Matrix Isolation Studies of the Bonding of Acetyl Groups in the Co-ordinatively Unsaturated Species Acetyltetracarbonylmanganese and Acetylmonocarbonyl(η-cyclopentadienyl)iron †

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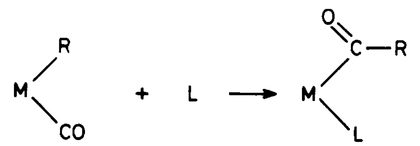
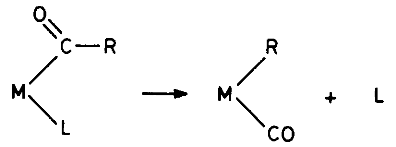
The infrared band positions of $\nu_{CO(acetyl)}$ for $[Mn(CO)_4(COCH_3)]$ and $[Fe(\eta^5\text{-}C_5H_5)(CO)(COCH_3)]$ are reported in CH_4 matrices at 12 K. It is proposed that the acetyl ligands have σ-acetyl type bonding in these co-ordinatively unsaturated species.

Three types of metal acyl bonding can be envisaged: σ-acyls (bonded through the C atom),[1] η^2-acyls (bonded through C and O atoms),[2] and μ-acyls (C and O atoms bridging two metals).[3] Definitive proof of bonding type comes only from *X*-ray crystallographic studies although strong inferences can be drawn from the position of the terminal infrared stretching band, $\nu_{CO(acyl)}$, in conjunction with *X*-ray crystallographic studies. In recent years a growing number of compounds with η^2-acyl bonding have been reported. This has increased the speculation that the assumed intermediate,[4,5] [M(COR)], in CO-insertion reactions [equation (1)] and decarbonylation reactions [equation (2)] might satisfy its co-ordinative unsaturation by η^2-acyl type bonding.


(1)


(2)

In the case of manganese, extended Hückel calculations[6] showed that there was nothing qualitatively wrong with an η^2-acetyl structure for the intermediate $[Mn(CO)_4(COCH_3)]$ but that the overlap match of the fragment orbitals was significantly worse for this structure compared to the σ-acetyl structure. Similarly, careful mechanistic studies[7] neither required nor eliminated an η^2-acetyl structure for $[Mn(CO)_4(COCH_3)]$ and so, in the absence of further information, an η^2-acetyl was assumed not to be present.

Ligand-exchange reactions in optically active iron complexes and investigations on ^{13}CO-labelled and η^5-C_5H_5-acyl bridged complexes were interpreted as showing[8] that the thermal decarbonylation of $[Fe(\eta^5\text{-}C_5H_5)(CO)(COCH_3)L]$ complexes [L=CO or $P(C_6H_5)_2NCH_3\text{-}S\text{-}CH(CH_3)(C_6H_5)$] begins with an intramolecular substitution of the ligand L by the acetyl oxygen with stereospecific formation of an η^2-acetyl intermediate. Attack by incoming ligands at the η^2-acetyl oxygen opens the η^2-bond of the acetyl and leads to the retention of configuration at the iron atom. In the photochemical decarbonylation of $[Fe(\eta^5\text{-}C_5H_5)(CO)(COCH_3)(PPh_3)]$ in tetrahydrofuran, however, the complex $[Fe(\eta^5\text{-}C_5H_5)(CO)(CH_3)(PPh_3)]$ is formed with an opposite configuration.[9] This is consistent[9] with the concept of a methyl migration into the position vacated by photochemical cleavage of the terminal CO ligand.[10] It follows, therefore, that the photochemical reaction cannot involve an η^2-acetyl intermediate.

Matrix isolation studies have been shown to be very useful for characterising unstable species. In previous papers we have presented evidence for the formation of $[Mn(CO)_4(COCH_3)]$[11] and $[Fe(\eta^5\text{-}C_5H_5)(CO)(COCH_3)]$[12] on photolysis of $[Mn(CO)_5(COCH_3)]$ and $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(COCH_3)]$ respectively in gas matrices at *ca.* 12 K. This evidence was based primarily on the terminal metal carbonyl stretching bands (ν_{CO}) because of the overlap of the weaker acetyl stretching bands [$\nu_{CO(acetyl)}$] with atmospheric water bands. In this paper we report the use of a Nicolet 7199 Fourier transform infrared spectrometer to obtain the $\nu_{CO(acetyl)}$ bands for $[Mn(CO)_4(COCH_3)]$ and $[Fe(\eta^5\text{-}C_5H_5)(CO)(COCH_3)]$ and discuss the data in relation to the bonding of the acetyl ligands.

