a less pure form were discarded.

All synthesized amines were found to be better than 99% pure by VPC. Structure assignments were carried out by ^1H NMR spectroscopy, mass spectroscopy, and elemental analysis data: ^1H NMR ($CDCl_3$) δ 5.4–6.1 (br m, 1 H, CH=C), 4.7–5.2 (br m, 2 H, CH_2=C), 1.8–2.5 (br m, with a prominent peak standing at 2.2, 10 H, $CH_2N(CH_3)_2$ and CH_2CH=), 1.0–1.8 (br m, "central methylene protons").

In the mass spectrum such compounds showed the expected molecular peaks: $n = 7$, m/e 127; $n = 8$, m/e 141; $n = 9$, m/e 155; $n = 11$, m/e 183; $n = 13$, m/e 211; $n = 16$, m/e 253. A base peak at m/e 58 was found in all cases and was probably due to the fragment $(CH_3)_2N^+{=}CH_2$.

Product Analysis. The identification of the components of the reaction mixture was accomplished by VPC comparison between the actual reaction mixtures and authentic samples of the products of the three competing reactions. For the comparison, two different types of column were used with identical results.

The product composition was determined under kinetic conditions by VPC measurements, according to a previously described procedure.[3] A Carbowax column and an Apiezon column were used for ring sizes with n = 8, 9, and 16 and for ring sizes with n = 7, 11, and 13, respectively.

Rate Measurements. The overall rates were measured by acid–base potentiometric microtitration of the total amine product formed according to a previously described procedure.[3]

Registry No. **1** (n = 7), 20422-15-5; **1** (n = 8), 27397-03-1; **1** (n = 9), 74366-38-4; **1** (n = 11), 74366-39-5; **1** (n = 13), 36735-08-7; **1** (n = 16), 74366-40-8; **2** (n = 7), 1192-95-6; **2** (n = 8), 19719-81-4; **2** (n = 9), 4802-48-6; **2** (n = 11), 19719-82-5; **2** (n = 13), 19719-84-7; **2** (n = 16), 74366-41-9; **3** (n = 7), 58390-19-5; **3** (n = 8), 74366-42-0; **3** (n = 9), 58390-20-8; **3** (n = 11), 74366-43-1; **3** (n = 13), 74366-44-2; **3** (n = 16), 74366-45-3; **3** (n = 16) picrate, 74366-46-4; **4** (n = 7), 52254-56-5; **4** (n = 8), 27397-04-2; **4** (n = 9), 16083-54-8; **4** (n = 11), 27397-10-0; **4** (n = 13), 21951-17-7; **4** (n = 16), 74366-47-5; **5** (n = 16), 50768-64-4; **6** (n = 7), 111-49-9; **6** (n = 8), 1121-92-2; **6** (n = 9), 5661-71-2; **6** (n = 11), 294-42-8; **6** (n = 13), 295-03-4; **6** (n = 16), 295-66-9; **7** (n = 8), 629-30-1; **7** (n = 9), 629-41-4; **7** (n = 11), 112-47-0; **7** (n = 13), 5675-51-4; **8** (n = 8), 10160-24-4; **8** (n = 9), 50816-19-8; **8** (n = 11), 53463-68-6; **8** (n = 13), 3344-77-2; **10** (n = 7), 74366-48-6; **10** (n = 8), 74366-49-7; **10** (n = 9), 74366-50-0; **10** (n = 11), 74366-51-1; **10** (n = 13), 74366-52-2.

Iron Carbonyl Promoted Additions of Perhalomethanes to Carbon–Carbon Double Bonds[1]

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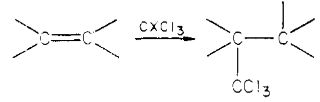
The addition of CCl_4 and $CBrCl_3$ to carbon–carbon double bonds, catalyzed by $Fe_2(CO)_9$ and $Me_3NFe(CO)_4$, is reported. In the case of CCl_4, these reactions afford $\alpha,\alpha,\alpha,\gamma$-tetrachloro-substituted derivatives with simple alkenes, whereas with norbornadiene and with the bicyclobutane bridged enone **1** and diene **2** rearranged products are obtained. The addition of CCl_4 to alkyl-substituted conjugated dienes leads to products that contain the iron carbonyl moiety. IR spectroscopic measurements revealed that the initial step of the catalyzed processes involves a reaction of the iron carbonyl with the perhalomethane to provide transient species of the type FeL_mX (L = CO, Me_3N; X = Cl, Br) and a trichloromethyl radical. A redox chain mechanism is proposed for the catalyzed process, implying addition of the (possibly complexed) trichloromethyl radical to the carbon–carbon double bond and subsequently abstraction of a halogen atom (X) by the (possibly complexed) substrate radical from FeL_mX to yield the $\alpha,\alpha,\alpha,\gamma$-tetrahalo derivative. The addition of CCl_4 to alkyl-substituted conjugated dienes supplies evidence for the possible intermediacy of σ complexes between substrate radical and species FeL_mX, trapped as stable diene iron tricarbonyl complexes in this particular case; the mode of addition was found to be consistent with the proposed mechanism for catalyzed additions by using deuterium-labeled 2,3-dimethylbutadiene.

