Schiff-base Complexes of Tetracarbonyliron from Enneacarbonyldi-iron

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The reaction between [$Fe_2(CO)_9$] and Schiff bases of the type PhCH=CH–CH=N–C_6H_4X (I; X = H, 4-Cl, 4-Br, 3-Br, 4-F, 4-I, 4-Me, and 4-OMe) and $R^1R^2R^3R^4C_6HCH$=N–C_6H_4OMe-4 (II; R^1,R^2,R^3,R^4 = H, Me, or OMe) has been re-examined. The first stage of the reaction leads to the formation of [$Fe(CO)_4L$] complexes (L = Schiff base) [III; L = (I)] and [IV; L = (II)]. I.r. and n.m.r. evidence suggests that the Fe is bonded to the nitrogen lone-pair electrons of the Schiff base. With ligands (I) the second stage of the reaction gives formation of [Fe(η-PhCH=CH–CH=N–C_6H_4X)$(CO)_3$] complexes (V). Ligands (II) having unsubstituted benzene ring *ortho* positions give complexes of the type [$Fe_2(CO)_6L$].

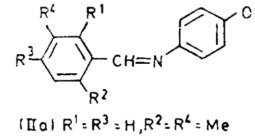
NITROGEN-DONOR ligands do not form stable carbonyl complexes,[1] in contrast to other ligands containing Group 5 donor atoms, unless the nitrogen is conjugated with a π system (such as pyridine,[2] *etc.*) which allows delocalisation of the metal *d* electrons. In several cases in which both olefinic bonds and nitrogen atoms are present in the ligands (*e.g.* CH_2=CH–CN) the two reactive centres compete for the metal and several products are obtained.[2,3] The formation of complexes of the type [Fe(η-PhCH=CH–CH=NPh)$(CO)_3$] has also been described,[4] but derivatives of tetracarbonyliron were not formed, unlike the ligands PhCH=CH–COR.[5] In an attempt to isolate tetracarbonyliron derivatives, the former reaction has been re-examined. We have found that the initial products are complexes in which the $Fe(CO)_4$ group is bonded to a nitrogen atom of the ligand. Other Schiff bases not containing olefinic bonds give complexes where the $Fe(CO)_4$ group is bonded to a nitrogen donor atom. This work describes the preparation and characterisation of these complexes.

EXPERIMENTAL

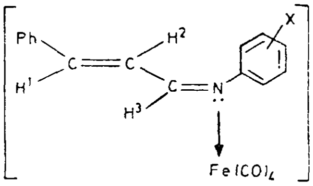
I.r. spectra were recorded on a Perkin-Elmer model 257 spectrophotometer. N.m.r. spectra were obtained with a Jeol JNM-C-60HL instrument using $SiMe_4$ as internal reference. All manipulations and reactions of the organometallic complexes were under nitrogen in thoroughly deaerated solvents, having first been dried using Na.

Preparation of the Schiff Bases.—The Schiff bases PhCH=CH–CH=N–C_6H_4X (I; X = H, 4-Cl, 4-Br, 3-Br, 2-Br, 4-F, 4-I, 4-Me, and 4-OMe) were prepared as follows. The substituted aniline $XC_6H_4NH_2$ in diethyl ether solution was added dropwise to a diethyl ether solution of PhCH=CH–CHO in equimolar proportions with stirring. The Schiff base formed immediately and precipitated from the diethyl ether solution. When the reaction was complete, the precipitate was redissolved by adding more diethyl ether. The solution was dried using magnesium sulphate and the pure Schiff base crystallised at −20 °C. The Schiff bases $R^1R^2R^3R^4C_6HCH$=N–C_6H_4OMe–4, (II), were prepared similarly. Since the reagents were only slightly soluble in diethyl ether, compound (IIc) was prepared from a suspension.

