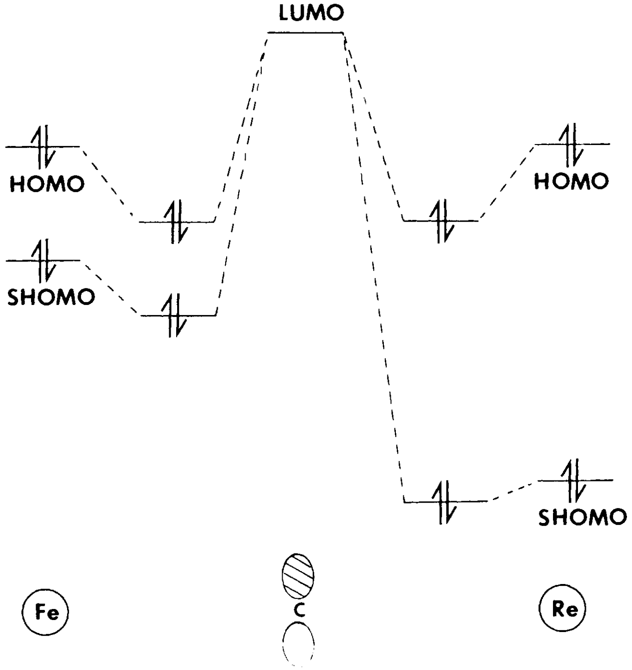
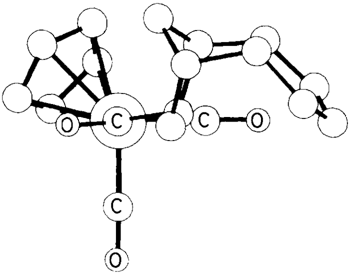


Figure 25 *Comparison of molecular orbital interactions for* [(η^5-C_5H_5)Fe(CO)(PPh_3)COR] *and* [(η^5-C_5H_5)Re(NO)(PPh_3)COR] *based on PMO theory*

complexes is where the acyl ligand lies perpendicular to the iron phosphorus bond to maximize overlap between the π* orbital of the carbonyl ligand and the HOMO on the metal. However, the orthogonal conformation will also allow d_π–p_{π^*} interaction to a similar extent for the iron auxiliary but to a very much lesser extent for the rhenium complex (Figure 25). This difference manifests itself in a strong stereoelectronic preference for the acyl to lie perpendicular to the phosphorus metal bond in rhenium but not in the iron acyl complexes. Note that steric repulsion continues to play a role in the rhenium complex by having the large CH(Me)CH_2Ph group *syn* to the small nitrosyl ligand and away from the more sterically demanding zone between the cyclopentadienyl and triphenylphosphine ligands (Figure 24).[5,43] Furthermore, the hydrogen atom and methyl group straddle the nitrosyl ligand with the small hydrogen atom residing in the sterically compressed zone between the carbon monoxide and triphenylphosphine ligands.[5,43]

Complexes where the steric interactions are greater than the stabilization that would be derived from resonance through d_π–p_{π^*} orbital overlap are complexes (26)[27] (see Section 2D, ii) and [(η^5-C_5H_5)Ru$(CO)_2$CO($C_{10}H_{15}$)] (40).[29b] Each of these complexes has a single lone pair of electrons as determined by the simple set of guidelines described above and, therefore, might be expected to adopt a con-



(40)

Figure 26 X-*Ray crystal structure of* $[(\eta^5\text{-}C_5H_5)Ru(CO)_2COC_{10}H_{15}]$ (40).[29b] *The diagram shows the Newman projection along the* alpha *carbon to ruthenium bond. The protons have been removed for clarity*

formation with the acyl ligand orthogonal to the HOMO. However, the solid state conformation for each of these complexes is the one where steric interactions are minimized. It is suggested that for these complexes the steric repulsion between the acyl moiety and the proximate ligands is greater than the energy potentially gained by electron delocalization. Note that for complex (40) a certain degree of electron delocalization may occur through back donation from the metal (HOMO) to acyl ligand (p_{π^*}) but steric effects preclude maximization of this type of stabilization.

