Journal of Organometallic Chemistry, 54 (1973) C39–C44

Preliminary communication

The interaction of Lewis bases with (acrylic acid) iron tetracarbonyl in solution

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(Received April 4th, 1973)

SUMMARY

(Acrylic acid) iron tetracarbonyl has been found to react with PCl_3 to give the complex $(CH_2{=}CHCOCl)Fe(CO)_4$ which undergoes further reaction with amines to give the amide derivatives. In addition, (acrylic acid) iron tetracarbonyl is found to form 1/1 complexes, $(CH_2{=}CHCOOH)Fe(CO)_4L$, in hexane solution with a variety of phosphine ligands (L).

We report the formation of mono(olefin) complexes derived from the reactions of (acrylic acid) iron tetracarbonyl and a variety of Lewis bases under very mild conditions.

(Acrylic acid) iron tetracarbonyl[1,2], $(CH_2{=}CHCOOH)Fe(CO)_4$, has been found to undergo reaction with phosphorus trichloride in hexane to form the acid halide complex, $(CH_2{=}CHCOCl)Fe(CO)_4$, in 90–95% yield. This product can be isolated from the hexane solution at −78° as a yellow solid which melts near room temperature to yield a bright yellow-orange liquid, which is readily converted back to the acrylic acid complex by moist air. The IR absorptions in the CO stretching region, together with the acyl carbonyl and C=C frequencies, are shown in Table 1. (Anal. Found: C, 32.6; H, 1.25; Cl, 13.53. $C_7H_3ClFeO_5$ calcd.: C, 32.5; H, 1.16; Cl, 13.78%).

The previously reported amide derivative[1], $(CH_2{=}CHCONH_2)Fe(CO)_4$, was prepared by the reaction of the acid chloride with NH_3 in hexane in >80% yield as a yellow solid (m.p. 115–116°). Its IR spectral absorptions are shown in Table 1 along with

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TABLE 1

INFRARED ABSORPTIONS OF $LFe(CO)_4$ COMPOUNDS AND ADDUCTS OF (ACRYLIC ACID) IRON TETRACARBONYL

Compound	$\nu(CO)/(cm^{-1})$ [a]				$\nu(C{=}O)/(cm^{-1})$	$\nu(C{=}C)/(cm^{-1})$
	$A_1^{(2)}$	$A_1^{(1)}$	B_2	B_1		
$(CH_2{=}CHCOOH)Fe(CO)_4$	2102.5	2037.4	2024.4	2000.6	1678	1425
$(CH_2{=}CHCOCl)Fe(CO)_4$	2106.0	2043.7	2031.3	2008.6	1756	1374
$(CH_2{=}CHCONH_2)Fe(CO)_4$	2094.6	2028.7	2011.2	1981.8	1650	1425
$(CH_2{=}CHCONC_5H_{10})Fe(CO)_4$	2095.0	2029.0	2011.0	1982.0	1652	1430
$(CH_2{=}CHCOO)Fe(CO)_4{}^-NH_4{}^+$	2084.5	2015.2	2005.3	1974.2	1630 (asym)	1462
$(CH_2{=}CHCOO)Fe(CO)_4{}^-NH_2C_5H_{10}{}^+$	2084.1	2015.6	2004.6	1973.8	1400 (sym)	
$(CH_2{=}CHCOO)Fe(CO)_4{}^-NH_2C_4H_8{}^+$	2084.8	2015.4	2006.0	1974.6		
$(CH_2{=}CHCOOH)Fe(CO)_4\cdot P(OCH_3)_3$	2095.5	2028.9	2017.5	1988.1		
$(CH_2{=}CHCOOH)Fe(CO)_4\cdot P(C_6H_5)_2C_2H_5$	2095.4	2028.7	2016.0	1987.1		
$(CH_2{=}CHCOOH)Fe(CO)_4\cdot P(C_6H_5)(CH_3)_2$	2093.6	2028.1	2015.5	1988.5		
$(CH_2{=}CHCOOH)Fe(CO)_4\cdot P(C_4H_9)_3$	2094.2	2027.1	2015.4	1987.0		
$(CH_2{=}CHCOOH)Fe(CO)_4\cdot P(C_6H_{11})_3$	2094.1	2026.1	2013.9	1985.5		
$(CH_2{=}CHCOOH)Fe(CO)_4\cdot NC_5H_5$	2097.0	2031.2	2016.1	1987.5		

