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Synthesis of Some Novel Iodo(η-cyclopentadienyl)iron Di-amine Complexes

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In continuation of our earlier studies [1–4] on the substitution reactions of η-cyclopentadienyliron dicarbonyl iodide with Group VA Donor ligands, we report here the preparation and characterization of some novel iodo(η-cyclopentadienyl)iron di-amine complexes of the type [(η-C_5H_5)Fe(Amine)$_2$I] instead of the formation of another common expected product of the types [(η-C_5H_5)Fe(CO)(Amine)I] and [(η-C_5H_5)Fe(CO)$_2$(Amine)] I from the reflux reaction of (η-C_5H_5)Fe(CO)$_2$I and amines (amines = cyclohexylamine, benzylamine, butylamine, piperidine and morpholine) in benzene as a solvent. Although only ionic products of the type [(η-C_5H_5)-Fe(CO)$_2$(Amine)] I [1] could be isolated from the reflux reaction of (η-C_5H_5)Fe(CO)$_2$I and the above amines in benzene as a solvent for a reaction period of *ca.* 2h, under milder conditions (*i.e.* by changing amounts of reactants and reaction periods), we have isolated some new derivatives of the type [(η-C_5H_5)-Fe(Amine)$_2$I].

Iododicarbonyl(η-cyclopentadienyl)iron [5] (0.4g) and cyclohexylamine (2.5 ml) were refluxed together in benzene (25 ml) for 4h under an atmosphere of dry nitrogen. The progress of the reaction was noticed even at room temperature, *i.e.* cyclohexylamine reacted sharply with the black crystals of (η-C_5H_5)Fe(CO)$_2$I and changed its colour to light red–brown. A dark red–brown reaction mixture was obtained after a reflux period of 4h. Evaporation of the solvent yielded a dark red–brown product from which unreacted cyclohexylamine and (η-C_5H_5)Fe(CO)$_2$I were removed by washing several times with water and hexane, respectively. The product was again washed with dichloromethane (25 ml) which removed a negligible amount of an unexpected reaction product, [(η-C_5H_5)Fe(CO)$_2$]$_2$. The major product (yield 60.3%) insoluble in all common organic solvents, was [(η-C_5H_5)Fe($C_6H_{11}NH_2$)$_2$I] which decomposed at higher temperature without melting. *Anal.* Found: C, 45.3; H, 6.6; N, 6.0; I, 28.1%. $C_{17}H_{31}FeIN_2$ calcd.: C, 45.7; H, 6.9; N, 6.2; I, 28.4%.

Reaction conditions, colours, yields and analyses of other substituted derivatives, prepared similarly, are given in the Table.

The infrared spectra (4000–600 cm^{-1} region in KBr disc) of [(η-C_5H_5)Fe(Amine)$_2$I] complexes exhibited bands at *ca.* 3350–3320 s(vbr), 2920 s(br), 2850 s, 1620 s, 1570–1560 s, 1445 sh, 1435 m, 1395 m(br), 1345 vw, 1310 s, 1260 m, 1240 s, 1225 m, 1180 m, 1155 m, 1085 s, 1065 w, 1045 m, and 890 s cm^{-1}. In the above i.r. spectral data the bands at *ca.* 3350–3320 s(vbr) cm^{-1} and 1620 s, 1570–1560 s cm^{-1} may be attributed to ν(N–H) and its deformation vibrations, respectively. The other bands at *ca.* 1435 m, 1395 m(br), 1085 s, 1065 w and 1045 m cm^{-1} may be attributed to (η-C_5H_5)–Fe bonding [6].

The products isolated [1] in the reaction period of 2h from the reflux reaction of (η-C_5H_5)Fe(CO)$_2$I and amines in benzene as a solvent exhibited two strong ν(CO) absorptions in the carbonyl region of their i.r. spectra [1] at *ca.* 2040–2020 s cm^{-1} and *ca.* 1990–1970 s cm^{-1}, which suggested the formation of ionic products of the type [(η-C_5H_5)Fe(CO)$_2$(Amine)] I.

TABLE. Reaction Times, Colours and Analytical Data for the Complexes.

Complex^{a,b}	Yield (%)	Analysis, Found (Calcd.) %			
		C	H	N	I
(η-C_5H_5)Fe($C_7H_7NH_2$)$_2$I	62.4	48.9 (49.3)	4.7 (4.9)	5.8 (6.0)	27.0 (27.4)
(η-C_5H_5)Fe($C_4H_9NH_2$)$_2$I	68.1	39.3 (39.5)	6.5 (6.8)	6.8 (7.1)	31.7 (32.2)
(η-C_5H_5)Fe($C_5H_{11}N$)$_2$I	61.5	42.7 (43.0)	6.1 (6.4)	6.4 (6.6)	29.9 (30.3)
(η-C_5H_5)Fe(C_4H_9NO)$_2$I	66.8	36.6 (36.9)	5.3 (5.4)	6.5 (6.6)	29.7 (30.0)

[a] Reflux period (in benzene solvent) *ca.* 4h.

[b] Red–brown coloured complexes which decomposed at higher temperature.

In the present investigations when the amounts of reactants (*i.e.* an excess of amines over 1:1 molar ratio) and reaction periods (*i.e.* from 2h to 4h) in the same solvent (benzene) were changed, the isolated products showed no ν(CO) absorptions in the carbonyl region of their i.r. spectra, indicating the formation of CO-free stable products of the type $[(\eta\text{-}C_5H_5)Fe(Amine)_2I]$ whose chemical compositions were also supported by the analytical data given in Table. These observations are also quite analogous to the reaction of $(\eta\text{-}C_5H_5)Fe(CO)_2I$ and $P(OC_6H_5)_3$ studied by Nesmeyanov *et al.* [7], which yielded a reaction product of the same type, $[(\eta\text{-}C_5H_5)Fe[P(OC_6H_5)_3]_2I]$.

A trace of an unidentified product observed during the synthesis of iododicarbonyl(η-cyclopentadienyl)-(Amine)iron complexes [1] which was removed by washing with dichloromethane has been identified as $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$ in this investigation by the help of i.r.spectral studies of this product. In the i.r. spectra of this product ν(CO) absorptions in the terminal and bridging carbonyl regions at *ca.* 1950 s and 1750 s cm^{-1} appeared, respectively, which are quite analogous to the carbonyl stretching frequencies of $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$ [8].

Hence, it is concluded that during the reaction of $(\eta\text{-}C_5H_5)Fe(CO)_2I$ and the above amines, a negligible amount of $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$ used to form whose presence may be detected by i.r. spectral studies) alongwith the desired products. This undesired product may be easily removed from the reaction mixture by washing with organic solvents such as benzene or dichloromethane.

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