Experimental

Details of the matrix isolation equipment, matrix gases, preparation of compounds, deposition of samples, and photolysis sources have been described previously.[11,12] Infrared spectra were recorded using a Nicolet 7199 Fourier transform i.r. spectrometer. The resolution was better than 0.5 cm^{-1} and the accuracy was ±0.01 cm^{-1}. Spectral subtraction[13] was accomplished by subtracting the absorbance spectrum of the parent complex after deposition from the absorbance spectrum of interest. Subtraction factors were adjusted iteratively until the ν_{CO} and $\nu_{CO(acetyl)}$ bands of the parent compounds had been removed. Spectra are displayed in the conventional percentage transmission form.

Results

Photolysis of $[Mn(CO)_5(COCH_3)]$ *and* $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(COCH_3)]$ *in* CH_4 *Matrices at* 12 K.—The i.r. spectra of $[Mn(CO)_5(COCH_3)]$ [Figure 1(*a*)] and $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(COCH_3)]$ [Figure 2(*a*)] isolated at high dilution in CH_4 matrices show two acetyl bands for each complex in the ketonic $\nu_{CO(acetyl)}$ region (1 700—1 500 cm^{-1}). Splitting of the acetyl band of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(COCH_3)]$ was also observed in Ar (1 680.3m, 1 670.6m, 1 631.9w, and 1 624.1w cm^{-1}), N_2 (1 677.1m, 1 672.3m, and 1 630.4w cm^{-1}), and CO (1 665.8m and 1 629.7w cm^{-1}) matrices.[12] Such splittings may be attributed to aggregation effects, matrix effects, or molecular conformation effects.[14] Aggregation which gives rise to discrete bands corresponding to monomers, dimers, trimers, and polymers is most pronounced for small molecules. In the case

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† *Non-S.I. unit employed:* cal = 4.184 J.

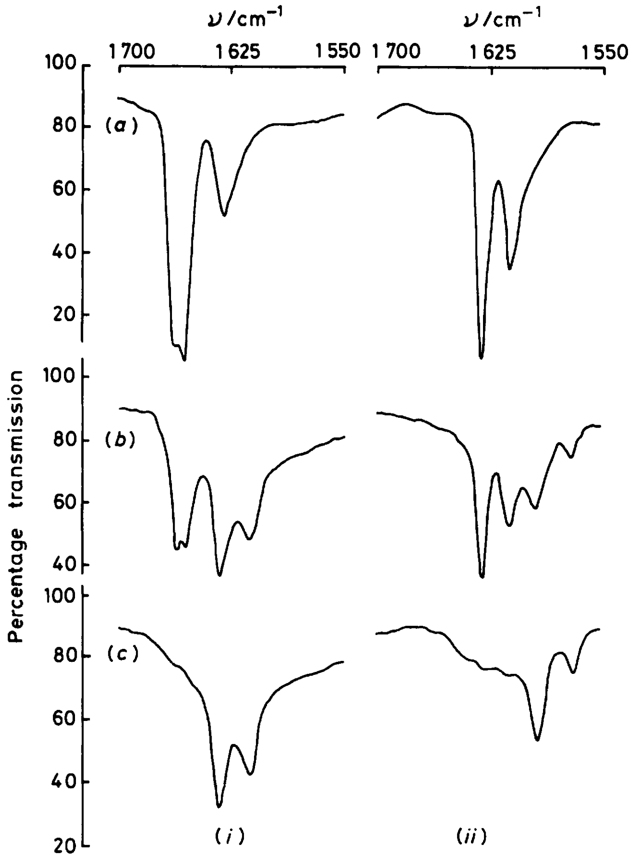

Figure 1. Infrared spectra from experiments with (*i*) [Mn(CO)$_5$(^{12}COCH$_3$)] and (*ii*) [Mn(CO)$_5$(^{13}COCH$_3$)] isolated in CH$_4$ matrices at 12 K: (*a*) after deposition, (*b*) after 50 min photolysis, and (*c*) after subtraction, *i.e.* (*b*) − *A*(*a*), where *A* is a scaling constant