B. Electrostatic Effects.—(i) *Dipolar Effects.* For most metal acyl complexes, a dipole exists in the acyl ligand as C(+ve)–O(−ve) due to electronic effects, and in consequence minimization of dipole–dipole interactions in the relatively non-polar solid-state environment will be favoured. The dipole–dipole interactions for an organotransition metal acyl complex will be small relative to steric interactions that would be present and, therefore, will not affect conformational preferences that are predicted from steric arguments. For formyl complexes, however, dipolar interactions may affect formyl orientation since the formyl ligand is sterically smaller than an acyl ligand. For example, the complex $\{[P(OEt)_3]_3Re(CO)_2CHO\}$ (41)[47] is determined to have one pair of electrons that is expected to align with the plane containing the two *trans* phosphorus atoms, the rhenium, and C_α carbon atoms. It is apparent from the *X*-ray crystal structure of complex (41)[47] a stereochemical preference does exist, such that the formyl ligand eclipses the *trans* carbon monoxide and phosphine ligands (Figure 27), whereby maximum overlap can be achieved between the single lone pair of electrons centred at the metal and the π* orbital of the formyl ligand. Since the metal–phosphorus bond is a polarized as M(−ve)–P(+ve)[9] the direction of the formyl ligand is opposite to that predicted by simple steric considerations and is directed towards the phosphine ligand to minimize the overall dipole in the solid state.

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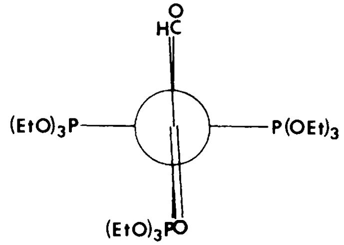
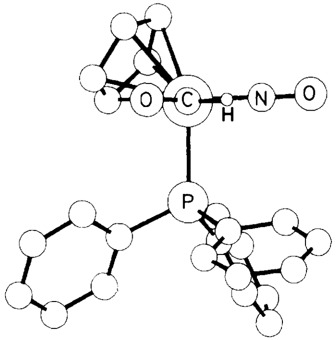
[47] C. Sontag, O. Orama, and H. Berke, *Chem. Ber.*, 1987, **120**, 559.



(41)

Figure 27 *Newman projection along* alpha *carbon rhenium bond showing the solid state conformation of* $\{[P(OEt)_3]_3Re(CO)_2CHO\}$ (41).[47]



(42)

Figure 28 X-*Ray crystal structure of* $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)_3CHO]$ (42).[35a,c] *The diagram shows the Newman projection along the* alpha *carbon to rhenium bond. Selected protons have been removed for clarity*

In the rhenium formyl complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)CHO]$ (42),[35a,c] shown in Figure 28, the formyl ligand lies perpendicular to the plane containing the phosphorus, rhenium, carbonyl carbon atoms, as determined by stereoelectronic requirements (see Section 3A), and the C–O dipole is directed opposite to the dipole associated with the nitrosyl ligand, thus minimizing its dipole–dipole interactions in the solid-state.

(ii) *Hydrogen Bonding.* Hydrogen bonding between an acyl oxygen atom and proximal ligands has been shown to play a role in determining acyl orientation[48] and is clearly illustrated in the complex $[Re(CO)_4(NH_2Ph)COMe]$ (43), shown in Figure 29.[48a] Cross-linking between adjacent molecules in the crystal lattice