The addition of CCl_4 and $CBrCl_3$ to alkenes has received considerable interest as a method to form new carbon–carbon single bonds. This reaction which involves a scission of a C–Cl bond in the case of CCl_4 and of a weaker C–Br bond in the case of $CBrCl_3$ usually gives rise to the formation of α,α,α-trichloro-γ-halo (chloro or bromo) derivatives (eq 1). Various methods are available for the conversion of the trichloromethyl moiety into other functionalities, for instance, into a carboxyl group by hydrolysis,[2,3] into a dichloromethylene group by dehydrohalogenation,[4-6] and into a (hydroxy)methyl group by reduction.[4,5,7]



X = Cl, Br

The addition of CCl_4 to alkenes has been accomplished either by a free-radical reaction initiated by peroxides or by UV irradiation[8,9] or by the application of transition-metal systems.[10] However, the former reaction is often inconvenient in the case of simple alkenes because of a competing telomerization;[8] therefore, the addition of

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(1) See for a preliminary communication J. Elzinga and H. Hogeveen, *J. Chem. Soc., Chem. Commun.*, 705 (1977).

(2) A. N. Nesmeyanov, R. K. Freidlina, and L. I. Zakharin, *Q. Rev., Chem. Soc.*, **10**, 330 (1956); A. N. Nesmeyanov, R. K. Freidlina, V. N. Kost, T. T. Vassilyeva, and B. V. Kopylova, *Tetrahedron*, **17**, 69 (1962).

(3) G. B. Gill and B. Wallace, *J. Chem. Soc., Chem. Commun.*, 380 (1977); H. Goldwhite, M. S. Gibson, and C. H. Harris, *Tetrahedron*, **20**, 1649 (1964); M. E. Hill, *J. Org. Chem.*, **25**, 1115 (1960).

(4) R. Dowbenko, *J. Am. Chem. Soc.*, **86**, 946 (1964).

(5) P. P. M. Rijsenbrij, Thesis, University of Amsterdam, 1977, Chapter 5; P. P. M. Rijsenbrij, R. Loven, J. B. P. A. Wijnberg, W. N. Speckamp, and H. O. Huisman, *Tetrahedron Lett.*, 1425 (1972).

(6) P. D. Klemmensen, H. Kolind-Andersen, H. B. Madsen, and A. Svendsen, *J. Org. Chem.*, **44**, 416 (1979).

(7) A. G. Yurchenko, L. A. Zosim, N. L. Dovgan, and N. S. Verpovsky, *Tetrahedron Lett.*, 4843 (1976).

(8) C. Walling, "Free Radicals in Solution", Wiley, New York, 1957, Chapter 6.2; C. Walling and E. S. Huyser, *Org. React.*, **13**, 91 (1963).

(9) G. Sosnovsky, "Free Radical Reactions in Preparative Organic Chemistry", Macmillan, New York, 1964, Chapter 2.

(10) This subject has been recently reviewed: J. K. Kochi, "Organometallic Mechanisms and Catalysis", Academic Press, New York, 1978.

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$CBrCl_3$, which gives higher yields of monomer, is preferred[8] to that of CCl_4 for the preparation of α,α,α-trichloro-γ-halo compounds. Redox systems that have been shown to be efficient catalysts for the addition of CCl_4 to olefins[10-12] are, for instance, iron and copper chlorides. In general, however, rather high temperatures (>80 °C) and a cocatalyst (alcohol, amine) are required.

Recently catalysis by organometallic compounds has gained strong interest. Among the catalysts that have been employed are $(CpFe(CO)_2)_2$ and $Co_2(CO)_8$ (temperature >130 °C),[13] $W(CO)_6$ with UV irradiation,[14] the (naphthalene)chromium tricarbonyl/THF system (room temperature),[15] $Fe(CO)_5$ (temperature >100 °C),[16] and $Ru(PPh_3)_4Cl_2$ (temperature >80 °C).[17] It has also been reported that some metal carbonyls in the presence of CCl_4 are capable of promoting polymerization reactions of olefins under the proper conditions.[18] Various mechanisms have been proposed to account for the catalyzed additions of perhalomethanes to carbon–carbon double bonds, some concerning radical intermediates (either free[10,11] or coordinated to the metal[12]) and others oxidative addition/reductive elimination steps.[13,15] Here we report the addition of CCl_4 (and in some cases $CBrCl_3$) to carbon–carbon double bonds at room temperature as catalyzed by iron carbonyls such as $Fe_2(CO)_9$ and $Me_3NFe(CO)_4$ (and in the case of $CBrCl_3$ also by $Fe(CO)_5$). Synthetic as well as mechanistic features of the reactions are discussed.