of larger molecules, such as metal carbonyls, aggregation effects are manifest in broad bands which tail to lower wavenumbers. In this work the amount of matrix gas sprayed on was increased until neither band broadening nor band tailing was observed. In such circumstances monomer isolation was assumed. Matrix splitting effects can arise from different trapping sites for small molecules, different packing arrangement of host matrix molecules around large molecules, and different phases of the solid host matrix.[14] Such effects produce splittings of the order of 0—10 cm^{-1} and are strongly host matrix dependent. The 20—40 cm^{-1} splittings observed for the acetyl complexes in CH$_4$ matrices (Table), therefore, may be attributed to some form of conformational isomerism, for example rotation of the acetyl group about the metal–acetyl bond (see Discussion section). The consistency of the acetyl band splitting for [Fe(η^5-C$_5$H$_5$)(CO)$_2$(COCH$_3$)] in a number of matrices (CH$_4$, 39.6; Ar, 47.7; N$_2$, 44.3; CO, 36.1 cm^{-1}) and the consistency of relative band intensities (m : w in all cases) reinforces the conclusion that conformational isomerism is occurring. Amongst the host matrices different patterns of smaller splittings were observed (see above and Table).

Irradiation of the matrices for 50 min using a filtered medium-pressure mercury arc ($320 < \lambda < 390$ nm) led to the production of new pairs of bands [Figures 1(*b*) and 2(*b*)] and these are shown more clearly in the difference spectra [Figure 1(*c*) and 2(*c*)]. Concomitantly new terminal carbonyl bands were observed in the 2 100—1 900 cm^{-1} region which corresponded to those obtained previously for [Mn(CO)$_4$(COCH$_3$)][11] and [Fe(η^5-C$_5$H$_5$)(CO)(COCH$_3$)].[12] The assignment of the new

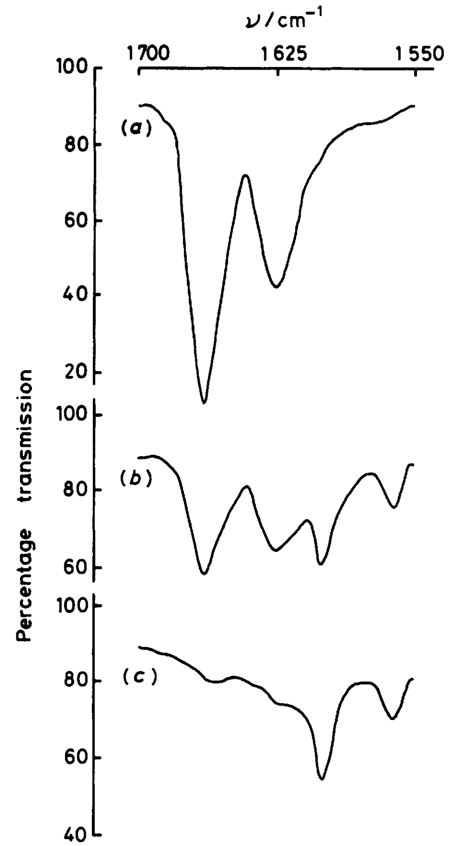

Figure 2. Infrared spectra from an experiment with [Fe(η^5-C$_5$H$_5$)(CO)$_2$(COCH$_3$)] isolated in a CH$_4$ matrix at 12 K: (*a*) after deposition, (*b*) after 50 min photolysis, and (*c*) after subtraction, *i.e.* (*b*) − *A*(*a*), where *A* is a scaling constant

bands in the 1 700—1 500 cm^{-1} region (Table) as $\nu_{CO(acetyl)}$ bands was conclusively confirmed by the appropriate ^{13}CO—^{12}CO shift for [Mn(CO)$_4$(^{13}COCH$_3$)] compared to [Mn(CO)$_4$(^{12}COCH$_3$)] in an experiment involving the photolysis of [Mn(CO)$_5$(^{13}COCH$_3$)].

