Reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNR)_n]$ (n = 1 or 2; R = Me, Et, or CH_2Ph) with Acetyl and Benzoyl Chlorides

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Complexes $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2L(CNR)]$ (L = CO or CNR; R = Me, Et, or CH_2Ph) react with R′COCl (R′ = Me or Ph) in tetrahydrofuran solution at room temperature to give $[Fe_2(\eta\text{-}C_5H_5)_2(CO_{\mu})(CO_t)L_t\{CN(R)COR'_{\mu}\}]X$ salts. These are unstable (*a*) with respect to hydrolysis to species such as $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{CN(Me)H\}]^+$, $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)\{CN(Me)H\}]^+$, and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{CN(Me)H\}_2]^{2+}$, and (*b*) with respect to metal–metal bond scission to species such as $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)_2]^+$.

THE nitrogen atom of the μ-RNC ligand of various $[Fe_2(\eta\text{-dienyl})_2(CO)_{4-n}(CNR)_n]$ complexes (dienyl = C_5H_5, C_5H_4Me, or C_9H_7; n = 1 or 2; R = alkyl or aryl) is susceptible to electrophilic attack by sources of protons or carbonium ions to give derivatives containing the $R(R')\overset{+}{N}{=}C{=}$ (R′ = alkyl or H) or iminium ligand which bridges two Fe atoms.[1-4] Richards and co-workers[5] have shown that isocyanides which are terminally co-ordinated to electron-rich metal centres, *e.g.* in $[M(CNR)_2(Ph_2PCH_2CH_2PPh_2)_2]$ (M = Mo or W), are also susceptible to electrophilic attack although they formulate the resultant terminal ligand as being one of the carbyne type, *e.g.* $[R(R')NC{\equiv}\overset{+}{M}L_n]$.

We describe here the reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNR)_n]$ (n = 1 or 2) with acyl chlorides R′COCl (R′ = Me or Ph) to give salts of the unstable $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2L\{CN(R)COR'\}]^+$ cations (L = CO or CNR). Chatt *et al.*[6] have shown that ligated dinitrogen also reacts with acyl chlorides to give complexes containing the $RCONN{\rightarrow}M$ moiety (W = W^0 or Re^I).

EXPERIMENTAL

The $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNR)_n]$ complexes were prepared as described elsewhere[7] from $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ and RNC. Their $\eta\text{-}C_5H_4Me$ counterparts were obtained similarly. Other chemicals were purchased. All reactions were carried out at room temperature under an atmosphere of nitrogen in solvents which had been purified by distillation from calcium hydride prior to use.

A solution of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNR)]$ (1 g) (R = Me, Et, or CH_2Ph) and MeCOCl (mol ratio 1 : 1) in tetrahydrofuran (thf, 50 cm^3) was stirred for 10 min during which time a solid precipitated. After another 40 min the solid was filtered off, washed with benzene and pentane, and dried. The reactions between $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNR)]$ and PhCOCl were carried out similarly but were much slower and required *ca.* 12 h for completion. The reactions between $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ and MeCOCl or PhCOCl were carried out as described above with reaction times of *ca.* 12 h.

The complex $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{CN(Me)COPh\}]Cl$ (0.1 g) was dissolved in MeOH (10 cm^3) and a saturated solution of $Na[BF_4]$ in MeOH (10 cm^3) added. The colour of the solution lightened, and yellow crystals of $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)_2][BF_4]$ precipitated.

Attempts to recrystallise $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)\{CN(Me)COMe\}]Cl$ from wet $CHCl_3$ gave a low yield of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{CN(Me)H\}_2]Cl_2{\cdot}2H_2O$.[3]

Infrared spectra in the 1 500—2 200 cm^{-1} region were run on a Perkin-Elmer **337** spectrometer fitted with a readout recorder. They were calibrated using DCl and H_2O vapour so that peak positions are accurate to ± 1 cm^{-1}. The spectra, together with the yields of the various products, their melting points, and analyses, are summarised in the Table. Analyses were determined in the Microanalytical Laboratory of University College, Dublin.

RESULTS AND DISCUSSION

Equimolar amounts of acyl chlorides, R′COCl (R′ = Me or Ph), and the purple $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2L(CNR)]$ complexes (L = CO or CNR; R = Me, Et, or CH_2Ph) react in tetrahydrofuran (thf) solution at room temperature. When L = CO, the reactions of MeCOCl are very rapid and are probably complete within 10 min. Those of PhCOCl and where L = CNR are much slower and require *ca.* 12 h.

In only three of the eight reactions attempted were we able to isolate and characterise unambiguously, by both analysis and i.r. spectroscopy, products which were salts of the acylimmonium cations, $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2L\{CN(R)COR'\}]^+$. In three other instances i.r. spectroscopy showed that the expected complexes were formed, but either the products were isolated in very low yields or they were unstable and consistent analytical data could not be obtained. Different products were formed in other reactions. They will be discussed later.

