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THE ACTIVATION OF CARBON—CHLORINE BONDS IN IRON CARBONYL COMPLEXES OF CHLOROBUTADIENES

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Summary

An investigation of the products of reaction of some chlorobutadienes with $Fe_2(CO)_9$ suggests that a chlorine substituent on a carbon atom of a coordinated double bond of a monodentately coordinated diene, or on a terminal carbon of a chelated diene, may be activated towards insertion of an iron carbonyl species into the carbon—chlorine bond. A chlorine substituent on a central carbon of a chelated diene appears unreactive in this respect. The results are discussed in terms of accepted bonding models for coordinated alkenes and 1,3-dienes.

The inert nature of halogen directly attached to olefinic carbon is well known. However, recent reports [1] of insertion of transition metals into vinyl—halogen bonds suggest that alkene coordination may serve to activate the carbon—halogen bond. There have been few studies [2-5] of the interaction of transition metal compounds with halogen-substituted 1,3-dienes other than fluorine-containing derivatives and only in one case has rupture of a carbon—halogen bond been observed. Thus, Greene et al. [4] found that reaction of 2-bromobutadiene with $Fe_2(CO)_9$ gave a distribution of products, of which, apart from polymer, only one, (bromoprene)$Fe(CO)_3$, contained bromine. The product distribution was explained in terms of insertion of iron carbonyl into the carbon—bromine bond of an initially formed (bromoprene)$Fe(CO)_3$ complex, followed by coupling, or CO insertion and coupling, to give mainly binuclear products. The corresponding chloro-compound was stated to be unreactive under the same conditions, yielding only polymer and the tricarbonyliron complex. We have confirmed these results with respect to 2-chlorobutadiene. However, 2,3-dichlorobutadiene be-

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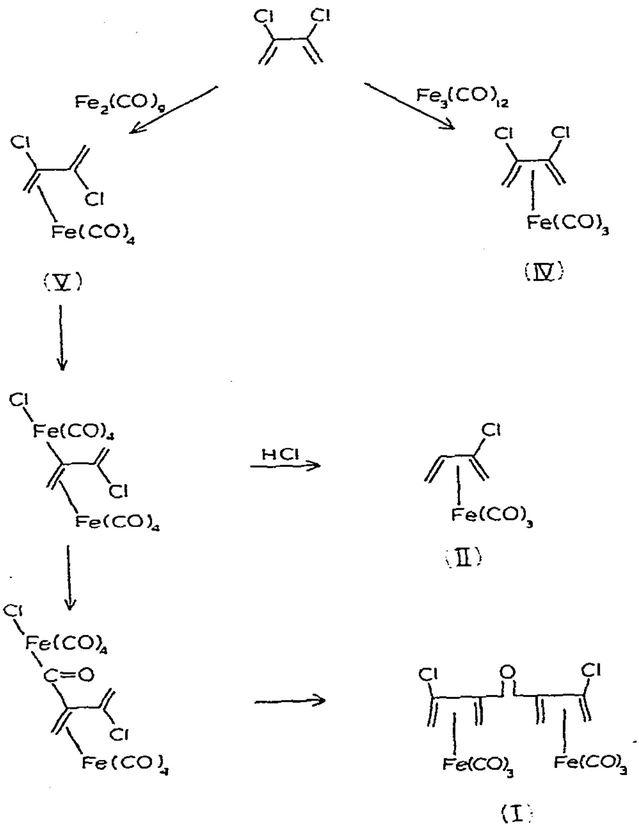
haves differently; we here report our observations and suggest a reason for the different reactivity of the two dienes.

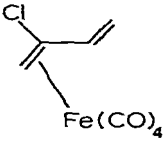
Reaction of 2,3-dichlorobutadiene with $Fe_2(CO)_9$ in refluxing hexane yielded the complexes I and II along with a smaller quantity of hexacarbonyl-(butatriene)diiron(0) (III) and some polymer. No complex of the reactant diene was obtained. Under the same reaction conditions treatment of the same diene with $Fe_3(CO)_{12}$ yielded only the corresponding diene—iron tricarbonyl complex (IV) along with some polymer and a trace of the butatriene compound (III), as found previously by Brune et al. [5]. Similarly, reaction of 2-chlorobutadiene with either $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ gave (2-chlorobutadiene)$Fe(CO)_3$ as the only isolable complex.