[a] Frequencies are accurate to ± 1 cm^{-1} and were measured in hexane solution; relative intensities may be seen in Fig.1.

those for $(CH_2{=}CHCONC_5H_{10})Fe(CO)_4$, which was prepared via the reaction with piperidine. (Anal. Found: C, 35.3; H, 2.21; N, 5.73. $C_7H_5FeNO_5$ calcd.: C, 35.2; H, 2.11; N, 5.86%.)

Strong Lewis bases were found to be readily protonated by $(CH_2{=}CHCOOH)Fe(CO)_4$ to give yellow salts, $(CH_2{=}CHCOO)Fe(CO)_4^-NH_2R_2^+$ ($R_2 = H_2$, cyclo-C_5H_{10}, cyclo-C_4H_8). The IR absorption bands (Table 1) are indicative of anion complexes, with ν(CO) occurring at considerably lower values than those of the parent acid derivative. The yellow ammonium derivative, $(CH_2{=}CHCOO)Fe(CO)_4^-NH_4^+$ (m.p. 108–110°), hydrolyzed in moist air to yield $(CH_2{=}CHCOOH)Fe(CO)_4$. (Anal. Found: C, 32.3; H, 2.62; N, 5.32. $C_7H_7FeNO_6$ calcd.: C, 32.7; H, 2.75; N, 5.45%.)

The relative acidity of bound and unbound acrylic acid was examined. Identical, reversible pH titrations were carried out on $CH_2{=}CHCOOH$ and $(CH_2{=}CHCOOH)Fe(CO)_4$ with NaOH in water solutions. A pK_a value of 5.16 was determined at 25° for $(CH_2{=}CHCOOH)Fe(CO)_4$ as compared with a value of 4.10 determined for acrylic acid. This sizable decrease in the acidity of $CH_2{=}CHCOOH$ upon complexation to iron carbonyl implies that the $CH_2{=}CHCOOH$ group is a net electron-withdrawing ligand in the complex. The slightly higher CO stretching force constant determined for the CO groups opposite to the acrylic acid in the $(CH_2{=}CHCOOH)Fe(CO)_4$ derivative (16.79 mdynes/Å) as compared with the corresponding force constant in $Fe(CO)_5$ (16.59 mdynes/Å)[3] further substantiates the electron-withdrawing property of the $CH_2{=}CHCOOH$ ligand. In addition, an upfield NMR shift of the acidic proton in $(CH_2{=}CHCOO\underline{H})Fe(CO)_4$ (9.38 ppm) relative to that in $CH_2{=}CHCOO\underline{H}$ (11.54 ppm) is in agreement with this conclusion[*].

Finally, we have observed that (acrylic acid) iron tetracarbonyl reacts with a variety of soft Lewis bases in solution to form 1/1 complexes, $(CH_2{=}CHCOOH)Fe(CO)_4L$ ($L = (CH_3O)_3P$, $C_2H_5(C_6H_5)_2P$, $(CH_3)_2(C_6H_5)P$, $(C_4H_9)_3P$, $(C_6H_{11})_3P$ and C_5H_5N). In each case, when the Lewis bases are added in excess to a hexane solution of (acrylic acid) iron tetracarbonyl at room temperature, an immediate reaction takes place. The extent of reaction is dependent upon the quantity of Lewis base added (Fig. 1). In the presence of a large excess of Lewis base (> 10 to 1) the yields of product are essentially quantitative as indicated by the intensity of the CO absorptions in the infrared spectra. The observed CO stretching frequencies for these proposed adducts are contained in Table 1. The spectrum in the CO stretching region for a typical Lewis base derivative, $(n\text{-}C_4H_9)_3P$, is illustrated in Fig. 1.