Results

Iron Carbonyl Catalyzed Additions of Tetrachloromethane to Carbon–Carbon Double Bonds. $Me_3NFe(CO)_4$ was prepared independently both by Shvo[19] and in our laboratory[1] by the reaction between Me_3NO and $Fe(CO)_5$; details concerning its preparation and properties[1] are described in the Experimental Section. Very recently Shvo and co-workers reported[20] a general synthesis of (trialkylamino)iron tetracarbonyl complexes by the reaction between trialkylamines and $Fe_2(CO)_9$. $Me_3NFe(CO)_4$ and $Fe_2(CO)_9$ are both capable of catalyzing the addition of CCl_4 at room temperature to certain carbon–carbon double bonds to afford $\alpha,\alpha,\alpha,\gamma$-tetrachloro-substituted derivatives (or isomeric products). The results are compiled in Table I. $Fe(CO)_5$ with or without triethylamine proves to be inactive as a catalyst at ambient temperature; however, catalysis by $Fe(CO)_5$ in this type of addition has been reported[16] to occur at higher temperatures (>100 °C). Although the turnover capability of the catalyst used is rather low in the case of simple alkenes, the yields of the products are high if calculated on the amount of consumed alkene (see Table I). It is synthetically favorable, therefore, to use $Me_3NFe(CO)_4$ and $Fe_2(CO)_9$ in stoichiometric amounts in the case of more difficultly accessible alkenes, $Me_3NFe(CO)_4$ and $Fe_2(CO)_9$ being easily available.

The addition to terminal alkenes proves to be more efficient than to internal alkenes (compare entries 1 and 2 with 3 and 4), probably due to steric factors. On the other hand, the addition to strained ring systems containing carbon–carbon double bonds such as norbornadiene (entry 6) and bicyclobutane-bridged derivatives **1** and **2** (entries 7 and 8) gives rise to formation of rearranged products in high yield (see Discussion). The addition to 1,5-hexadiene (entry 2) gives incorporation of only 1 equiv of CCl_4, no diadduct being observed under the present reaction conditions.[21] However, entries 9–11 show that in other cases diadducts are formed.

Entries 4 and 9–11 show that since a dehydrohalogenation side reaction can occur, this does not result from a reaction between initially formed adduct and the original iron carbonyl catalyst, because when a mixture of compounds **7** and **8** was treated with excess $Me_3NFe(CO)_4$, no reaction occurred. On the other hand, when the mixture of **7** and **8** was treated with silver perchlorate, compound **7** was converted into **8** (yield 70%).

Iron Carbonyl Catalyzed Additions of Bromotrichloromethane to Carbon–Carbon Double Bonds. Usually the addition of $CBrCl_3$ to alkenes is a facile process; sometimes exposure to daylight is sufficient to initiate the radical chain reaction.[8] $Me_3NFe(CO)_4$ and $Fe_2(CO)_9$ and also $Fe(CO)_5$ prove to be active as catalysts in this addition, as shown for the examples listed in Table II.

The addition of $CBrCl_3$ to diene **2** proceeds spontaneously in the daylight when a quartz vessel is used, but in a Pyrex vessel UV irradiation or a catalyst is required to drive the reaction to completion;[22] the addition to enone **1** does not occur without a catalyst or irradiation.

The rearranged products, viz., **9**, **10**, and **12**, are obtained in good yields as in the case of CCl_4 addition; compound **11** is formed in a thermal reaction from the *endo*-Br isomer of compound **12** as has been discussed in a previous paper.[22]

Iron Carbonyl Promoted Additions of Tetrachloromethane to Alkyl-Substituted Conjugated Dienes. Whereas treatment of diene **2** with CCl_4 in the presence of $Fe_2(CO)_9$ affords CCl_4-incorporated products (Table I), the alkyl-substituted dienes, represented in Table III, show a different behavior. Instead of a catalyzed addition, a stoichiometric reaction with respect to $Fe_2(CO)_9$ takes place to afford, in low yield, products containing a trichloromethyl as well as an iron tricarbonyl moiety; the same products are formed by irradiation of the diene in CCl_4 solution in the presence of $Fe(CO)_5$ and by treatment of the diene with $Me_3NFe(CO)_4$ in CCl_4 solution (see Table III).

In the case of $Fe_2(CO)_9$- and $Fe(CO)_5/h\nu$-promoted additions the diene iron tricarbonyl complexes compiled in Table III were the only products that could be isolated from complicated reaction mixtures by applying preparative TLC. Attempts to increase the yields of these complexes by varying the iron carbonyl/alkene ratio and the concentrations of the reagents were unsuccessful. In the case of the $Me_3NFe(CO)_4$-promoted addition of CCl_4 to

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[11] F. Minisci, *Acc. Chem. Res.*, **8**, 165 (1975); M. Asscher and D. Vofsi, *Chem. Ind. (London)*, 209 (1962); *J. Chem. Soc.*, 1887 (1963); *J. Chem. Soc. B*, 947 (1968); A. Orochov, M. Asscher, and D. Vofsi, *J. Chem. Soc., Perkin Trans. 2*, 1000 (1973).