The isolation of I and II as the major products of reaction of 2,3-dichlorobutadiene with $Fe_2(CO)_9$ suggests a similar sequence of reactions to those proposed by Greene et al. [4] for the case of 2-bromobutadiene, namely insertion of an iron carbonyl fragment, probably $Fe(CO)_4$, into a carbon—chlorine bond followed by CO insertion and coupling to give I, or by reaction with by-product HCl to give II (See Scheme 1). However, it cannot be the diene—tricarbonyl complex (IV) which undergoes the insertion step, as suggested [4] for the bromobutadiene reaction. This was proven by treating complex IV with $Fe_2(CO)_9$ under identical conditions. The reactant complex was recovered in quantitative

SCHEME 1



yield. Conceivably it is the uncoordinated diene which reacts to give the insertion intermediate. This seems very unlikely in view of the fact that the diene forms complex IV but no insertion products on treatment with $Fe_3(CO)_{12}$. We propose that the oxidative addition occurs while the diene is coordinated via one double bond only (structure V). There is precedent for the occurrence of monodentately coordinated 1,3-dienes not only as reactive intermediates but also as isolable species [6]. It is further proposed that the iron carbonyl fragment inserts into the carbon—chlorine bond on the coordinated double bond. These considerations suggest an explanation for the non-reactivity of 2-chlorobutadiene. Of the two possible monodentately coordinated diene structures VI and VIII the preferred one is expected to be VII. The evidence for this comes from studies of the products of the insertion of 2-chlorobutadiene into palladium π-allyl complexes [3]. Moreover, stability constant measurements on rhodium(I) complexes have shown that chloroethylenes form less stable complexes than ethylene itself [7]. Thus, it is concluded that since the chlorine atom in VII is not attached to a coordinated alkene group it is not activated to reaction.



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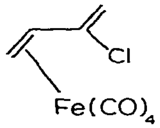
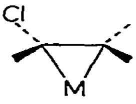
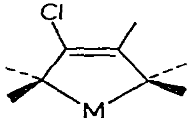


(VII)

It is now necessary to account for the activation of chlorine on a coordinated vinyl group but not on a bidentately coordinated 1,3-diene. This may be understood by considering the nature of the carbon—halogen bond in the two cases. It is generally accepted that the σ-bonded "metallocyclopropane" valence bond (VB) structure VIII may make a significant contribution to the bonding in alkene complexes, particularly, as in the present case, where the metal is in a low valence state and the alkene bears electron-withdrawing substituents [8]. In the VB structure VIII the carbon atoms are sp^3 hybridized and the chlorine therefore acquires some of the character of an alkyl chloride; specifically it should be more reactive to substitution. In the coordinated 1,3-diene case contributions from the VB "metallocyclopentene" structure IX do not alter the hydridization of C(2) or C(3) and a chlorine atom on these positions is not activated. Application of these considerations to the reaction of 2-bromobutadiene with $Fe_2(CO)_9$ suggests that the bromine on an uncoordinated double bond or on a central carbon of the chelated diene is sufficiently labile to react under the conditions of the experiment; this may be attributed to the well established greater reactivity of organic bromides vis-a-vis organic chlorides. It may be significant that in the reactions described by Greene et al. [4] substantial proportions of unreacted



(VIII)



(IX)

2-bromobutadiene-iron tricarbonyl complex were always isolated among the insertion products where as, with 2,3-dichlorobutadiene, no complex of the reactant diene could be detected, an observation consistent with the greater reactivity of monodentately coordinated 2,3-dichlorobutadiene and with the proposed mechanism.