Discussion

The wavenumber ranges of $\nu_{CO(acyl)}$ for σ-acyls (1 700—1 620 cm^{-1}) and η^2-acyls (1 620—1 450 cm^{-1}, Table) have been established [5] using i.r. spectroscopy in conjunction with *X*-ray crystallography.* Since the values of $\nu_{CO(acetyl)}$ for [Mn(CO)$_5$(COCH$_3$)] (1 662.8 cm^{-1} in n-hexane) and [Fe(η^5-C$_5$H$_5$)(CO)$_2$(COCH$_3$)] (1 670.4 cm^{-1} in n-hexane) fall in the upper range it may safely be concluded that the acetyl groups are bonded in a σ-acyl manner. Additionally the close correspondence of the band positions in n-hexane for the two compounds, which may be regarded as isoelectronic, indicates that the metal–acetyl bonding must be very similar in the two parent compounds. Before using i.r. data to discuss the metal–acetyl bonding in [Mn(CO)$_4$(COCH$_3$)] and [Fe(η^5-C$_5$H$_5$)(CO)-

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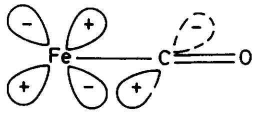
* *Note added at proof:* On the basis of n.m.r. and i.r. spectroscopy the complexes [Fe(η^5-C$_5$H$_5$)(PMe$_3$)$_2$(COC$_2$H$_5$)] ($\nu_{CO(acyl)}$ 1520 cm^{-1}) and [Fe(η^5-C$_5$H$_5$){P(OMe)$_3$}$_2$(COC$_2$H$_5$)] ($\nu_{CO(acyl)}$ 1528 cm^{-1}) were thought to possess η^2-propionyl ligands. *X*-Ray crystallography, however, has shown that the first contains a normal σ-propionyl ligand (H. G. Alt, M. E. Eichner, B. M. Jansen, and H. Thewalt, *Z. Naturforsch.*, *Teil B*, in the press). The range for $\nu_{CO(acyl)}$ in σ-bonded acyls would seem, therefore, to extend to much lower wavenumbers than previously envisaged.[5]

Table. Acetyl stretching band positions [$\nu_{\text{CO(acetyl)}}$] for compounds in CH_4 matrices, solutions, and Nujol mulls

Compound	$\nu_{\text{CO(acetyl)}}$/cm^{-1}		
	CH_4	Solution	Nujol
$[Mn(CO)_5(^{12}COCH_3)]$	1 665.4 1 656.9 [a] 1 629.6	1 662.8 [b]	1 661.5
$[Mn(CO)_5(^{13}COCH_3)]$	1 629.3 1 610.5	1 627.2 [b]	1 625.9
$[Fe(\eta^5\text{-}C_5H_5)(CO)_2(COCH_3)]$	1 666.0 1 626.4	1 670.4 [b]	1 667.9
$[Mn(CO)_4(^{12}COCH_3)]$	1 633.7 1 612.7		
$[Mn(CO)_4(^{13}COCH_3)]$	1 592.6 1 569.7		
$[Fe(\eta^5\text{-}C_5H_5)(CO)(COCH_3)]$	1 602.0 1 564.7		
$[Ti(\eta^5\text{-}C_5H_5)_2Cl(COCH_3)]$ [c,d]			1 620
$[Zr(\eta^5\text{-}C_5H_5)_2(CH_3)(COCH_3)]$ [c,e]		1 540 [f]	1 545
$[Hf(\eta^5\text{-}C_5H_5)_2(CH_3)(COCH_3)]$ [c,g]		1 550 [f]	1 550
$[Th(\eta^5C_5Me_5)_2Cl(COCH_2CMe_3)]$ [c,h]		1 469 [i] 1 434	
$[Ru(CO)_2(COCH_3)(PPh_3)_2]$ [j,k]		1 505 [i]	1 505
$[V(\eta^5\text{-}C_5H_5)_2(CO)(COCH_3)]$ [j,l]		1 605 [m]	
$[W(\eta^5\text{-}C_5H_5)(CO)(C_2H_2)(COCH_3)]$ [j,n]		1 591 [i]	