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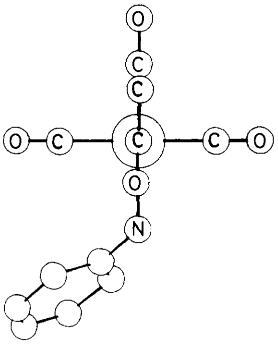
[48] (*a*) C. M. Lukehart and J. V. Zeile, *J. Am. Chem. Soc.*, 1978, **100**, 2774; (*b*) A. J. Baskor, C. M. Lukehart, K. Srinivasan, *J. Am. Chem. Soc.*, 1981, **103**, 1461; (*c*) J. D. Korp and I. Bernal, *J. Organomet. Chem.*, 1981, **220**, 355; (*d*) C. M. Lukehart and J. V. Zeile, *J. Organomet. Chem.*, 1977, **140**, 309; (*e*) C. M. Lukehart and J. V. Zeile, *J. Am. Chem. Soc.*, 1976, **98**, 2365; (*f*) V. G. Albano, P. L. Bellon, and M. Sarson, *Inorg. Chem.*, 1969, **8**, 298; (*g*) F. A. Cotton, B. A. Frenz, and A. Shauer, *Inorg. Chim. Acta*, 1973, **7**, 161.



(43)

Figure 29 *X-Ray crystal structure of* [Re(CO)$_4$(NH$_2$Ph)COMe] (43).[48a] *The diagram shows the Newman projection along the* alpha *carbon to rhenium bond. The protons have been removed for clarity*

through hydrogen bonding has been proposed for certain complexes and may also affect acyl orientation.[49]

4 Conformational Analysis of Ligands other than η^1-Acyl

The guidelines for determining acyl conformation set forth here may also be applied to other ligands, such as for example carbenes[50] and vinylidenes.[51] Thus, the preferred conformation of a carbene or vinylidene ligand in an organotransition metal complex will be primarily governed by steric interactions with a stereoelectronic preference existing only when there is a single lone pair of electrons on the metal fragment.[52] *X*-Ray crystal structure determinations of a number of carbene[51,53,54] complexes have been reported; the complexes shown in Figure 30

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[49] (*a*) D. M. Chipman and R. A. Jacobson, *Inorg. Chem. Acta*, 1967, **1**, 393; (*b*) G. L. Breneman, D. M. Chipman, E. J. Galles, and R. A. Jacobson, *Inorg. Chem. Acta*, 1969, **3**, 447; (*c*) A. J. Lindsay, S. Kim, R. A. Jacobson, and R. J. Angelici, *Organometallics*, 1984, **3**, 1523; (*d*) D. Messer, G. Landgraf, and H. Behren, *J. Organomet. Chem.*, 1979, **172**, 34; (*e*) H. Wagner, A. Jungbauer, G. Thiele, and H. Z. Behren, *Naturforsch., Teil B*, 1979. **34**. 1487.

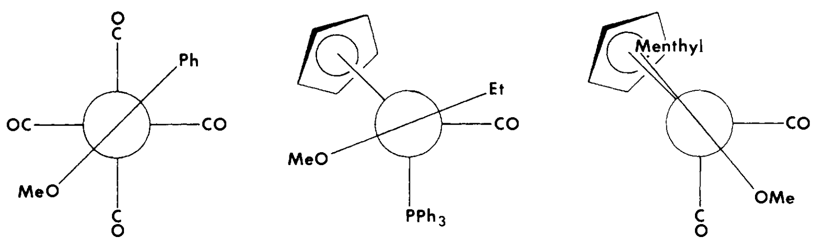
[50] For leading references see: (*a*) U. Schubert, *Coord. Chem. Rev.*, 1984, **55**, 272; (*b*) K. H. Dötz, H. Fischer, P. Hofmann, F. R. Kreisgl, U. Schubert, and K. Weiss, 'Transition Metal Carbene Complexes', Verlag Chemie: Weinheim, 1983; (*c*) F. J. Brown, *Prog. Inorg. Chem.*, 1980, **27**, 1; (*d*) D. J. Cardin and R. J. Norton. *Organomet. Chem.*, 1982, **12**, 213; (*e*) K. H. Dötz, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 587; (*f*) J. E. Hahn, *Prog. Inorg. Chem.*, 1984, **31**, 205; (*g*) D. B. Pourreau and G. L. Geoffroy, *Adv. Organomet. Chem.*, 1985, **24**, 249; (*h*) T. Aratani, *Pure Appl. Chem.*, 1985, **57**, 1839; (*i*) M. Brookhart and W. B. Studabaker, *Chem. Rev.*. 1987, **87**, 411.