The $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2L\{CN(R)COR'\}]X$ salts are orange crystalline solids which decompose in air at room temperature and more slowly at −25 °C under nitrogen. Although insoluble in benzene or pentane, they dissolve in polar solvents, *e.g.* CH_2Cl_2, $CHCl_3$, thf, or MeOH, but are generally very unstable in solution. Consequently product purification by recrystallisation was not possible, and consistent analyses were difficult to obtain. This instability prevented us from measuring meaningful conductivities and n.m.r. spectra. However, the i.r. spectra discussed below are consistent with the structure we attribute to these compounds.

The i.r spectra of the solids in the 1 500—2 200 cm^{-1} region sometimes varied from sample to sample due to the presence of by-products, but it was possible to select the absorption bands which were due to the C–O and C–N stretching vibrations of the desired complexes. In other instances clear spectra of good quality were obtained, but the compounds decomposed rapidly in chloroform or thf solutions. The new absorption bands could be identified readily and discounted. The results are summarised in the Table.

The spectra are very similar to those of *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO_\mu)(CO_t)_2\{CN(R)R''_\mu\}]^+$ and $[Fe_2(\eta\text{-}C_5H_5)_2(CO_\mu)(CO_t)(CNR_t)\{CN(R)R''_\mu\}]^+$ cations,[3,4] but contain an extra absorption band, B or G. Consequently we can assume that the alkyl and acyl adducts are isostructural and that the latter are salts of the *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO_\mu)(CO_t)_2\{CN(R)COR'_\mu\}]^+$ and $[Fe_2(\eta\text{-}C_5H_5)_2(CO_\mu)(CO_t)(CNR_t)\{CN(R)COR'_\mu\}]^+$ cations. Then absorption bands A and F are assigned to $\nu(C{=}N_\mu)$, C and H to $\nu(CO_\mu)$, D, E, and I to $\nu(CO_t)$, and J to $\nu(CN_t)$. The arguments supporting this assignment may be found in refs. 3 and 4. The extra absorption bands B and G are clearly due to the C–O stretching vibrations of the RCO groups, $\nu(CO_a)$. When R′ = Ph these are single peaks with frequencies at *ca.* 1 740 cm^{-1} (*cf.* 1 640 cm^{-1} for $PhCONEt_2$ or 1 773 cm^{-1} for PhCOCl[8]). In the acetyl derivatives $\nu(CO_a)$ has a higher frequency and for $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{CN(Et)COMe\}]^+$ it appears to have two components. If the CN(R)COR′ moiety is planar, isomerism is possible with R′ *cis* or *trans* to R. When R = Et and R′ = Me the two isomers might be expected to have comparable stabilities, but if the size of R or R′ were increased, steric interactions would destabilise one with respect to the other.

Melting points, analyses, and i.r. spectra (1 500—2 200 cm^{-1})

Compound	M.p.[a] (θ_c/°C)	Analysis (%) [b] C	H	N	Absorption bands (cm^{-1}) [c] A	B	C	D	E
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{CN(Me)COPh\}]Cl$	22—24	50.4	3.4	2.6	*d* 1 594	1 741	1 837	1 995	2 032
		(52.0)	(3.4)	(2.7)	(1.0)	(1.7)	(3.1)	(2.8)	(10)
					e 1 594w	1 741m	1 849s	1 973s	2 023s,br
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{CN(Et)COMe\}]Cl$	25	47.3	3.7	3.1	*e* 1 593w	1 764w 1 794w	1 807m	1 975s	2 022s,br
		(47.1)	(3.9)	(3.0)					
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{CN(CH_2Ph)COMe\}]Cl$	25	53.0	4.0	2.7	*c* 1 593w	1 753w	1 807m	1 983m	2 013s,br
		(52.9)	(3.8)	(2.7)					
$[Fe_2(\eta\text{-}C_5H_5)_3(CO)_3\{CN(Et)COPh\}]Cl$					*d* 1 594	1 740	1 827	1 996	2 032
					(1.4)	(3.2)	(5.9)	(3.2)	(10)
					e 1 593w	1 740m	1 823m	1 989s	2 012s,br
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{CN(CH_2Ph)COPh\}]Cl$					*e* 1 590w	1 788	1 811m	1 988s	2 016s,br
					F	G	H	I	J
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)\{CN(Me)COPh\}]Cl$					*d* 1 598	1 737	1 804	1 987	2 182
					(3.2)	(2.4)	(5.7)	(10)	(9.0)
					e 1 597m	1 722m	1 801s	2 000s	2 181s
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)\{CN(Me)H\}][PF_6]$	>360	36.0	3.4	5.6	*d* 1 599		1 803	1 986	2 182
		(36.5)	(3.2)	(5.3)	(3.5)		(3.2)	(10)	(6.2)
					e 1 593m		1 798m	2 003s	2 182
									(6.0)

[a] Measured in sealed tubes. [b] Calculated values in parentheses. [c] Relative peak heights in parentheses; w = weak, m = medium, s = strong, and br = broad. [d] Chloroform solution. [e] Nujol mull.

