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CONFORMATIONAL ANALYSIS OF THE IRON ACETYL COMPLEX $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_3]$

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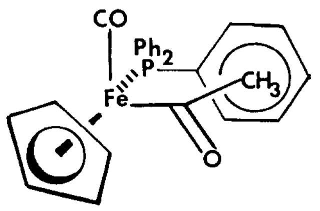
Summary: A conformational analysis for the complex $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_3]$ based on extended Huckel and ab initio SCF MO calculations is described which indicates that the conformational preference for the acyl oxygen is approximately anti periplanar to CO due to steric interactions between the acyl ligand and two of the phenyl groups of the triphenylphosphine.

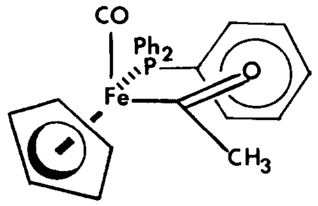
The iron moiety $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)]$ is a highly versatile chiral auxiliary allowing excellent stereochemical control to be achieved in a variety of carbon-carbon bond forming reactions of attached acyl ligands.[1] Although the high stereoselectivities observed in these reactions are consistent with preferential reactivity of conformations in which the acyl derived oxygen and the carbon monoxide ligand are anti[1,2] no detailed conformational analysis of such iron acyl complexes has been reported. We describe here a conformational analysis of the parent acetyl complex $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_3]$ 1 based on extended Huckel and ab initio SCF MO calculations performed upon simplified model complexes.

We have previously reported[3] a detailed conformational analysis for alkyl complexes of the type $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)R]$ which highlighted their pseudo-octahedral nature and the controlling steric influence exerted by the triphenylphosphine ligand. Based on this conformational analysis the iron acetyl complex 1 would be expected to have a pseudo-octahedral geometry with one of the phenyl groups of the triphenylphosphine ligand positioned approximately parallel to a plane containing the carbon monoxide, the iron atom and the oxygen and two carbon atoms of the acetyl ligand. However this qualitative analysis gives no indication concerning any conformational preference for the acyl oxygen to be oriented anti or syn with respect to the CO ligand. Examination of the X-ray crystal structure of the acetyl complex 1 and those of several analogues confirmed the above predictions.[4,5] Furthermore, without exception, in the solid state the acyl oxygen is always anti and close to periplanar to the carbon monoxide ligand.

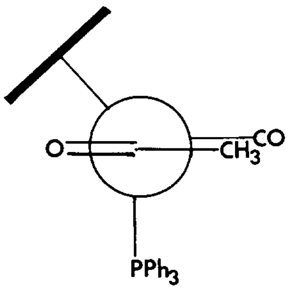
Extended Huckel calculations on compound 1 would be too complex to perform and therefore the model complex $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPhH_2)COCH_3]$ 2 was chosen. Furthermore, in order to ensure that $PPhH_2$ provided a realistic model for interactions between PPh_3 and the acetyl ligand in 1, rotation about the metal phosphorus bond was restricted such that the $Fe\text{-}C(=O)(CH_3)$ bond essentially eclipsed the $P\text{-}C_{ipso}$ bond with the two ortho carbons essentially equidistant from

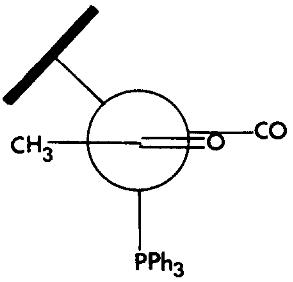


I-anti



I-syn





the acetyl-carbonyl-carbon. The calculations were performed as described previously with a weighted Hij formula.[3] Two energy minima corresponding to the anti and syn conformations are observed. These minima are surprisingly similar in energy with the syn conformation being marginally, but not significantly (<1 kcal mol^{-1}), favoured. Furthermore, the calculations clearly indicate that the only reasonable rotational pathway for interconverting the anti and syn conformations is the one via eclipsed C=O and Fe-P.

ab initio SCF MO calculations were performed for the anti and syn conformations upon a simplified model complex [(η^5-C_5H_5)Fe(PH_3)(CO)(COMe)], obtained from the structure used in the extended Huckel calculations above by replacement of the basal phenyl group by a hydrogen atom. Huzinaga's MINI-2' basis[6] for iron was augmented by a set of gaussian p-functions with exponent 0.2 to represent the 4p shell.[7] Huzinaga's (333/33) basis for phosphorus and (33/3) bases for carbon and oxygen were employed[8] together with the STO-3G basis for hydrogen.[9] The calculations used the CADPAC program[10] as implemented on the Cambridge University IBM 3081 computer. Distributed multipole analysis[11] for each conformer revealed overall group charges (sums of atomic monopoles) of 0.07 for PH_3, about -0.85 for C_5H_5 and about -0.10 for the CH_3 group of the acetyl ligand, together with atomic charges as shown in Figure 1. The syn-conformer has a more favourable electrostatic arrangement and is energetically preferred over the anti-conformer by 2.7 kcal mol^{-1} (Table 1).