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[15] O. Gandolfi and M. Cais, *J. Organomet. Chem.*, **125**, 141 (1977).

[16] A. N. Nesmeyanov, R. K. Freidlina, E. C. Chukovskaya, R. G. Petrova, and A. B. Belyavsky, *Tetrahedron*, **17**, 61 (1962); E. C. Chukovskaya, A. A. Kamyshova, and R. K. Freidlina, *Dokl. Akad. Nauk SSSR*, 602 (1965); R. K. Freidlina, and E. C. Chukovskaya, *Synthesis*, 477 (1974).

[17] H. Matsumoto, T. Nakano, K. Takasu, and Y. Nagai, *J. Org. Chem.*, **43**, 1734 (1978); H. Matsumoto, T. Nakano, T. Nikaido, and Y. Nagai, *Chem. Lett.*, 115 (1978); H. Kono, H. Matsumoto, and Y. Nagai, *J. Organomet. Chem.*, **148**, 267 (1978).

[18] C. H. Bamford and C. A. Finch, *Proc. Chem. Soc., London*, 110 (1962); C. H. Bamford, G. C. Eastmond, and D. Whittle, *J. Organomet. Chem.*, **17**, P33 (1969); *Pure Appl. Chem.*, **12**, 183 (1966).

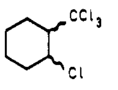
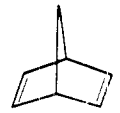
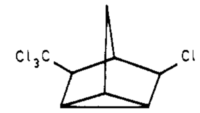
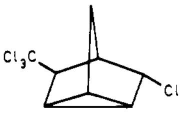
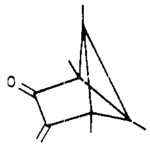
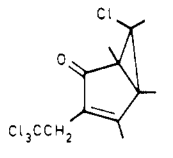
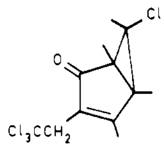
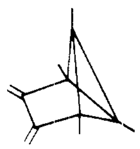
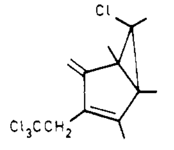
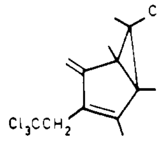
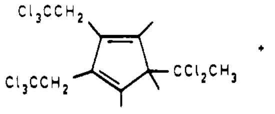
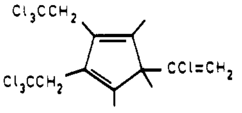
[19] Y. Shvo and E. Hazum, Abstracts of the 7th International Conference on Organometallic Chemistry, Venice, 1975, p 122.

[20] F. Birencwaig, H. Shamai, and Y. Shvo, *Tetrahedron Lett.*, 2947 (1979).

[21] The same result was obtained when (naphthalene)chromium tricarbonyl was used as catalyst.[15]

[22] J. Elzinga and H. Hogeveen, *J. Org. Chem.*, **44**, 2381 (1979).

Table I. Iron Carbonyl Catalyzed Addition of CCl_4 (Solvent) to Carbon-Carbon Double Bonds[a]

entry	substr	ratio of catal/substr	products		yield with catalyst, %	
					$Me_3NFe(CO)_4$	$Fe_2(CO)_9$
1	$CH_2{=}CH(CH_2)_4CH_3$	0.1	$Cl_3CCH_2CHCl(CH_2)_4CH_3$		50[b](95)[c]	40[b](90)[c]
2	$CH_2{=}CH(CH_2)_2CH{=}CH_2$	0.1	$Cl_3CCH_2CHCl(CH_2)_2CH{=}CH_2$		40(95)	30(90)
3		0.1			10(85)	10(80)
4	$(CH_3)_2C{=}C(CH_3)_2$	0.1	$Cl_3CC(CH_3)_2C(CH_3)_2Cl$ + $Cl_3CC(CH_3)_2C(CH_3){=}CH_2$	(g)	10(90)	(d)
5	ibid	0.5	ibid	(g)	40(90)	(d)
6		0.1	 + 	(h)	90(90)	80(90)
7[e]	 1	0.1	 3 +  4	(i)	95(95)	95(95)
8[e]	 2	0.1	 5 +  6	(j)	90(90)	90(90)
9	5 + 6 (j)	0.1	 7 +  8	(k)	7(70)	(f)
10	ibid	0.5	ibid	(k)	35(70)	(f)
11	ibid	1.1	ibid	(k)	70(70)	(f)