[51] For leading references see: (*a*) M. I. Bruce and A. G. Swincer, *Adv. Organomet. Chem.*, 1983, **22**, 59; (*b*) S. Abbot, D.Phil. Thesis, Oxford University, 1984; (*c*) S. G. Davies S. Abbott, and P. Warner, *J. Organomet. Chem.*, 1983, **256**, C65; (*d*) A. G. M. Barrett and M. A. Sturgess, *J. Org. Chem.*, 1987, **52**, 3811; (*e*) G. Consiglio and F. Morandini, *Inorg. Chim. Acta*, 1987, **127**, 79.

[52] Note that steric interactions in vinylidene complexes are tempered due to the greater distance between the groups on the allenic ligand and proximal ligands.

[53] (*a*) G. Huttner and H. Lorenz, *Chem. Ber.*, 1975, **108**, 1864; (*b*) S. G. Davies, T. R. Maberly, R. H. Jones, M. E. C. Polywka, and G. Baird, in preparation; (*c*) T. R. Maberly, D.Phil. Thesis, Oxford University, 1986; (*d*) S. Fontana, U. Schubert, and E. O. Fisher, *J. Organomet. Chem.*, 1978, **146**, 39.

[54] P. Helquist, C. Knors, G.-H. Kuo, J. W. Lauher, and C. Eigenbrot, *Organometallics*, 1987, **6**, 988.



(44) (45) (46)

Figure 30 *Newman projections along* alpha *carbon metal bond showing the solid state conformations for the carbene complexes* $[Cr(CO)_5C(OMe)Ph]$ (44),[53a] $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)C(OMe)Et]^+$ (45),[53b,c] *and* $[(\eta^5\text{-}C_5H_5)Mn(CO)_2C(OMe)\text{menthyl}]$ (46).[53d,55]

illustrate the steric and stereoelectronic influences on conformation in these types of complexes. Complexes $[Cr(CO)_5C(OMe)Ph]$ (44)[53a] and $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)C(OMe)Et]$ (45)[53b,c] are determined to have zero and two lone pairs of electrons, respectively (see Section 3A), and therefore adopt a conformation that reduces all steric interactions. Complex $[(\eta^5\text{-}C_5H_5)(CO)_2MnC(OMe)\text{menthyl}]$ (46)[53d,55] has a single lone pair of electrons on the metal fragment and thus adopts a conformation in which the π^* orbital of the ligand (LUMO) is aligned parallel to the lone pair (HOMO). This stereoelectronic conformational preference is also seen in the homologous vinylidene complex $[(\eta^5\text{-}C_5H_5)Mn(CO)_2CCMe_2]$ (47),[56] shown in Figure 31.

It should be noted that in certain cases steric interactions may be so great as to overwhelm stereoelectronic preferences.[54] For example, complex (48) $[(\eta^5\text{-}C_5H_5)Fe(CO)_2C(SMe)Me]^+$ adopts a conformation that reduces steric interactions by placing the thiomethyl and methyl groups bound to the carbene carbon atom in the least sterically congested space between the carbon monoxide and cyclopentadienyl ligands (Figure 32).[54] However, the complex $[(\eta^5\text{-}C_5H_5)(CO)_2FeCH(SPh)]^+$ (49),[54] a closely related complex to (48), adopts the conformation that is predicted on stereoelectronic arguments (Figure 32). In the crystal structure determination of complex (49) there was identified two randomly distributed contributors to the structure that were determined to be (49a) (80%) and (49b) (20%). Despite the problems associated with disorder in the solid state, the crystal structure determinations for (48) and (49) are sufficient to reveal their conformational preferences. Comparison of complexes (48) and (49) shows that (49) does not contain the same