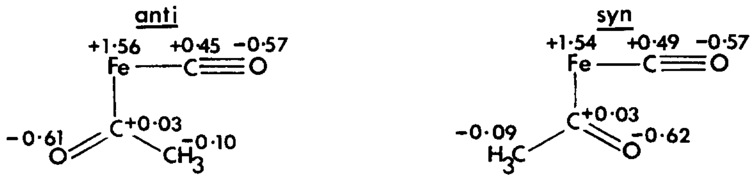


FIGURE 1: Calculated atomic charges for [(η^5-C_5H_5)Fe(CO)(PH_3)$COCH_3$] conformers.

Table 1: Ab initio SCF energies for $[(\eta^5\text{-}C_5H_5)Fe(CO)(PH_3)COCH_3]$ conformers.

conformer	total energy/hartrees	relative energy/kcal mol^{-1}
anti	-2051.75930	0.00
syn	-2051.76360	-2.70

Calculations upon a model complex lacking both the Fe atom and the PH_3 ligand, i.e. $[C_5H_5^-.CO.COMe^+]$, also predicted the syn-conformer to be lower in energy than the anti-conformer by 0.8 kcal mol^{-1}. This result suggests that (a) the iron atom serves primarily as a template for the ligands, (b) steric interactions between the acyl ligand and a model PH_3 ligand do not account for the experimentally observed[4,5] preference for anti-conformers of $[(\eta^5\text{-}C_5H_5)Fe(PPh_3)(CO)COR]$ compounds and (c) the observed preference for the anti-conformer does not have its origin in steric interactions between the alkyl group R of the acyl ligand and the cyclopentadienyl ring.

Inspection of all the available X-ray crystal structures of $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COR]$ complexes reveals the additional stereochemical feature that the twist of the PPh_3 propellar is always the same with one particular C-H bond of a second, proximate, phenyl group consistently orientated towards the acyl oxygen as shown in Figure 2. This oxygen-hydrogen distance was 1.6A for the acetyl complex 1.[4] This further suggested that steric interactions involving the acyl ligand and two of the phenyl groups of the phosphine ligand might determine the conformational preference. Consequently ab initio SCF MO calculations were performed for a complex $[C_2H_4.C_2H_4.COMe]^+$ (Figure 2) in which the -CH=CH- "leading edges"

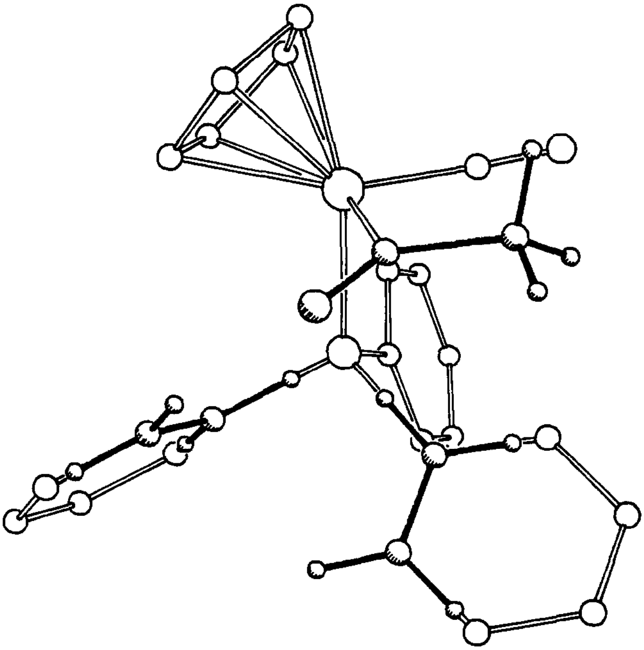


Figure 2: A composite illustration of $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_3]$ 1 overlaid with $[C_2H_4.C_2H_4.COMe]^+$ model.

of these phenyl rings in 1, adjacent to the acyl ligand, were modelled by a pair of ethylene molecules with geometries based upon the crystallographic structural data.[5] The anti-conformer is calculated to be 8.3 kcal mol^{-1} more stable than the syn-conformer for this *model, in accord with the experimentally observed preference.*

The above conformational analysis for the acetyl complex 1 allows the following conclusions to be made: (1) it is the steric interaction between the acetyl ligand and one of the phenyl groups of PPh_3 that is responsible for the acetyl group preferring to be in the plane containing the iron atom, carbon monoxide and the acetyl-carbonyl-carbon, and (2) it is the steric interaction between the acetyl ligand and a second phenyl group that is responsible for the anti carbonyl-oxygen to CO conformation being preferred. This conformational analysis is also applicable to the general acyl complexes $[(\eta^5-C_5H_5)Fe(CO)(PPh_3)COR]$ where the anti conformational preference will be more pronounced the larger the group; it is equally applicable to alkoxycarbene and alkoxyvinyl complexes of $[(\eta^5-C_5H_5)Fe(CO)(PPh_3)]$ where a conformational preference for alkoxy-oxygen anti to CO is also observed.[12] Consideration of this second phenyl group is expected to influence considerably the conformational analysis of the alkyl complexes $[(\eta^5-C_5H_5)Fe(CO)(PPh_3)R]$ which we have previously based on $PPhH_2$ as a model for PPh_3. More detailed ab initio calculations for both acyl and alkyl complexes are presently being undertaken.

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