[a] Reaction conditions: room temperature, N_2 atmosphere, reaction time 16 h (if not otherwise indicated). [b] Yields based on the intake of alkene (determined by ^1H NMR spectroscopy using benzene as standard). [c] Yields based on consumed alkene (determined by ^1H NMR spectroscopy using benzene as standard). [d] These reactions were also performed with $Fe_2(CO)_9$ as catalyst; however, complicated mixtures were obtained which contained the monoadduct in low yield. [e] Reaction time 3 h. [f] The reaction with $Fe_2(CO)_9$ gave complicated mixtures containing compound 8 but no 7. [g] Tetrachloro and trichloro derivatives were formed in a ratio of 5:1. [h] *exo*-Chloro and *endo*-chloro derivatives were formed in a ratio of 3:2. [i] Compounds 3 and 4 were formed in a ratio of 85:15. [j] Compounds 5 and 6 were formed in a ratio of 68:32. [k] Compounds 7 and 8 were formed in a ratio of 2:1.

2,3-dimethylbutadiene, the formation of the complex 15 is a minor reaction compared to formation of large amounts of unstable and unidentified materials.

IR Measurements of the Reactions between Iron Carbonyls and Perhalomethanes. In order to obtain more information about the mechanism of the iron carbonyl catalyzed additions of CCl_4 and $CBrCl_3$ to carbon-carbon double bonds, an IR investigation of the reactions between iron carbonyls and perhalomethanes was performed.

When $Fe(CO)_5$ was added to $CBrCl_3$, the initially yellow solution rapidly turned orange. The IR spectrum of a sample taken from the orange solution within 10 min after mixing showed absorptions in the CO region at 2150, 2110, 2100, and 2075 cm^{-1} along with bands at 2020 and 1980 cm^{-1} due to $Fe(CO)_5$ and at 1810 cm^{-1} due to $COCl_2$. Gradually the intensities of the absorptions at 2150, 2110, 2100, and 2075 cm^{-1} increased at the expense of those due to $Fe(CO)_5$ which had completely disappeared after 2 h. The structure of the complex exhibiting bands at 2150, 2110, 2100, and 2075 cm^{-1} proved to be[23] $Fe(CO)_4Br_2$ as

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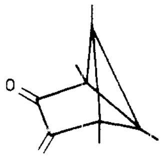
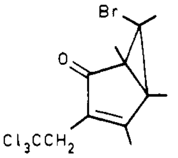
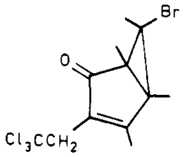
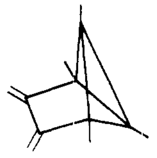
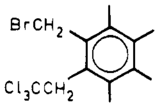
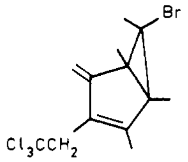
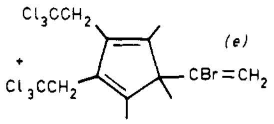
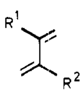
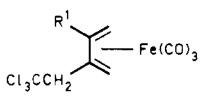
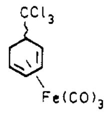
[23] K. Noack, *Helv. Chim. Acta*, 45, 1847 (1962).

Table II. Iron Carbonyl Catalyzed Addition of $CBrCl_3$ (Solvent) to Carbon-Carbon Double Bonds[a]

substr	ratio of catal/substr	products	yield[b] with catalyst, %: Me_3N-$Fe(CO)_4$	$Fe_2(CO)_9$	$Fe(CO)_5$
 1	0.1	 9 +  10 (c)	70	70	70
 2	0.1	 11 +  12 (d)	70	70	70
2	1.1	11 +  13 (e)	70	70	70
12	0.1	13	8		8
12	1.1	13	70		70

[a] Reaction conditions: room temperature, N_2 atmosphere, reaction time 3 h. [b] Yields are based on the intake of alkene (determined by ^1H NMR spectroscopy with benzene as standard). [c] Compounds 9 and 10 were formed in a ratio of 78:22. [d] For the formation of 11 see the text and ref 22; compounds 11 and 12 were formed in a ratio of 73:27. [e] Compounds 11 and 13 were formed in a ratio of 4:1.

Table III. Iron Carbonyl Promoted Addition of CCl_4 (Solvent) to Conjugated Dienes[a]

substr	iron carbonyl	product	yield,[b] %
			
$R^1 = H, R^2 = CH_3$	$Fe_2(CO)_9$	14, $R^1 = H$	15
$R^1 = R^2 = CH_3$	$Fe_2(CO)_9$	15, $-CH_3$	15
ibid	$Me_3NFe(CO)_4$	ibid	5[c]
ibid	$Fe(CO)_5/h\nu$	ibid	15
	$Fe_2(CO)_9$	 (d) 16	10

[a] Reaction conditions: 1 equiv of iron carbonyl (if not otherwise indicated), N_2 atmosphere, reaction time 16 h. [b] Yield of isolated product. [c] 0.1 equiv of $Me_3NFe(CO)_4$ was used. [d] Only one geometrical isomer of 16 was obtained; its stereochemistry is unknown. In addition to 16, cyclohexadiene iron tricarbonyl was isolated in 10% yield.