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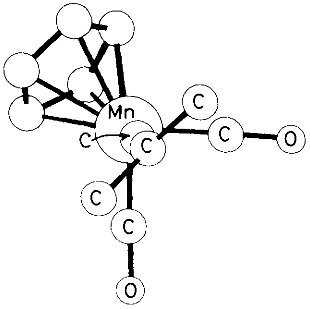
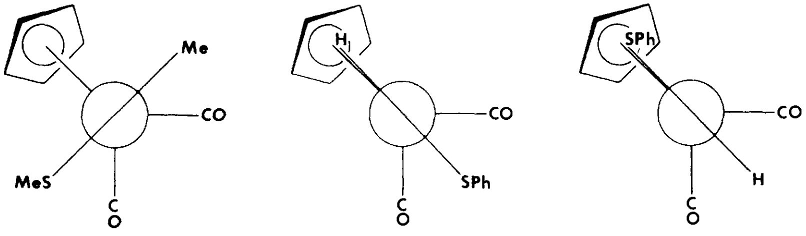
[55] Several authors have noted that complex (46) adopts a conformation where the methoxy group occupies the space between the cyclopentadienyl and carbon monoxide ligands, but, as seen by its Newman projection in Figure 30 this is clearly not the case. [(*a*) U. Schubert, *Organometallics*, 1982, **1**, 1085; (*b*) W. M. Jones, F. J. Manganiello, and M. D. Radcliffe, *J. Organomet. Chem.*, 1982, **228**, 271.][47a]

[56] H. Berke, G. Huttner, and J. von Seryerl, *J. Organomet. Chem.*, 1981, **218**, 193. For other *X*-ray crystal structure determinations of vinylidene complexes see: (*a*) A. N. Nesmeyanov, G. G. Aleksandrov, A. E. Antonova, K. N. Anisimov, N. E. Kolobova, and Y. T. Struchkov, *J. Organomet. Chem.*, 1976, **110**, C36; (*b*) M. I. Bruce, F. S. Wong, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1982, 2203; (*c*) R. M. Kirchner and S. Iber, *Inorg. Chem.*, 1974, **13**, 1667; (*d*) G. L. Geoffroy, D. B. Pourreau, A. L. Rheingold, and S. J. Geib, *Organometallics*, 1986, **5**, 1337.



(47)

Figure 31 *X-Ray crystal structure of* $[(\eta^5\text{-}C_5H_5)Mn(CO)_2CCMe_2]$ (47).[56] *The diagram shows the Newman projection along the* alpha *carbon to manganese bond. The protons have been removed for clarity*

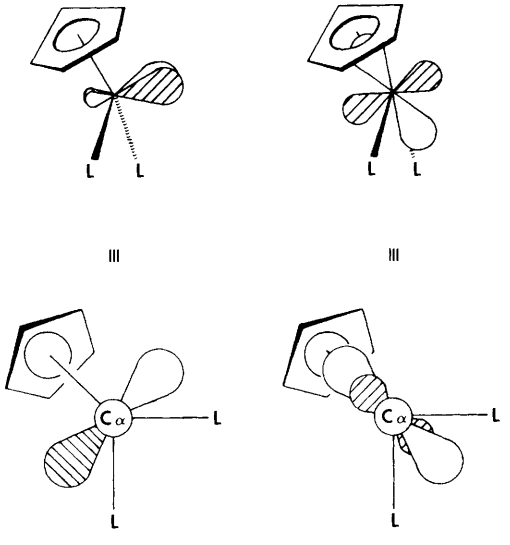


(48) (49a) (49b)

Figure 32 *Newman projections along* alpha *carbon metal bond showing the solid state conformations for the cationic carbene complexes* $[(\eta^5\text{-}C_5H_5)Fe(CO)_2C(SMe)Me]^+$ (48),[54] *and* $[(\eta^5\text{-}C_5H_5)Fe(CO)_2C(SPh)H]^+$ (49):(49a) 80% *contributor*, (49b) 20% *contributor*[54]

steric demands as in (48)—there being a greater steric requirement for a methyl group relative to a hydrogen atom—and thus adopts the stereoelectronically preferred conformation.