This reaction probably involves a hydrogen bonded Lewis base with the acidic proton of acrylic acid (L•••H–O) although attack at the iron atom leading to production of a stable six-coordinated iron(0) species in solution is not ruled out. However, the

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[*] The acidic proton resonance for free $CH_2{=}CHCOOH$ appears as a sharp signal on a neat sample indicating rapid proton exchange. However, in $(CH_2{=}CHCOOH)Fe(CO)_4$ a broad acidic proton resonance is observed which is indicative of slow exchange. When the $(CH_2{=}CHCOOH)Fe(CO)_4$ derivative is mixed with free $CH_2{=}CHCOOH$ in $CDCl_3$ the acidic proton signal in the iron derivative sharpens and moves towards the signal of that in the free ligand as the quantity of free acrylic acid is increased.

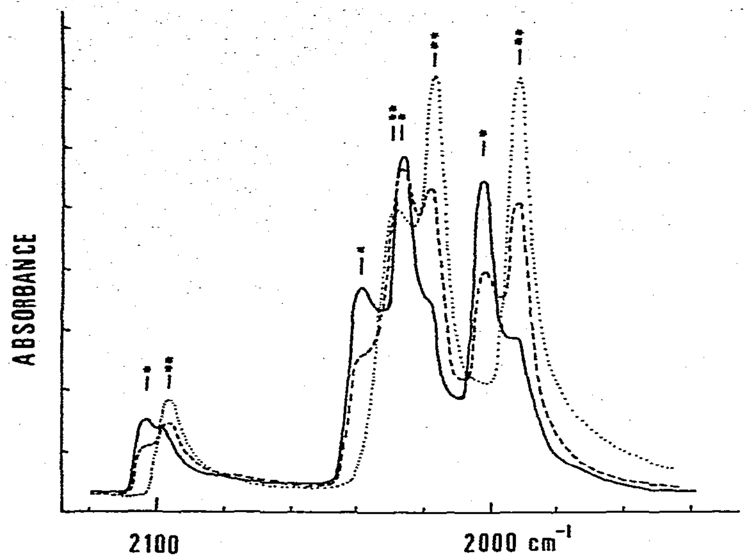

Fig.1. Infrared spectra of $(CH_2CHCOOH)Fe(CO)_4$ in hexane with increasing $(C_4H_9)_3P$ concentration in the order: —— (1/1), – – – – (1/6), ···· (1/12). ★ $(CH_2CHCOOH)Fe(CO)_4$ ν(CO) bands and ★★ $(CH_2CHCOOH)Fe(CO)_4[(C_4H_9)_3P]$ ν(CO) bands.

small shifts observed for ν(CO) as L is varied leads us to favor the hydrogen-bonding type of interaction. Although these adducts are stable only in solution in the presence of excess phosphines and cannot be isolated, evidence for the proposed type of interaction comes from NMR spectral measurements as well as IR spectral measurements. The ABX NMR pattern for free $CH_2=CHCOOH$ is moved significantly to higher field upon complex formation with the $Fe(CO)_4$ moiety[★1]. This pattern remains upon addition of Lewis bases with some slight changes in chemical shifts and coupling constants (Fig. 2) which indicates that the $CH_2=CH$ grouping remains intact and bound to iron tetracarbonyl. There is also a downfield shift in the acidic proton of $CH_2=CHCOOH$ upon addition of these Lewis bases. In addition, the ν(C=O) frequency of the acrylic acid group (1710–1730 cm^{-1}) is still present after Lewis base addition has occurred.