[a] Matrix splitting. [b] In n-hexane. [c] η^2-Acetyl bonding established by *X*-ray crystallography. [d] Data from G. Fachinetti, C. Floriani, and H. Stoekli-Evans, *J. Chem. Soc., Dalton Trans.*, 1977, 2297. [e] Data from ref. 2. [f] In CH_2Cl_2. [g] Data from G. Fachinetti, G. Fochi, and C. Floriani, *J. Chem. Soc., Dalton Trans.*, 1977, 1946. [h] Data from ref. 18. [i] In C_6H_6. [j] η^2-Acetyl bonding inferred on the basis of $\nu_{\text{CO(acetyl)}}$. [k] Data from R. R. Hitch, S. K. Gondal, and C. T. Sears, *Chem. Commun.*, 1971, 777. [l] Data from G. Fachinetti, S. D. Nero, and C. Floriani, *J. Chem. Soc., Dalton Trans.*, 1976, 203. [m] In tetrahydrofuran. [n] Data from H. G. Alt, *J. Organomet. Chem.*, 1977, **127**, 349.

$(COCH_3)]$ it is important to establish the significance or otherwise of any specific effects which the matrix isolation experiment might have on $\nu_{\text{CO(acetyl)}}$. For example both $[Mn(CO)_5(COCH_3)]$ and $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(COCH_3)]$ show single $\nu_{\text{CO(acetyl)}}$ bands at ambient temperatures in solution and in Nujol whereas at 12 K both show two well separated bands (Table).



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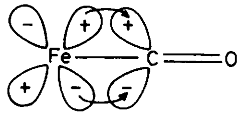

II

The i.r. spectra of a number of σ-acyl complexes show *two* $\nu_{\text{CO(acyl)}}$ bands in a variety of media, *e.g.* neat, Nujol mull, cyclohexane solution, and CCl_4 solution, although the relative intensities of the two bands vary with the medium and from compound to compound. The corresponding ^{1}H n.m.r. spectra, however, show only one acyl environment. These observations have been attributed [15,16] to conformational isomerism about the metal–acyl bond with a barrier to rotation estimated [15] as $\leqslant 10$ kcal mol^{-1}. The fact that *two* acyl bands are observed in a situation where *three* [16] $\{[Pt(\eta^5\text{-}C_5H_5)(CH_3)_2(COCH_3)]$ or $[Pt(\eta^5\text{-}C_5H_5)(C_2H_5)_2(COC_2H_5)]\}$ or *four* [15] $\{[Fe\{HB(pz)_3\}(CO)_2(COCH_3)]$ (pz = pyrazol-1-yl)$\}$ bands had been expected can be explained by recognising that an acyl ligand is a single-faced π-acceptor ligand [6] which should have a definite preference for a particular orientation of its π-acceptor orbital. A favourable orientation of the acyl ligand should lead to an increased metal–carbon bond order, a decreased carbon–oxygen bond order, and a substantial shift of $\nu_{\text{CO(acyl)}}$ to lower wavenumbers. This is borne out by the 30—40 cm^{-1} separation of the acetyl bands of $[Fe\{HB(pz)_3\}(CO)_2(COCH_3)]$ [$\nu_{\text{CO(acetyl)}}$ = 1 683m and 1 648m cm^{-1} in cyclohexane] [15] and of $[Pt(\eta^5\text{-}C_5H_5)(CH_3)_2(COCH_3)]$ [$\nu_{\text{CO(acetyl)}}$ = 1 693s and 1 663m cm^{-1} in CCl_4].[16] It is interesting to note that at ambient temperatures the intensity of the lower acetyl band, corresponding to the favourable orientation and an increased metal–carbon bond order (type II conformer), is equal to that of the upper band (type I conformer) in $[Fe\{HB(pz)_3\}(CO)_2(COCH_3)]$,[15] is lower in $[Pt(\eta^5\text{-}C_5H_5)(CH_3)_2(COCH_3)]$ or $[Pt(\eta^5\text{-}C_5H_5)(C_2H_5)_2(COC_2H_5)]$ [16] complexes, while for the remainder of σ-acetyl complexes in solution, *e.g.* $[Mn(CO)_5(COCH_3)]$ and $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(COCH_3)]$ (Table), no lower acetyl bands are observed. The observation of two acetyl bands for $[Mn(CO)_5(COCH_3)]$ and $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(COCH_3)]$ in matrices at 12 K with similar separations to those for $[Fe\{HB(pz)_3\}(CO)_2(COCH_3)]$ [15] and $[Pt(\eta^5\text{-}C_5H_5)(CH_3)_2(COCH_3)]$ [16] is consistent with the trapping of two acetyl conformers at low temperatures. In other words, although free rotation of the acetyl group on the i.r. time-scale may be taking place at ambient temperatures, type I (upper band) and type II (lower band) conformers are trapped by depositing the compounds onto a low-temperature window. Interestingly, the band positions of the type I conformers in CH_4 matrices are very close to positions of the bands observed for solutions and mulls (Table) where the acetyl groups are freely rotating. Additionally, the relative intensities of the bands at 12 K are similar to those for $[Pt(\eta^5\text{-}C_5H_5)(CH_3)_2(COCH_3)]$ or $[Pt(\eta^5\text{-}C_5H_5)(C_2H_5)_2(COC_2H_5)]$.[16]

