Journal of Organometallic Chemistry, 397 (1990) C13–C19
Elsevier Sequoia S.A., Lausanne
JOM 21301

Preliminary communication

Conformational analyses for acetyl and formyl ligands bound to transition metal auxiliaries

Stephen G. Davies * and **Andrew J. Smallridge**
The Dyson Perrins Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QY (U.K.)

(Received July 27th, 1990)

Abstract

Conformational analyses for acetyl and formyl ligands bound to transition metal auxiliaries reveal that, after considering primary stereoelectronic effects where appropriate, the conformations adopted by acetyl ligands are determined primarily by steric interactions while the corresponding formyl conformations are determined primarily by dipolar and electrostatic forces. No evidence for secondary stereoelectronic effects is apparent.

We have previously reported extensive conformational analyses for acetyl ligands bound to transition metal moieties [1,2]. Acetyl complexes may be divided into two classes depending on whether the metal fragment will exert a primary stereoelectronic effect or not. Firstly for those complexes with two lone pairs on the metal fragment of appropriate symmetry and energy to interact with the acetyl carbonyl π-orbital, therefore exerting no primary stereoelectronic effect, e.g. $[(C_5H_5)Fe(CO)(PPh_3)COCH_3]$ *, the acetyl conformation is determined solely by steric effects with the relatively bulky methyl group preferring to occupy the least congested space. Secondly, for those complexes where, due to the presence of a single lone pair on the metal fragment, there is a primary stereoelectronic effect, e.g. $[(C_5H_5)Re(NO)(PPh_3)COCH_3]$, the conformation of the acetyl ligand is such that it lies orthogonal to the HOMO on the metal fragment, and is orientated so as to place the relatively bulky methyl group in the least congested of the two possible spaces.

We further extended our conformational analysis to include transition metal formyl complexes [1,2]. We appreciated that, due to the small size of both the oxygen and hydrogen of the formyl ligand, steric effects were less likely to dominate the conformational preference of the formyl group and proposed that dipole and

---

* The descriptor η^5 for the cyclopentadienyl ligand has been omitted throughout for clarity.

0022-328X/90/$03.50

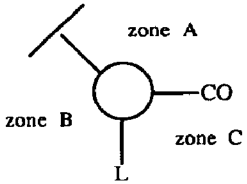

Fig. 1. Newman projection towards the auxiliary $[(C_5H_5)Fe(CO)(L)]$ showing the three zones: zone A between the cyclopentadienyl and carbon monoxide; zone B between the cyclopentadienyl and ligand L; zone C between the carbon monoxide and the ligand L.

charge interactions would become important. Recently Schreiber and coworkers [3], while apparently not considering much of our work in this area, have proposed that secondary stereoelectronic effects are important in determining formyl and acetyl ligand conformations. Herein we elaborate further our conformational analysis for these ligands by considering the full range of formyl complexes and confirm our conclusions that, after consideration of primary stereoelectronic effects where appropriate, their conformations are determined primarily by steric and dipole/electrostatic effects. Contrary to the Schreiber et al. analysis we can find no experimental evidence to support their hypothesis that secondary stereoelectronic effects, whether or not they exist at all, have any bearing on determining conformational preferences for acetyl or formyl ligands.

Complexes derived from the iron chiral auxiliaries $[(C_5H_5)Fe(CO)(L)]$ are pseudo-octahedral in geometry; the cyclopentadienyl ligand occupying three of the six coordination sites with carbon monoxide and the ligand L taking one site each leaving one site available for another ligand, e.g. acetyl or formyl. Figure 1 shows the Newman projection from this latter site to the iron. The mutually orthogonal geometry of the three sites not occupied by the cyclopentadienyl ligand is apparent from this view. Whatever the size of the ligand L, zone C between the carbon monoxide and the L ligand will always be the least accessible due to the small (ca. 90°) bond angle. Due to the small size of the carbon monoxide ligand, zone A, between the cyclopentadienyl and carbon monoxide ligands, will always be sterically more accessible than zone B, between the relatively larger ligand L and the cyclopentadienyl ligand. This effect is exacerbated in the case of L being triphenylphosphine since the propellor structure of the triphenylphosphine places an *ortho* hydrogen on one of the phenyl groups in zone B. When L is carbon monoxide the two zones A and B become equivalent but zone B is never preferred sterically to zone A. Thus for the acetyl complexes $[(C_5H_5)Fe(CO)(PPh_3)COCH_3]$ [4] (Fig. 2) and $[(C_5H_5)Fe(CO)(PPhMe_2)COCH_3]$ [5] (Fig. 3) the conformation may be predicted solely on the basis of the steric requirement of placing the methyl group in

Fig. 2. Newman projection derived from the X-ray crystal structure of $[(C_5H_5)Fe(CO)(PPh_3)COCH_3]$ ($\theta = 161°$, $\nu(C{=}O) = 1603\ cm^{-1}$). θ is defined as the torsion angle $O_{formyl(acetyl)}-C_\alpha-metal-CO$.