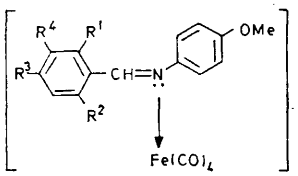
Preparation of the Complexes.—[$Fe(CO)_4${N(C_6H_4X)=CH–CH=CHPh}], (III). The method described refers to the preparation of the complexes with X = H, 4-Me, 4-Cl, 4-I, 4-F, 4-Br, and 3-Br. The reaction times varied slightly depending on the substituent X. Enneacarbonyldi-iron and Schiff base (mol ratio 1 : 3) were allowed to react in deaerated benzene at 8—10 °C. The formation of [Fe-$(CO)_5$] and complex (III) was observed during the reaction. The reaction was allowed to continue for 1—2 d until the complex [Fe(η-PhCH=CH–CH=N–C_6H_4X)$(CO)_3$], (V), began to form. The solution was filtered and dried, care being taken to keep the temperature below 5 °C. The residue was redissolved in the minimum of cold anhydrous diethyl ether. Only the Schiff base precipitated at −80 °C from this solution. The solution, of the almost pure complex (III) in excess of ligand, was again dried and the residue dissolved in n-pentane at −20 °C. Red-brown crystals were obtained which were stable at room temperature in the absence of air. During the last operation the temperature was kept below 0 °C, since the rate of formation of complex (V) increases with decreasing excess of the Schiff base. Some physical and spectroscopic properties of the complexes are reported in Table 1.



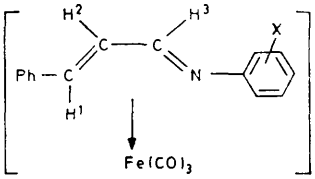
(IIa) $R^1 = R^3 = H$, $R^2 = R^4 = Me$
(IIb) $R^1 = R^2 = R^3 = R^4 = H$
(IIc) $R^4 = H$, $R^1 = R^2 = R^3 = OMe$



(III)



(IVa) $R^2 = R^4 = Me$, $R^1 = R^3 = H$
(IVb) $R^1 = R^2 = R^3 = R^4 = H$
(IVc) $R^1 = R^2 = R^3 = OMe$, $R^4 = H$



(V)

[$Fe(CO)_4${N(C_6H_4OMe-4)=CH–$C_6HR^1R^2R^3R^4$}], (IV). When the *ortho* positions of the benzene rings in (II) are not substituted (R^1 and/or R^2 = H) formation of complexes (IV) could be observed spectroscopically during the reaction between [$Fe_2(CO)_9$] and (II). These complexes could not be isolated because they rapidly formed complexes of the type [$Fe_2(CO)_6$(Schiff base)] described previously.[6] The spectroscopic characteristics of some of these complexes, in n-pentane, are: (IVa) ν(CO) at 2 050, 1 967, 1 948, and

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TABLE 1

Analytical data and CO-stretching frequencies for complexes (III)

X	M.p.	Yield	Analysis (%) Found			Analysis (%) Calc.			$\tilde{\nu}$(CO) [a]/cm^{-1}
	(θ_c/°C)	(%)	C	H	N	C	H	N	
H	81—83	10	60.5	3.35	3.90	60.85	3.50	3.75	2 052, 1 971, 1 952, 1 940
4-Me	73—75	15	59.75	4.10	3.80	60.15	3.90	3.60	2 053, 1 970, 1 954, 1 940
4-OMe	76—77	8	58.2	3.50	3.60	58.3	3.75	3.45	2 051, 1 968, 1 952, 1 938
4-Cl	100—101	10	55.95	3.05	3.35	55.7	2.95	3.40	2 054, 1 973, 1 954, 1 943
4-I	94—96	5	45.75	2.30	2.95	45.55	2.40	2.80	2 051, 1 972, 1 954, 1 942
4-F	67—69	5	58.3	2.95	3.45	58.35	3.10	3.60	2 052, 1 972, 1 955, 1 943
4-Br [b]	91—93	15	50.55	2.95	3.00	50.25	2.65	3.10	2 051, 1 972, 1 953, 1 942
2-Br	62—63	5	50.0	2.75	3.35	50.25	2.65	3.10	2 052, 1 971, 1 955, 1 945
3-Br		5							2 053, 1 972, 1 954, 1 942

[a] In pentane. [b] Molecular weight (CH_2Cl_2): 472 (calc. 454); ν(C=N) (in n-pentane) at 1 610 cm^{-1}; n.m.r. spectrum (in CS_2) δ(H^3) 9.40 (ligand 9.65), δ(Ph) 7.75 (ligand 7.85), and δ(C_6H_4) 7.40 p.p.m. (ligand 7.52 p.p.m.).