Benzoyl chloride reacted more rapidly and acetyl chloride much more rapidly with $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2L(CNR)]$ than did methyl iodide. This is consistent with the greater susceptibility of acyl halides towards nucleophilic attack. At the same time the products were less stable because the R′CO group is more bulky than a primary alkyl group, and the steric interactions between the $\mu\text{-}C\overset{+}{N}(R)COR'$ ligand and the $Fe(\eta\text{-}C_5H_5)(L_t)$ moieties would be greater. Although delocalisation of electrons throughout the μ-ligand may be enhanced this would only be possible if the whole was planar, and steric effects may prevent this. The benzoyl derivatives are more difficult to form, perhaps a steric effect, but when obtained they are more stable. This may be a consequence of further delocalisation in the phenyl ring.

Another factor which must be considered is the susceptibility of the $C{=}\overset{+}{N}(R)COR'$ moiety to nucleophilic attack. Although the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2L\{CN(R)R'\}]^+$ cations are dealkylated by liquid ammonia to $[Fe_2(\eta\text{-}C_5H_5)(CO)_2L(CNR)]$, they are stable towards water. On the other hand their acyl counterparts, especially the acetyl derivatives, are very susceptible to hydrolysis, with the formation of salts containing the $\mu\text{-}C{=}\overset{+}{N}(R)H$ ligand. Of interest in this respect is the product isolated from the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$–MeCOCl reaction by the addition of $K[PF_6]$ or $[NEt_4][PF_6]$. This, and its precursor in the reaction mixture in the absence of $[NEt_4][PF_6]$, has an i.r. spectrum similar to that anticipated for $[Fe_2(\eta\text{-}C_5H_5)_2(CO_\mu)(CO_t)(CNMe_t)\{CN(Me)COMe_\mu\}][PF_6]$ except that absorption band G, due to $\nu(CO_a)$, is absent. Furthermore, although the analytical data are consistent with this formulation together with two molecules of water of crystallisation (C, 35.8; H, 3.8; N, 4.7%; *cf.* Table), in the light of the earlier discussion we feel that the latter are unlikely to be present. Consequently we formulate this product as $[Fe_2(\eta\text{-}C_5H_5)_2(CO_\mu)(CO_t)(CNR_t)\{CN(Me)H_\mu\}][PF_6]$, a salt of a type which we have been unable to isolate before, but which we have detected in phenolic solutions of various $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNR)_2]$.[9] Its i.r. spectrum shows a $\nu(NH)$ frequency (3 280 cm^{-1}) in the same region as the related compounds $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{CN(C_6H_{11})H\}][PF_6]$ and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{CN(Me)H\}_2][PF_6]_2$ (3 275 and 3 280 cm^{-1} respectively; all as Nujol mulls). If, instead of $[NEt_4][PF_6]$, aqueous HPF_6 is added to the reaction mixture the only product is $[Fe_2(\eta\text{-}C_5H_5)_2(CO_t)_2\{CN(Me)H\}_2]X_2$ ($X = PF_6$) whilst water allows isolation of the related salt where $X = Cl{\cdot}H_2O$. Under the same conditions, the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)]$–MeCOCl–$HPF_6$ reaction gives $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{CN(Me)H\}][PF_6]$.[3]

The $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2L\{CN(R)COR'\}]X$ salts are also unstable towards a form of decomposition which results in the disappearance of all bridging ligands. It can take place slowly in the solid state, but more rapidly in solution. It is virtually instantaneous for $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{CN(Et)COMe\}]Cl$ in chloroform solution, but proceeds more slowly for other compounds, especially the benzoyl derivatives. The i.r. spectra of the final species show only absorption bands due to the stretching vibrations of the terminal carbonyl and isocyanide ligands. In most solutions two species appear to be present. In one instance, dissolution of the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$–MeCOCl product in MeOH gave $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)_2]^+$ isolated as its $[BF_4]^-$ salt. This breakdown into mononuclear fragments is a common feature of the chemistry of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNR)_n]$ complexes with strong Lewis acids such as BF_3.[10]

No adducts could be detected as products of the reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ with $p\text{-}MeC_6H_4SO_2Cl$. Infrared spectroscopic studies showed that, under the same conditions as those used for acyl halides, species which did not possess μ-ligands were formed immediately. The reaction was not studied further.

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