Fig. 3. Newman projection derived from the X-ray crystal structure of $[(C_5H_5)Fe(CO)(PPhMe_2)COCH_3]$ ($\theta = 163°$).

zone A, there being no primary stereoelectronic effect for these complexes. In neither case is it necessary to invoke a secondary stereoelectronic effect to explain the conformation, indeed any such stereoelectronic effect would favour the strictly antiperiplanar (acyl oxygen to CO) conformation, which is not observed.

In the case of the rhenium acetyl complex $[(C_5H_5)Re(NO)(PPh_3)COCH_3]$ the acetyl ligand is constrained to lie periplanar with the nitrosyl ligand due to the primary stereoelectronic effect since this arrangement maximises the overlap of the acetyl carbonyl π-orbital with the HOMO on the rhenium. Steric and dipole/electrostatic interactions will orientate the acetyl ligand such that the oxygen is *anti* to the nitrosyl ligand. The substantial backbonding from the rhenium to the nitrosyl and acetyl ligands results in a build up of electron density on the acetyl oxygen and nitrosyl ligand. In the antiperiplanar conformation the resultant dipole and electrostatic repulsive forces are minimised. In addition the antiperiplanar conformation keeps the acetyl methyl out of the restricted zone B with the eclipsing interaction being accommodated by the methyl hydrogens straddling the nitrosyl. Unfortunately the structure of the rhenium acetyl has not been determined; however, Fig. 4 shows the X-ray structure of a related acyl complex, $[(C_5H_5)Re(NO)(PPh_3)$-$COCH(CH_3)CH_2Ph]$, [6] which exhibits the predicted conformation.

For the formyl ligand in $[(C_5H_5)Re(NO)(PPh_3)CHO]$ [7] (Fig. 5) neither the oxygen nor the hydrogen will have significant steric interactions with either the cyclopentadienyl or the triphenylphosphine and thus they both can occupy zones A or B. However the primary stereoelectronic effect forces either the oxygen or hydrogen to eclipse the nitrosyl ligand and therefore, since oxygen is relatively larger than hydrogen, the antiperiplanar arrangement is preferred. In addition and probably more importantly the antiperiplanar conformation minimises the dipole and electrostatic repulsive forces between the formyl oxygen and the nitrosyl ligand as discussed above.

Fig. 4. Newman projection derived from the X-ray crystal structure of $[(C_5H_5)Re(NO)(PPh_3)COCH(CH_3)CH_2Ph]$ ($\theta = 180°$, $\nu(C{=}O) = 1545\ cm^{-1}$)

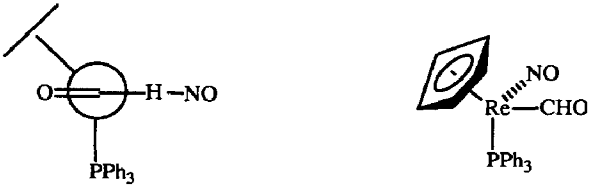

Fig. 5. Newman projection derived from the X-ray crystal structure of $[(C_5H_5)Re(NO)(PPh_3)CHO]$ ($\theta = 176°$).

For the complex $[(C_5Me_5)Ru(CO)(PPhMe_2)CHO]$ [8] (Fig. 6) there is no primary stereoelectronic effect to determine the conformation of the formyl ligand. The conformation of the phosphine is determined by the very bulky pentamethylcyclopentadienyl ligand with the result that zone B is extremely encumbered and thus the occupancy of this zone by the formyl oxygen is disfavoured. In complexes of this type the phosphorus will bear a partial positive charge and the formyl oxygen a partial negative charge with the result that the the preferred conformation on electrostatic/dipole grounds will put the formyl oxygen *syn* periplanar to the phosphorus. The conformation adopted by the formyl ligand is therefore a compromise between maximising the dipole/electrostatic attraction and minimising the steric interactions between the formyl and the methyl groups on the cyclopentadienyl and phosphine ligands.