TABLE 2

Analytical data, CO-stretching frequencies, and n.m.r. data for complexes (V)

X	M.p. (θ_c/°C)	Analysis (%) Found			Analysis (%) Calc.			$\tilde{\nu}$(CO) [a]/cm^{-1}	δ [b]/p.p.m.			J(H^1H^2)/Hz
		C	H	N	C	H	N		H^1	H^2	X	
H [c]	122—124	62.4	3.95	4.20	62.3	3.80	4.05	2 063, 2 003, 1 991	6.80	4.47		12
4-Me	137—140	63.25	4.25	3.90	63.2	4.20	3.90	2 060, 2 002, 1 990	6.72	4.45	7.82	11
4-OMe [d]	>215	60.2	4.10	3.80	60.5	4.00	3.70	2 059, 1 998, 1 987	6.68	4.42	6.30	9
4-Cl [d]	132—135	56.9	3.20	3.60	56.65	3.15	3.65	2 062, 2 003, 1 992	6.70	4.45		11
4-I	145 (decomp.)	45.6	2.60	3.00	45.7	2.55	2.95	2 062, 2 003, 1 992	6.72	4.40		11
4-F	108—111	59.0	3.45	3.85	59.2	3.30	3.85	2 060, 2 001, 1 998	6.68	4.40		11
4-Br	147—150	50.8	3.00	3.20	50.75	2.85	3.30	2 064, 2 008, 1 994	6.72	4.38		9
2-Br	126—127							2 063, 2 007, 1 996				
3-Br	98—99							2 064, 2 005, 1 994				

[a] In pentane. [b] Solvent, CCl_4. [c] Described in ref. 4. [d] Described in ref. *5b*.

1 932 cm^{-1}; (IVb) ν(CO) at 2 064, 2 026, 1 992, 1 982, and 1 975 cm^{-1}; [$Fe_2(CO)_6(\eta^2$-$C_6H_4CH_2$–N–C_6H_4OMe-4)] ν(CO) at 2 069, 2 030, 1 998, 1 987, and 1 976 cm^{-1}. When R^1 and R^2 are different from hydrogen only complexes (IV) were formed as *ortho*-metallation of the benzene ring is not possible. In this case, complexes (IV) may be isolated, even though they are very unstable in solution. As an example, the preparation is described of complex (IVc) formed from the Schiff base (IIc).

Compound (IIc) was allowed to react with [$Fe_2(CO)_9$] in deaerated benzene (mol ratio 4 : 1) for 24 h; after this time the concentration of (IVc) did not increase since its rate of formation is the same as that of its decomposition. The solution was filtered and rapidly dried, taking care that the temperature was always < 0 °C. The residue was dissolved in anhydrous deaerated diethyl ether. Crystallisation at -80 °C removed most of the Schiff base. The diethyl ether solution was dried and the residue redissolved in n-hexane. Complex (IVc) was obtained in low yield (5%) as red crystals by crystallisation at -20 °C. This crystallisation also gave crystals of the Schiff base, so it was necessary to separate the crystals of (IVc) mechanically. However, it was not possible to entirely remove the Schiff base since it is formed on decomposition of the complex. Complex (IVc) decomposes at 83—84 °C without fusion; ν(CO) at 2 048, 1 962, 1 947, and 1 937 cm^{-1} (in n-pentane) (Found: C, 53.5; H, 4.20; N, 3.00. Calc.: C, 53.75; H, 4.10; N, 3.00%).

[Fe(η-PhCH=CH–CH=N–C_6H_4X)$(CO)_3$], (V; X = H, 4-Me, 4-OMe, 4-Cl, 4-I, 4-F, 4-Br, 2-Br, *and* 3-Br). Equimolar quantities of [$Fe_2(CO)_9$] and (I) were mixed in deaerated benzene with stirring at 40 °C. The reaction went to completion after 8—10 h. The solution was filtered and dried to eliminate any [$Fe(CO)_5$] formed. The residue was recrystallised from dichloromethane–n-hexane. Some physical properties of the complexes are listed in Table 2.

RESULTS

I.r. Spectra.—Complexes (III) and (IV) showed four bands in the CO stretching region, which indicates that at least four CO groups are present. The highest and lowest absorption frequencies correspond to those found in [$Fe(CO)_4$(py)] (py = pyridine) [2] and [$Fe(CO)_4(PPh_3)$] [7] which show only three CO-stretching bands and have trigonal-bipyramidal structures with the substituent py and PPh_3 in apical positions. The two central bands are caused by the lowering of symmetry of complexes (III) and (IV) from the ideal C_{3v} due to distortion of the trigonal bipyramid by the bulky Schiff base. The C=N stretching frequencies of the Schiff base, in the region 1 600—1 630 cm^{-1}, were not shifted in the complexes.