While a bonding contribution from the "metallocyclopentene" structure IX does not alter the hybridization of the central carbon atoms it might be expected to have an activating effect upon chlorine bound to a terminal carbon. In attempt to test this prediction some experiments were performed with *trans*-1-chlorobutadiene. Reaction with $Fe_3(CO)_{12}$ yielded the corresponding diene—iron tricarbonyl complex, along with some of the butatriene derivative, as found with the other chlorobutadienes. With $Fe_2(CO)_9$ two products were isolated together with only a trace of the tricarbonyl compound. The major product was shown by elemental analysis, infrared, ^{1}H NMR and mass spectra to be (1-chlorobutadiene)$Fe(CO)_4$ in which the chlorine-bearing double bond is uncoordinated. This compound constitutes an interesting new example of a monodentately coordinated 1,3-diene. The second product was unstable and was not identified; an NMR spectrum could not be obtained. However, it contained no chlorine and an infrared spectrum showed, in addition to carbonyl stretching vibrations at 2070, 2010 and 1980 cm^{-1}, a split band at ~1690 cm^{-1}. The absence of any significant quantity of chelated 1-chlorobutadiene among the reaction products and the isolation of a chlorine-free material showing IR absorption in the ketonic C=O region are therefore consistent with the occurrence of a similar type of oxidative addition reaction, leading to carbonyl insertion, as proposed for monodentately coordinated 2,3-dichlorobutadiene.

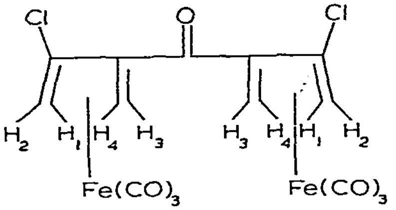
Experimental

Reaction of 2,3-dichlorobutadiene with $Fe_2(CO)_9$

2,3-Dichlorobutadiene (25 ml) was added to a suspension of $Fe_2(CO)_9$ (25 g) in hexane (150 ml) and refluxed for 2 h. The cooled solution was filtered and the solvent, plus $Fe(CO)_5$ generated in the reaction, pumped off to leave a dark brown oily residue. This was extracted with dichloromethane (4 × 25 ml). The combined extracts were concentrated (10 ml) and chromatographed on a silica gel column. Elution with hexane gave a red oil (1.2 g) which was shown by TLC to consists of two components. These were separated by cooling a hexane solution of the oil to −78° when a red solid (III) (0.48 mg) separated. The residual orange solution was decanted off and an orange oil (II) (0.74 mg) was obtained on removal of hexane. TLC on each component confirmed an efficient separation. The red solid (III) was identified as hexacarbonyl(butatriene)diiron(0) by elemental analysis and comparison of its melting point, IR, mass and ^{1}H NMR spectra with data reported in the literature [9]. The orange oil (II) was identified as tricarbonyl(2-chlorobutadiene)iron(0) also on the basis of elemental analysis, IR, mass and ^{1}H NMR spectra and the agreement of these with data published by Brune et al. [5].

Continued elution of the column with a 3/1 hexane—dichloromethane solution afforded a yellow oil (1.54 g). TLC of this oil indicated a single component. Trituration and recrystallisation from hexane gave a yellow solid (I) which melted at 104-106°. This complex was identified as hexacarbonyl(2,6-dichloro-3,5-dimethylenehepta-1,6-diene-4-one)diiron(0) on the basis of the following data. Found: C, 37.4; H, 1.7; Cl, 14.7%. $C_{15}H_8Cl_2Fe_2O_7$ calcd.: C, 37.3; H, 1.6; Cl, 14.7%. Parent ion peaks in the mass spectrum were observed at m/e = 482, 484 and 486. Formula mol. wt. = 483. Peaks corresponding to the consecutive loss of six CO groups were observed. IR spectral bands included 2076 s(sharp), 2060 s(sharp) and 2020 s(broad cm^{-1} attributable to the carbonyl ligands, and 1982 s(sharp) cm^{-1} due to the ketonic CO group.