shown by comparison with an authentic sample prepared by the reaction between $Fe(CO)_5$ and Br_2 according to the literature.[24] $Fe_2(CO)_9$ was found to dissolve in $CBrCl_3$ with formation of $Fe(CO)_4Br_2$ and $Fe(CO)_5$ as shown by IR spectroscopy; no signals originating from $Fe_2(CO)_9$ were observed.[25]

Upon the addition of $CBrCl_3$ to $Me_3NFe(CO)_4$ a vigorous reaction took place with the evolution of CO. The IR spectrum recorded just after mixing showed the complete decomposition of $Me_3NFe(CO)_4$ (IR absorptions at 2050, 1960, and 1940–1920 cm^{-1} in the CO region); instead the IR spectrum revealed two strong sharp signals at 2110 and 2060 cm^{-1} in the CO region and less intense signals at about 3000 cm^{-1} (Me_3N). Attempts to isolate the complex were unsuccessful due to its rapid decomposition into (mainly) $FeBr_2$ upon removal of the $CBrCl_3$ in vacuo; it proved to be moderately stable in dilute $CBrCl_3$ solution, however. Although the structure of the complex exhibiting bands at 2110, 2060 (CO), and 3000 cm^{-1} (Me_3N) cannot unequivocally be derived from these data, the values of the observed CO frequencies suggest the complex to have a structure of the type $Me_3NFe(CO)_mBr_n$ (monomeric or dimeric): replacement of iron-bonded CO groups by halogen atoms is known to shift the absorptions of the remaining CO groups to higher frequencies.[23] It is of interest to note that this complex is not formed on treatment of $Me_3NFe(CO)_4$ with bromine.

$Fe(CO)_5$ has been reported[26] to decompose into $FeCl_2$

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(24) W. Hieber and G. Bader, *Chem. Ber.*, 61, 1717 (1928).

(25) $Fe_2(CO)_9$ has been reported to display IR absorptions in the CO region at 2087, 2023, and 1831 cm^{-1}. N. Hagihara, M. Kumada, and R. Okawara, Eds., "Handbook of Organometallic Chemistry", W. A. Benjamin, Amsterdam, 1968, p 878.

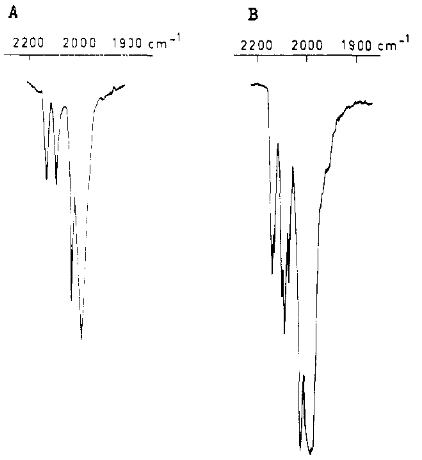


Figure 1. IR spectra of the reaction between $Fe_2(CO)_9$ and CCl_4 (only the iron carbonyl CO region is shown): A, after 10 min; B, after 25 min. See the Experimental Section for the experimental conditions.

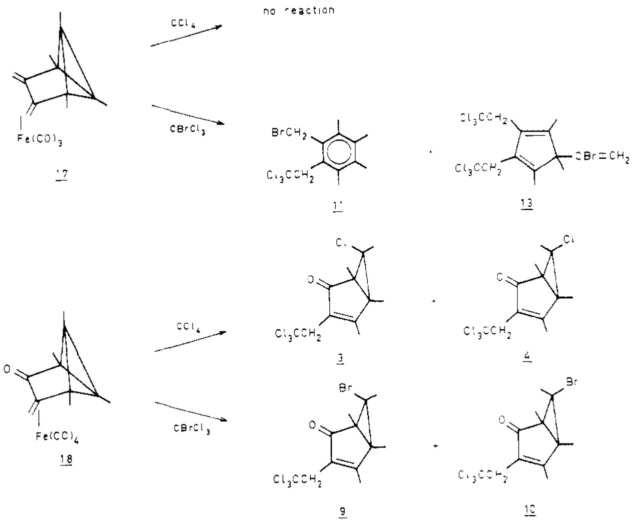
and C_2Cl_6 upon photolysis or thermolysis in CCl_4 solution; but when kept at room temperature in the dark, $Fe(CO)_5$ proves to be reasonably stable for some days in CCl_4 solution. On the contrary, $Fe_2(CO)_9$ was found to decompose completely in CCl_4 within 3 h to yield a mixture of $FeCl_2$, $Fe(CO)_5$, and C_2Cl_6. Samples taken from the supernatant orange solution of a mixture of $Fe_2(CO)_9$ and CCl_4 were monitored by IR spectroscopy. A spectrum taken within 5 min after mixing showed absorptions in the CO region at 2130 and 2090 cm^{-1} along with the bands due to $Fe(CO)_5$ at 2020 and 1990 cm^{-1} (Figure 1) and a signal at 1810 cm^{-1} due to $COCl_2$. Absorptions originating from $Fe_2(CO)_9$ were not observed[25] which shows that $Fe_2(CO)_9$ dissolves into CCl_4 with complete decomposition. After 25 min the intensities of the signals at 2130 and 2090 cm^{-1} decreased with the simultaneous appearance of bands at 2135, 2100, and 2075 cm^{-1} (Figure 1b); the latter signals disappeared consecutively. The structures of these unstable species are not known, but they may be of the type $Fe(CO)_mCl_n$ in view of the high frequencies of the observed CO absorptions.[23] The formation of the complex $Fe(CO)_4Cl_2$ (which is known[23] to have absorptions at 2164, 2124, 2108, and 2084 cm^{-1}, C_2Cl_4 solution) was not observed, however, contrary to the formation of $Fe(CO)_4Br_2$ from the reaction between $Fe_2(CO)_9$ and $CBrCl_3$.

