Insertion of Chlorosulphonyl Isocyanate into a Transition-metal–Carbon Bond

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Summary A novel dicarbonyl-π-cyclopentadienyliron-amido-complex, cpFe(CO)$_2$[N(SO$_2$Cl)C(O)CH$_2$C(Me)=CH$_2$] (cp = π-cyclopentadienyl), is the product of the first reported insertion of chlorosulphonyl isocyanate into a transition-metal–carbon bond; this reaction is believed to proceed *via* a dipolar iron–olefin complex.

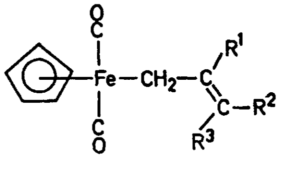
Unsaturated electrophilic reagents such as SO$_2$,[1] SO$_3$,[2] and (CN)$_2$C=C(CN)$_2$[3] are known to engage in insertion reactions with metal-organic compounds. We now report the first example of insertion of ClSO$_2$NCO into a transition-metal–carbon bond.

Treatment of (Ia) with ClSO$_2$NCO in CH$_2$Cl$_2$ at < − 20° for 10—30 min affords in *ca.* 45% yield an orange-red 1 : 1 adduct† (IIa), m.p. 90·5—91·5°; ν(C≡O) (CHCl$_3$) 2075 and 2028 cm^{-1}; ν(C=O) (KBr pellet) 1670 cm^{-1}; ν(SO) (KBr pellet) 1353 and 1133 cm^{-1}; τ 8·23 (3H, Me), 6·39 (2H, -CH$_2$-) 5·23—5·07 (2H, =CH$_2$), and 4·87 (5H, cp). The unusually high values of ν(C≡O) militate against an Fe–C bonded cycloaddition structure (IIIa)[4] or an iron-carboxamido-linkage, Fe–C(O)N<,[5] whilst the n.m.r. data accord with the intact methylallyl fragment.[6] When treated with gaseous HCl in CHCl$_3$ for 2 h, (IIa) furnishes CH$_2$=C(Me)-CH$_2$C(O)NH$_2$,[7] m.p. 117—118°, (M^+) 99, and cpFe(CO)$_2$Cl (*ca.* 66%), thus providing good evidence in support of structure (IIa).

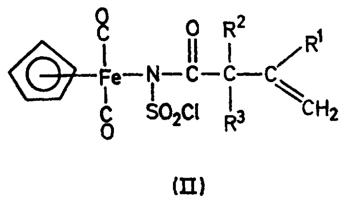
The novel iron–amido-complex reacts with PhNH$_2$ (CH$_2$Cl$_2$ soln.; 25°) [reaction (1)] and yields cp$_2$Fe$_2$(CO)$_4$ upon treatment with Et$_3$N (CH$_2$Cl$_2$ soln.; reflux).

$$\text{(IIa)} \xrightarrow{\text{PhNH}_2} \text{cpFe(CO)}_2\text{[N(SO}_2\text{NHPh)C(O)CH}_2\text{-C(Me)=CH}_2] \qquad (1)$$

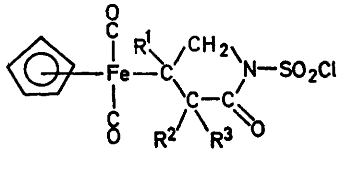
Since the alkyls cpFe(CO)$_2$R (R = Me or CH$_2$Ph) do not react with ClSO$_2$NCO under comparable conditions, the formation of (IIa) is probably related to the allylic nature of (Ia). We believe that the initial electrophilic attack of ClSO$_2$NCO at the C=C of (Ia) leads to the formation of a



(I)



(II)



(III)

a; R^1 = Me, R^2=R^3=H
b; R^1 = H, R^2=R^3=Me
c; R^1 = R^3=H, R^2=Ph

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† Satisfactory C, H, N, and Cl (or S) analyses were obtained for all new complexes reported herein.

dipolar olefin complex,[8] which affords (IIa) *via* displacement of the co-ordinated C=C by the nitrogen.

Interestingly, the related iron–allyl complexes (Ib) and (Ic) yield (IIIb) and (IIIc) rather than (IIb) and (IIc) upon treatment with $ClSO_2NCO$.[9] This difference in behaviour may be ascribed to the relative stabilities of the respective olefin intermediates, with the least substituted and therefore most stable olefin zwitterions collapsing *via* attack of the nitrogen at the terminal carbon rather than at the metal.

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