The ^1H NMR spectrum ($CDCl_3$) was assigned as indicated below:



τ:7.67 (d, H_2); 7.88 (d, H_3); 9.26 (d, H_1); 9.96 (d, H_4). $J(H_1H_2)$ = 4.2; $J(H_3H_4)$ = 3.2 Hz.

Reaction of 2,3-dichlorobutadiene with $Fe_3(CO)_{12}$

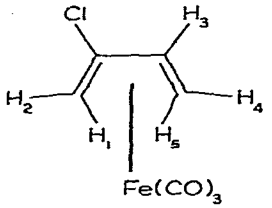
2,3-Dichlorobutadiene (25 ml) was added to a suspension of $Fe_3(CO)_{12}$ (25 g) in tetrahydrofuran (100 ml) and refluxed for 2 h, during which the colour changed from dark green to red. The cooled solution was filtered and the solvent and $Fe(CO)_5$ generated in the reaction pumped off to leave a dark brown oily residue. This was extracted with dichloromethane (3 × 25 ml) and the combined extracts concentrated to 5 ml. Hexane elution on a silica gel column gave a red oil (2.5 g) which was shown by TLC to consist of two components. These were separated in a micro-distillation apparatus. The first fraction (1.9 g) (b.p. 92-93°, 10 mm Hg) was identified as tricarbonyl (2,3-dichlorobutadiene)iron(0) (compound IV). (Found: C, 32.2; H, 1.6; Cl, 26.9%. $C_7H_4Cl_2FeO_3$ calcd.: C, 32.0; H, 1.5; Cl, 27.0%.) The parent ion peaks occur at 262, 264 and 266, cf. mol. wt. = 263. In the IR spectrum ν(CO) are observed at 2066 s(sharp) and 2000 s(broad) cm^{-1}. The ^1H NMR spectrum consisted of two doublets at τ 7.80 and τ 9.80 attributable, respectively, to the *syn*- and *anti*-protons on C(1) and C(4); $J(H_sH_a)$ = 4.1 Hz. The second fraction (b.p. 100-102°, 10 mm Hg) solidified in the condenser. It was shown by analysis and ^1H NMR spectra to be complex III.

Reaction of tricarbonyl(2,3-dichlorobutadiene)iron(0) with $Fe_2(CO)_9$

One gram of complex IV was refluxed with 10 g $Fe_2(CO)_9$ in hexane for 2 h. No colour change occurred. On cooling unreacted $Fe_2(CO)_9$ was filtered off. The solvent was removed from the orange filtrate to give a red oil. Elution with hexane on a silica gel column afforded 1.0 g of a red oil shown by IR and ^1H NMR spectroscopy to be unreacted complex IV.

Reaction of 2-chlorobutadiene with $Fe_2(CO)_9$

2-Chlorobutadiene (25 ml) was refluxed with $Fe_2(CO)_9$ (25 g) in hexane for 2 h. The cooled solution was filtered and the solvent, plus $Fe(CO)_5$, removed to yield a brown oily residue. This was extracted with dichloromethane (3 × 25 ml) and the combined extracts concentrated to 5 ml. Elution with hexane on a silica gel column gave an orange oil (0.95 g) which was shown by TLC to consist of one component only. It was purified by distillation (b.p. 72°, 10 mm Hg) and identified by elemental analysis, IR, mass and ^1H NMR spectra as tricarbonyl(2-chlorobutadiene)iron(0). Continued elution with hexane produced a small quantity of $Fe_3(CO)_{12}$. Elution with dichloromethane did not yield any further products. (Found: C, 37.1; H, 2.3; Cl, 15.7%. $C_7H_5ClFeO_3$ calcd.: C, 36.8; H, 2.2; Cl, 15.6%.) m/e = 228, 230, cf. mol. wt. = 228.5. $\nu(CO)$ = 2060 s and 1980 s(br) cm^{-1}. Proton assignments in the ^1H NMR spectrum ($CDCl_3$) are as indicated below:



τ: 4.26 (t, H_3); 7.73 (dd, H_2); 8.36 (dd, H_4); 9.43 (dd, H_1); 10.21 (dd, H_5). $J(H_3H_5)$ = 9.0; $J(H_3H_4)$ = 7.5; $J(H_4H_5)$ = 2.6; $J(H_2H_3)$ = 1.8; $J(H_1H_3)$ = 1.3; $J(H_1H_2)$ = 4.4 Hz.