The conformation adopted by the formyl ligand in $[Os(CO)(dppe)_2CHO]$ [9] (Fig. 7) is determined by steric constraints there being no primary stereoelectronic effect and dipole/electrostatic effects being essentially nondirectional due to symmetry.

The trigonal bipyramidal formyl complexes $[Fe(L)(CO)_3CHO]$ provide particularly germane examples when considering the possibility of secondary stereoelectronic effects. Two crystal structures are known for L = $P(OPh)_3$ [10] (Figure 8) and $P(O\text{-}3,5\text{-}C_6H_3Me_2)$ [11] (Figure 9) where the phosphite ligands are trans to the formyl ligands. The nearest neighbours to the formyl ligand are therefore the three carbon monoxide ligands. There is no primary stereoelectronic effect to influence the formyl conformation and the dipole/electrostatic effects are also likely to have minimal influence. Steric effects will be small favouring two conformational energy minima, one with the formyl eclipsing one carbon monoxide with the formyl oxygen antiperiplanar, the other with the formyl ligand orthogonal to one carbon monoxide. These will be of similar energy since one eclipsing (H/CO) interaction is exchanged for two gauche (H/CO and O/CO) interactions. However, any secondary stereoelectronic effect of the type proposed by Schreiber et al. should favour only the antiperiplanar conformation. As shown in Fig. 8 and 9, for the two very similar

Fig. 6. Newman projection derived from the X-ray crystal structure of $[(C_5Me_5)Ru(CO)(PPhMe_2)CHO]$ ($\theta = 28°$, $\nu(C{=}O) = 1601\ cm^{-1}$).

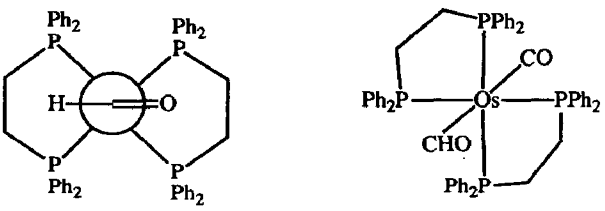

Fig. 7. Newman projection derived from the X-ray crystal structure of [Os(CO)(dppe)$_2$CHO] (ν(C=O) = 1575 cm^{-1}).

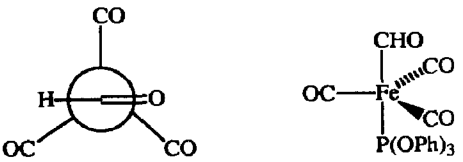

Fig. 8. Newman projection derived from the X-ray crystal structure of [Fe(P(OPh$_3$))(CO)$_3$CHO] (θ = 74°, ν(C=O) = 1580 cm^{-1}).

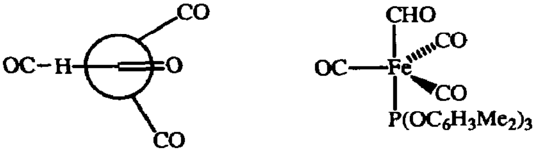

Fig. 9. Newman projection derived from the X-ray crystal structure of [Fe(P(O-3,5-C$_6$H$_3$Me$_2$))(CO)$_3$CHO] (θ = 175°).

Fig. 10. Newman projection derived from the X-ray crystal structure of [Mn(CO)$_2$(P(OPh))$_3$CHO] (θ = 179°, ν(C=O) = 1585 cm^{-1}).

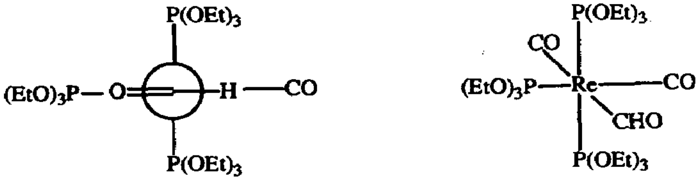

Fig. 11. Newman projection derived from the X-ray crystal structure of [Re(CO)$_2$(P(OEt))$_3$CHO] (θ = 180°, ν(C=O) = 1570 cm^{-1}).