Two pieces of information are relevant in the discussion of the bonding of the acetyl ligands in $[Mn(CO)_4(COCH_3)]$ and $[Fe(\eta^5\text{-}C_5H_5)(CO)(COCH_3)]$. These are (*i*) the $\nu_{\text{CO(acetyl)}}$ band position, and (*ii*) the band multiplicity.

In relation to (*i*) it should be noted that when a CO ligand is removed from a metal carbonyl complex to give a 16-electron co-ordinatively unsaturated species then the bonding of the remaining ligands is strengthened. In the case of terminal CO ligands this strengthening is manifested by a shift in ν_{CO} to lower wavenumbers. On the basis of a ~35 cm^{-1} shift to lower wavenumbers in ν_{CO} for $[\mathrm{M(CO)}_{n-1}\mathrm{L}_m]$ species compared to $[\mathrm{M(CO)}_n\mathrm{L}_m]$ complexes,[17] a shift in $\nu_{\mathrm{CO(acetyl)}}$ to lower wavenumbers of approximately 30 cm^{-1} might be expected.

In relation to *(ii)* it should be noted that the bands corresponding to both conformers are depleted equally during photolysis and that both the product species show two acetyl bands with splittings analogous to those of the parent compounds. In the following discussion of $\nu_{\mathrm{CO(acetyl)}}$ band shifts, the positions of the more intense upper bands will be used.

The $\nu_{\mathrm{CO(acetyl)}}$ band position for $[\mathrm{Mn(CO)_4(COCH_3)}]$ (1 633.7 cm^{-1}, Table) is within the range for σ-acyl complexes. The downwards shift (32 cm^{-1}) from the band position of $[\mathrm{Mn(CO)_5(COCH_3)}]$ is also consistent with that expected on removing a CO ligand. It seems probable, therefore, that the acetyl ligand in $[\mathrm{Mn(CO)_4(COCH_3)}]$ is bonded in a σ-acyl manner as predicted by the extended Huckel calculations.[6] These calculations also predict that rotation round the metal–acetyl bond will be a difficult process requiring some 20 kcal mol^{-1}. The observation of two acetyl bands for $[\mathrm{Mn(CO)_4(COCH_3)}]$ with similar relative intensities to those for $[\mathrm{Mn(CO)_5(COCH_3)}]$ supports the prediction of a high barrier to rotation. If the barrier had been low then the excess energy from the photolysis, after the ejection of a CO ligand, could perhaps have been dissipated by rotation of the acetyl ligand. It seems likely, therefore, that the two orientations of the acetyl ligand are retained during the photolysis step to form $[\mathrm{Mn(CO)_4(COCH_3)}]$.