Reaction of 2-chlorobutadiene with $Fe_3(CO)_{12}$

2-Chlorobutadiene (25 ml) was refluxed with $Fe_3(CO)_{12}$ (25 g) in tetrahydrofuran (100 ml) for 2 h. The colour changed from green to red. The cooled solution was filtered and the solvent and $Fe(CO)_5$ removed to leave a dark red oil. This was extracted with dichloromethane and chromatographed on silica gel as before. The only product was tricarbonyl(2-chlorobutadiene)iron(0) (2.4 g).

Reaction of 1-chlorobutadiene with $Fe_3(CO)_{12}$

trans-1-Chlorobutadiene (2 ml) was refluxed with $Fe_3(CO)_{12}$ (12 g) in tetrahydrofuran for 2 h. The colour changed from dark green to red-brown. The solution was cooled, filtered and concentrated and chromatographed on a silica gel column. Elution with light petroleum ether yielded a yellow-orange liquid (0.72 g) followed by an orange solid (0.18 g) shown by its physical properties to be the butatriene complex (III). The yellow-orange liquid was identified as tricarbonyl-(1-chlorobutadiene)iron(0). (Found: C, 38.1; H, 2.3%. $C_7H_5ClFeO_3$ calcd.: C, 36.8; H, 2.2%.) m/e = 228, 230, cf. mol.wt. = 228.5. $\nu(CO)$ = 2063 s, 2000 s, 1994 s cm^{-1} in hexane; 2065 s, 2015-1970 s cm^{-1} (thin film). The ^1H NMR spectrum in $CDCl_3$ consisted of resonances at τ 4.2-5.0 (multiplet), τ 7.52 (complex doublet), τ 8.2 (d), τ 8.2 (d), τ 9.7 (d).

Reaction of 1-chlorobutadiene with $Fe_2(CO)_9$

1-Chlorobutadiene (2 ml) was refluxed with $Fe_2(CO)_9$ (8 g) in hexane for 2 h during which time the colour of the reaction mixture changed from pale orange to brown-green. Removal of solvent from the cooled, filtered solution gave a brownish green oil. This was chromagraphed on a silica gel column. Elution with light petroleum ether afforded, successively, a yellow liquid (1.1 g), $Fe_3(CO)_{12}$, and a pale yellow oil (0.32 g) which darkened on isolation. The yellow liquid was identified as tetracarbonyl(1-chlorobutadiene)iron(0). (Found: C, 37.7; H, 2.0%. $C_8H_5ClFeO_4$ calcd.: C, 37.5; H, 2.0%.) The mass spectrum did not show a peak corresponding to the parent ion. The fragmentation pattern indicated loss of diene followed by successive loss of CO. This contrasts with the behaviour of complexes of chelated diene where CO is lost first. A hexane solution showed IR bands at 2080 s, 2000 vs and 1991 vs cm^{-1} due to ν(CO) and another at 1616 m cm^{-1} attributable to uncoordinated C=C. The ^{1}H NMR spectrum showed resonances at τ 3.8-4.6 (multiplet), τ 5.5-6.07 (multiplet) and τ 7.2-7.7 (multiplet) in the integrated intensity ratio of 2/1/2. The pale yellow viscous oil deteriorated rapidly after isolation darkening to a brown oil; it was not characterized. Analysis gave C, 63.9; H, 8.1%. An NMR spectrum could not be obtained. The infrared spectrum showed, inter alia, bands at 2965 s, 2928 s, 2856 s, 2070 s, 2010 (sh), 1980 s(br), 1697 m, 1683 m, 1446 m, 1423 s, 1243 s, 1030 m, 735 m, 620 s, 596 s, 571 s cm^{-1}.

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