Complexes (V) showed three CO-stretching bands. These correspond to those found in the complex with X = H, described previously,[4] for which a structure determination has been performed.[8]

N.M.R. Spectra.—Complexes (III) and (IV) were too unstable to permit reliable assignment of the n.m.r. absorptions. Only for the complex with X = 4-Br could reproducible spectra be obtained, and showed that the chemical shifts for the Schiff base are not greatly changed in the complex (see Table 1).

Complexes (V) showed H^1 and H^2 absorptions shifted to high-field because of co-ordination to the $Fe(CO)_3$ group (see Table 2).[4,9] The H^3 absorption was also shifted to high-field for the same reason, but is not reported in Table 2 because it was masked by the signals of the phenyl groups.

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DISCUSSION

The i.r. spectra show that complexes (III) and (IV) have a trigonal-bipyramidal structure. The absorption frequencies indicate that the Schiff bases lie in an apical position of the bipyramid. Thus, when a substituent L in $[\mathrm{Fe(CO)_4L}]$ is in the apical position the higher-frequency CO-stretching vibration lies at 2 050—2 070 $\mathrm{cm^{-1}}$,[7] whilst with an equatorial L substituent the band shifts to 2 080—2 110 $\mathrm{cm^{-1}}$.

Complexes (III) may have three different types of Fe–L bond: *via* the C=C olefinic bond, *via* the imidine C=N group, or utilising the nitrogen lone-pair electrons. With the ligand PhCH=CHCHO bonding to the $\mathrm{Fe(CO)_4}$ group occurs *via* the olefinic bond.[5] However, this may be excluded for complexes (III) as the ' soft ' character of the olefinic bond would require that it occupied the equatorial position of the trigonal bipyramid.[10] Bonding *via* the C=N group may also be excluded since this should give rise to a strong shift in the C=N stretching frequency which is not observed. The third type of bonding therefore appears to be present. Since the nitrogen atom is a ' hard ' group, substitution occurs in the apical position of the bipyramid and the structure obtained should be similar to that of $[\mathrm{Fe(CO)_4(py)}]$.[11] Further evidence excluding bonding to the olefinic group is the formation by ligands (II) of complexes (IV), in which the olefinic bond is absent. Since complexes (IV) have the same structure as (III), a π bond in the latter may be excluded. In addition, the n.m.r. spectra show no appreciable up-field shifts for H^1, H^2, and H^3, a clear indication that neither a bond to C=C nor to C=N is present.

The formation of a σ bond between a nitrogen atom and an $\mathrm{Fe(CO)_4}$ group has been recently demonstrated in the reaction of $[\mathrm{Fe_2(CO)_9}]$ with azo-compounds.[12] This type of bonding has also been suggested to explain *ortho*-metallation and catalytic insertion of carbon monoxide in reactions of imidine organic compounds with $[\mathrm{Fe_2(CO)_9}]$ or $[\mathrm{Co_2(CO)_8}]$.[13] The different behaviour of the Schiff bases (I) compared with aldehydes or ketones of the type PhCH=CHCOR shows that the imidine nitrogen atom is more nucleophilic than the olefinic double bond and the latter is more nucleophilic than the carbonyl oxygen atom. The reactivity order towards $\mathrm{Fe(CO)_4}$ is thus $-\mathrm{C{=}N}- \; > \; {>}\mathrm{C{=}C}{<} \; > \; {>}\mathrm{C{=}O}$. It is to be noted that this sequence does not correspond to the stability sequence for these complexes. The olefinic complexes are more stable than the σ-N complexes because of the contribution of π back bonding to the bond.[14]

The i.r. and n.m.r. spectra of complexes (V) are similar to those reported previously for $[\mathrm{Fe(\eta\text{-}PhCH{=}CH{-}CH{=}NPh)(CO)_3}]$.[4] The high-field shifts of H^1, H^2, and H^3 indicate a delocalisation of the $\mathrm{CH^1{=}CH^2{-}CH^3{=}N}$ system with consequent formation of η^4 complexes.

This work was supported in part by the Italian National Research Council (C.N.R.).

[6/419 *Received, 2nd March,* 1976]

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