By contrast, the $\nu_{\mathrm{CO(acetyl)}}$ band position for $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{(CO)(COCH_3)}]$ (1 602.0 cm^{-1}) falls in the range expected for an η^2-acyl. The downwards shift in $\nu_{\mathrm{CO(acetyl)}}$ (~65 cm^{-1}) is more than that expected on removal of a CO ligand, *cf.* the 32 cm^{-1} shift for $[\mathrm{Mn(CO)_4(COCH_3)}]$. This is underlined by noting that the corresponding shift in ν_{CO} is 43 cm^{-1} {ν_{CO} (mean) for $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{(CO)_2(COCH_3)}]$ − ν_{CO} for $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{(CO)(COCH_3)}]$},[12] which is the magnitude of shift expected. It would seem, therefore, that the ketonic C–O order in $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{(CO)(COCH_3)}]$ is significantly lower than in $[\mathrm{Mn(CO)_4(COCH_3)}]$ and this could be consistent with η^2-acyl bonding in $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{(CO)(COCH_3)}]$. However, the observation of two acetyl bands for $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{(CO)(COCH_3)}]$ suggests the retention of type I (1 602.0 cm^{-1}) and type II (1 564.7 cm^{-1}) forms of a σ-acetyl ligand on photolysis (see above). If the bonding had changed from σ-acetyl type to η^2-acetyl type on going from $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{(CO)_2(COCH_3)}]$ to $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{(CO)(COCH_3)}]$ it seems likely that there would be much less difference between different orientational forms, and a much smaller $\nu_{\mathrm{CO(acetyl)}}$ splitting because of the strength of the Fe–O interaction in the η^2-acetyl geometry and also because of the lack of steric crowding in the co-ordinatively unsaturated species. Two instances of doublet $\nu_{\mathrm{CO(acetyl)}}$ bands have been reported.[18,19] A large splitting (~35 cm^{-1}) was reported for $[\mathrm{Th}(\eta^5\text{-}\mathrm{C_5Me_5})_2\mathrm{Cl}(\eta^2\text{-}\mathrm{COCH_2CMe_3})]$ [18] and a smaller splitting (~25 cm^{-1}) was reported for $[\mathrm{Zr}(\eta^5\text{-}\mathrm{C_5H_5})_2(\eta^2\text{-}\mathrm{COC_6H_4Me}\text{-}p)(\mathrm{C_6H_4Me}\text{-}p)]$ [19] and in both compounds the observation of a split acetyl band was ascribed to the high degree of steric crowding. There would appear to be very little steric crowding in $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{(CO)(COCH_3)}]$. Since the splitting of the acetyl bands depends on band position,[18] a splitting of less than 20 cm^{-1} might have been expected if the acetyl ligand in $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{(CO)(COCH_3)}]$ was to adopt the η^2-bonding mode. On the basis of the very large (37 cm^{-1}) splitting of the $\nu_{\mathrm{CO(acetyl)}}$ bands it seems more likely that σ-acetyl bonding is retained in $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{(CO)(COCH_3)}]$. Differences in band positions between $[\mathrm{Mn(CO)_4(COCH_3)}]$ and $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{(CO)(COCH_3)}]$ can be rationalised in terms of the considerably greater π-acceptor capabilities of four CO ligands *versus* an $\eta^5\text{-}\mathrm{C_5H_5}$ ligand and a CO ligand respectively.

The identification of the acetyl bonding as σ-acyl type in $[\mathrm{Mn(CO)_4(COCH_3)}]$ and $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{(CO)(COCH_3)}]$ is consistent with the dissociative mechanism proposed[9,10] for photochemical decarbonylation reactions where CO loss is followed by methyl migration into the site vacated by the CO ligand rather than the formation of an η^2-acetyl intermediate.

Future studies will investigate the matrix photochemistry of acetyl complexes whose η^2-acetyl bonding has been established unequivocally by *X*-ray crystallography for example $[\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{Cl(COCH_3)}]$ and $[\mathrm{Zr}(\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{(CH_3)(COCH_3)}]$.

Acknowledgements

We thank Dr. H. Berke and Professor H. Brunner for helpful discussions, the Universiti Teknologi Malaysia for a Research Studentship (to R. B. H.), and the S.E.R.C. for support (to A. J. R.).

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Received 9*th July* 1982; *Paper* 2/1160