When $Me_3NFe(CO)_4$ was dissolved in CCl_4, the IR spectrum in the CO region showed only the absorptions due to $Me_3NFe(CO)_4$ at 2050, 1960, and 1940–1920 cm^{-1}; this complex decomposed slowly (within 10 h) into ultimately $FeCl_2$, no new absorptions with reasonable intensities due to intermediate species being detected by IR spectroscopy.

The reactions between perhalomethanes and iron carbonyls were also performed in the presence of substrates prone to incorporation of perhalomethanes, viz., bicyclobutane-bridged derivatives 1 and 2 (Tables I and II); no new IR absorptions due to intermediate species in addition to those already cited were observed, however.

In conclusion, the reported reactions between iron carbonyls and perhalomethanes lead to formation of unstable complexes of the general type FeL_mX_n (L = CO, Me_3N; X = Cl, Br). The dehalogenating capability of iron carbonyls as shown here has been observed with various organic halide derivatives[27] and has been applied in organic synthesis;[28,29] furthermore, certain organic halides have been used as precursors for the preparation of diene iron tricarbonyl complexes.[30]

Scheme I



Reactions of Some Bicyclobutane-Bridged Iron Carbonyl Complexes with Perhalomethanes. Also some organic derivatives of iron carbonyls were treated with perhalomethanes. Whereas diene iron tricarbonyl 17[31] proved to be stable in CCl_4 solution even at reflux temperature for several hours,[32] enone iron tetracarbonyl 18[33] decomposed within 1 day in CCl_4 solution at room temperature to afford a mixture of CCl_4-incorporated products 3 and 4 (ratio 85:15, Scheme I). No intermediates could be observed by IR measurements taken during the course of the reaction. In $CBrCl_3$ solution 18 decomposed within 1 h to provide a mixture of $CBrCl_3$-incorporated products 9 and 10 (ratio 78:22). When the reaction was monitored by IR spectroscopy, absorptions at 2150, 2110, 2100, and 2075 cm^{-1} due to $Fe(CO)_4Br_2$ were observed. Complex 17 also decomposed in $CBrCl_3$ solution (in contrast to its behavior in CCl_4 solution) to afford a mixture of compounds 11 and 13, the formation of $Fe(CO)_4Br_2$ being observed by IR spectroscopy.[34]

Discussion

(A) General Remarks. In order to discuss the mechanism of the iron carbonyl catalyzed additions of CCl_4 and $CBrCl_3$ to carbon–carbon double bonds, one should keep in mind the following features of the reactions.

(1) The catalyzed additions of CCl_4 to simple alkenes afforded $\alpha,\alpha,\alpha,\gamma$-tetrachloro-substituted derivatives; the same products were obtained upon the addition of CCl_4 under free-radical conditions with initiation by UV irra-

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(26) E. Koerner von Gustorf, M. J. Jun, H. Huhn, and G. O. Schenck, *Angew. Chem.*, **75**, 1120 (1963); E. Koerner von Gustorf and F. W. Grevels, *Top. Curr. Chem.*, **13**, 366 (1969).

(27) C. R. Eady, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1706 (1976).

(28) H. Alper in "Organic Synthesis via Metal Carbonyls", Vol. 2, I. Wender and P. Pino, Eds., Wiley, New York, 1977, Chapter 4; J. Tsuji, *Top. Curr. Chem.*, **28**, 41 (1972); M. Ryang, *Organomet. Chem. Rev., Sect. A*, **5**, 67 (1970).

(29) R. Noyori, *Acc. Chem. Res.*, **12**, 61 (1979).

(30) W. R. Roth and J. D. Meier, *Tetrahedron Lett.*, 2053 (1967); G. F. Emerson, K. Ehrlich, W. P. Giering, and P. C. Lauterbus, *J. Am. Chem. Soc.*, **88**, 3172 (1966); G. F. Emerson, L. Watts, and R. Pettit, *ibid.*, **87**, 131 (1965).