When small quantities of piperidine (Fe/piperidine/R_3P ratio 1/5/50) are added to hexane solutions of the Lewis base adducts containing excess phosphine, $(CH_2=CHCOO)Fe(CO)_4^-NH_2C_5H_{10}^+$ is produced quantitatively. Heating the $(CH_2=CHCOOH)Fe(CO)_4L$ adducts in the presence of excess phosphines in refluxing hexane produces the known axially substituted $LFe(CO)_4$ and *trans*-$L_2Fe(CO)_3$ compounds.

Giese and Vallee[4] have employed the related complex, (maleic anhydride)-iron tetracarbonyl, as a probe for proteins via presumed reaction of the amino acid side chains of the protein at the maleic anhydride site. The $(CH_2=CHCOCl)Fe(CO)_4$ derivative reported in this communication should prove useful for chemically modifying

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[★1] δ in ppm (relative to TMS 0.0 ppm) 5.95, 6.50 and 6.20 ppm for the free ligand *vs.* 2.58, 2.82 and 3.20 ppm for the complexed ligand.

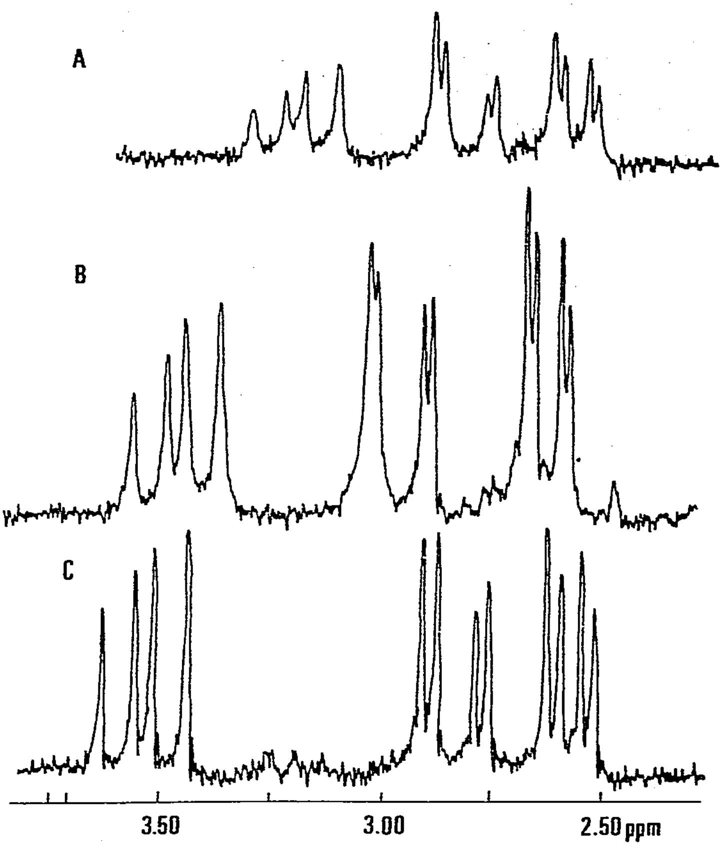

Fig. 2. Proton NMR spectra in $CDCl_3$: (A) $(CH_2CHCOOH)Fe(CO)_4$, (B) $(CH_2CHCOOH)Fe(CO)_4NC_5H_5$, (C) $(CH_2CHCOCl)Fe(CO)_4$.

proteins, specifically, at the lysine, serine, threonine, tyrosine, and cysteine residues. Bulkin and Lynch[5] have also reported a reaction involving (maleic anhydride) iron tetracarbonyl and pyrrolidine in which they observe an intermediate reaction followed by very slow formation of $(C_4H_8NH)Fe(CO)_4$.

Interactions of the type discussed in this communication are worthy of extensive study and work along these lines is in progress in our laboratory.

ACKNOWLEDGEMENT

We thank the Research Corporation for financial support of this project.

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