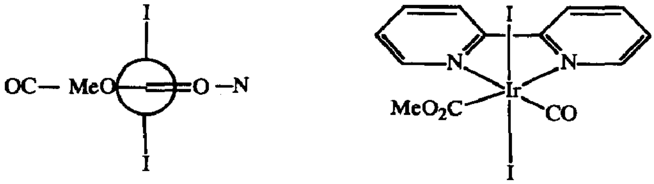

Fig. 12. Newman projection derived from the X-ray crystal structure of [Ir(bipyridyl)(CO)I_2CO_2Me] ($\theta = 176°$).

structures one exhibits the orthogonal conformation and the other the antiperiplanar conformation. While both conformations are compatible with steric interactions the former belies the importance of secondary stereoelectronic effects.

For the octahedral manganese complex [Mn$(CO)_2$(P(OPh_3))CHO] [12] the formyl ligand has two mutually *trans* carbon monoxide ligands and two mutually trans phosphite ligands as near neighbours (Fig. 10). The formyl lies orthogonal to the P–Mn–P axis due to a primary stereoelectronic effect. This places the formyl, therefore, periplanar with the two carbon monoxide ligands. In the analogous rhenium complex [Re$(CO)_2$(P(OEt)$)_3$CHO] [13] (Fig. 11) the formyl has three phosphite and one carbon monoxide ligands as near neighbours. Again, the primary stereoelectronic effect operates to restrict the formyl orthogonal to the P–Re–P axis. In contrast to the manganese case, however, the two orientations of the formyl are not degenerate and the preference for the synperiplanar orientation of the formyl oxygen to the phosphite can be rationalised in dipolar/electrostatic terms; the phosphorus bearing a partial positive charge and the formyl oxygen bearing a partial negative charge. A similar rationalisation accounts for the conformation of the carboxymethyl group in the complex [Ir(bipyridyl)(CO)I_2CO_2Me] [14] (Fig. 12) where the negative charge on the ester carbonyl oxygen is attracted by the adjacent positive nitrogen but repelled by the adjacent partial negative charges on the iodines.

In line with our previous analyses we have demonstrated that, after considering primary stereoelectronic effects where appropriate, the conformations adopted by acetyl ligands bound to transition metal fragments are determined primarily by steric interactions while the corresponding formyl conformations are determined primarily by dipolar and electrostatic forces. In no case is it necessary to invoke a secondary stereoelectronic effect to explain conformational preferences, and hence the existence of such an effect is questionable.

Acknowledgement. We thank the SERC for support (to AJS) and BP International for a Venture Research award (to SGD).

References

1 B.K. Blackburn, S.G. Davies, K.H. Sutton and M. Whittaker, Chem. Soc. Rev., 17 (1988) 147.
2 B.K. Blackburn, S.G. Davies and M. Whittaker, in I. Bernal (Ed.), Stereochemistry of Organometallic and Inorganic Compounds, Vol. 3, Elsevier, Amsterdam, 1988.
3 S. Shambayati, W.E. Crowe and S.L. Schreiber, Angew. Chem., Int. Ed. Engl., 29 (1990) 256.
4 I. Bernal, H. Brunner and M. Muschiol, Inorg. Chim. Acta, 142 (1985) 235.
5 J.W. Herndon, C. Wu and H.L. Ammon, J. Org. Chem., 53 (1988) 2873.
6 D.E. Smith and J.A. Gladysz, Organometallics, 4 (1985) 1480.

7 G.S. Bodner, A.T. Patton, D.E. Smith, S. Georgiou, W. Tam, W.K. Wong, C.E. Strouse and J.A. Gladysz, Organometallics, 6 (1987) 1954.

8 G.O. Nelson and C.E. Summer, Organometallics, 5 (1986) 1983.

9 G. Smith, D.J. Cole-Hamilton, M. Thornton-Pett and M.B. Hursthouse, J. Chem. Soc., Dalton Trans., (1985) 387.

10 C.P. Casey, M.W. Meszaros, S.M. Neumann, I.G. Cesa and K.J. Haller, Organometallics, 4 (1985) 143.

11 C.P. Casey, D.R. McAlister, J.C. Calabrese, S.M. Neumann, M.A. Andrews, M.W. Meszaros and K.J. Haller, Cryst. Struct. Commun., 11 (1982) 1015.

12 H. Berke, G. Huttner, O. Scheidsteger and G. Weiter, Angew. Chem., Int. Ed. Engl., 23 (1984) 735.

13 C. Soutas, O. Orama and H. Berke, Chem. Ber., 120 (1987) 559.

14 V.G. Albano, P.L. Bellon and M. Sansoni, Inorg. Chem., 8 (1969) 298.