Interestingly, all the known pseudo-octahedral cyclopentadienyl manganese dicarbonyl complexes adopt the conformation where maximum orbital overlap between the *p*-orbital on the carbene and HOMO on the metal can be achieved, whereas the majority of the corresponding iron complexes adopt a conformation predicted on steric interactions. This result is surprising, since all of these types of complexes are isoelectronic and, therefore, are predicted to have a single lone pair of electrons. It is postulated that this difference stems from the energetic imbalance between the HOMO and an orbital of lower energy, that lies orthogonal to the HOMO and is also available for backbonding (Figure 33),[38] on the iron and manganese fragments. A similar argument was presented above for the observed difference between the acyl complexes of $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)]$ and its rhenium analogue (Figure 25). In order to rationalize the results observed for the iron and manganese systems it is suggested that for most of the iron complexes



HOMO **secondary orbital**

Figure 33 *Illustration of the orientation of the HOMO and the secondary lower energy orbital*

steric interactions are greater than the energy gained by preferentially mixing the empty carbene *p*-orbital with the HOMO relative to the lower lying orbital, which was calculated to be approximately 6 kcal mol^{-1}.[38] For the manganese complexes that are known, however, this energy difference is greater than the steric interactions present and they therefore adopt the conformation where the carbene *p*-orbital can efficiently interact with the HOMO. The difference described for these two complexes is commonly observed for similar types of complexes of the iron triad relative to the manganese triad.

A single lone pair of electrons on the metal, in addition to the stereoelectronic conformational preferences, will also manifest itself in an increase in the barrier to rotation.[55b,57–59] For example, essentially free rotation about the iron to *alpha* carbon bond is observed for carbene ligands attached to the iron chiral auxiliary [(η^5-C$_5$H$_5$)Fe(CO)(PPh$_3$)],[57a] predicted to have two lone pairs (Section 3A), whereas *syn* and *anti* rotomers can be isolated for carbene ligands attached to the rhenium chiral auxiliary [(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)],[58] calculated to have one lone

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[57] For example: (*a*) M. Brookhart, J. R. Tucker, T. C. Flood, and J. Jensen, *J. Am. Chem. Soc.*, 1980, **102**, 1203; (*b*) U. Guerchais and C. Lapinte, *J. Chem. Soc., Chem. Commun.*, 1986, 894; (*c*) A. Davison and D. L. Reger, *J. Am. Chem. Soc.*, 1972, **94**, 9273; (*d*) M. Brookhart, J. R. Tucker, and G. R. Husk, *J. Am. Chem. Soc.*, 1983, **105**, 258.

[58] A. M. Crespi and D. F. Schriver, *Organometallics*, 1985, **4**, 1830.

[59] (*a*) W. E. Buhro, S. Georgiou, J. M. Fernandez, A. T. Patton, C. E. Strouse, and J. A. Gladysz, *Organometallics*, 1986, **5**, 956; (*b*) W. A. Kiel, W. E. Buhro, and J. A. Gladysz, *ibid.*, 1984, **3**, 879; (*c*) W. G. Hatton and J. A. Gladysz, *J. Am. Chem. Soc.*, 1983, **105**, 6157.

pair of electrons on the metal (Section 3A). In the former case the electronic effect is not significantly directional whereas in the latter a strong directional stereoelectronic effect is apparent. Similar results are observed for the corresponding vinylidene complexes of $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)]$[60] and $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]$.[61]

5 Conclusions

The dominant force that controls acyl conformation in transition metal η^1-acyl complexes is steric interactions. Therefore, the preferred conformation of an η^1-acyl complex can, in general, be rapidly, and correctly predicted by taking into account the steric interactions that would be present between the acyl ligand and its proximate ligands. We have shown this to be the case by correlating the sterically preferred conformation, as determined by using the CHEM-X molecular modelling program only calculating van der Waals interactions,[11,12] to the corresponding *X*-ray crystal structures available. Only in exceptional cases, where a stereoelectronic conformational preference is present in the system, is the sterically preferred conformation not strictly adhered to. We have provided a set of guidelines where the electronic contribution of the metal fragment can be readily predicted, including several examples of their use on known complexes. Furthermore, this hypothesis can be successfully extrapolated to ligands other than acyl; for example, Fischer carbenes and vinylidenes.

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