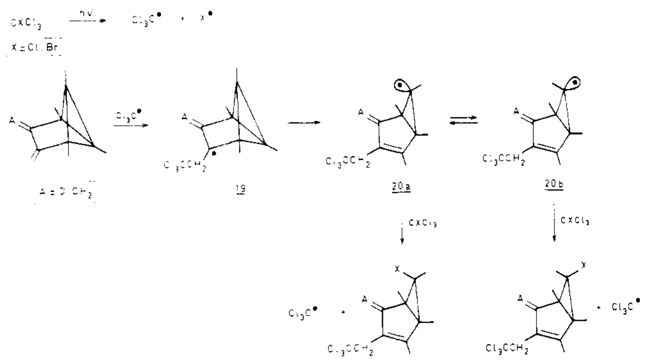
(31) J. Elzinga and H. Hogeveen, *Tetrahedron Lett.*, 2383 (1976).

(32) Upon UV irradiation of a CCl_4 solution of 17, decomposition occurred within 3 h to produce a mixture of unidentified products.

(33) J. Elzinga and H. Hogeveen, *J. Org. Chem.*, **43**, 745 (1978).

(34) Hence, an iron tetracarbonyl complex is formed from an iron tricarbonyl complex by a disproportionation reaction. Similar conversions of $Fe(CO)_{n-1}$ into $Fe(CO)_n$ complexes have been reported. D. H. Gibson and R. L. Vonnahme, *J. Am. Chem. Soc.*, **94**, 5090 (1972).

Scheme II



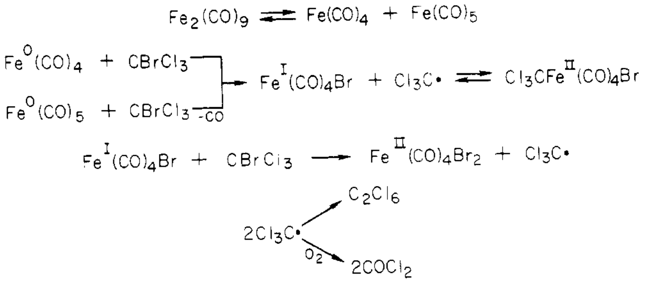
diation or peroxides, although in the latter case the formation of monoadducts was accompanied by formation of side products (telomers).[8] In the case of norbornadiene,[35] enone **1**,[22] and diene **2**,[22] the iron carbonyl catalyzed addition of CCl_4 afforded a mixture of rearranged products (Table I), identical with those as obtained upon the addition of CCl_4 under free-radical conditions. The mechanism of the free-radical additions to **1** and **2**, which involves a homoallylic rearrangement of a bicyclobutylcarbinyl radical, **19**, to a cyclopropyl radical, **20**, is shown in Scheme II.[22] Since the mixtures of products obtained in the iron carbonyl catalyzed processes are equal (within experimental error) to those obtained in the free-radical additions, it is likely that intermediate radicals are also involved in the catalyzed additions.

(2) It is well-known that free-radical chain reactions are inhibited or retarded in the presence of small amounts of radical scavengers such as hydroquinone and *p*-benzoquinone.[36] However, the $Me_3NFe(CO)_4$- and $Fe_2(CO)_9$-catalyzed additions of CCl_4 to enone **1** were not measurably retarded in the presence of a large excess (10 equiv, with respect to the catalyst) of hydroquinone or *p*-benzoquinone. This observation leads to the conclusion that the catalyzed addition of CCl_4 does not occur according to a free-radical chain mechanism in which the iron carbonyl complex functions only as the initiator to generate trichloromethyl radicals, analogously to the role of dibenzoyl peroxide in the free-radical additions of CCl_4. The observation, however, does not exclude the possibility of radical intermediates.[37]

(3) In the course of the catalyzed additions of CCl_4, the catalysts, viz., $Me_3NFe(CO)_4$ and $Fe_2(CO)_9$, decomposed to give ultimately $FeCl_2$ [and $Fe(CO)_5$ in the case of $Fe_2(CO)_9$]. Although $FeCl_2$[10,11] and $Fe(CO)_5$[16] have been used as catalysts to achieve the addition of CCl_4 to alkenes at high temperatures, it was shown that under the present conditions both $FeCl_2$ and $Fe(CO)_5$ (with or without triethylamine) were unable to accomplish the addition to carbon–carbon double bonds, viz., to diene **2**.

(4) The addition of CCl_4 to a mixture of dienes **5** and **6** promoted by $Me_3NFe(CO)_4$ afforded a mixture of diadducts **7** and **8**. Attempts to accomplish a free-radical addition of CCl_4 to **5** and **6** (initiated by UV irradiation or by peroxides) were unsuccessful.[22] Similar attempts to perform a free-radical addition of $CBrCl_3$ to diene **12** (initiated by UV irradiation) resulted only in decomposition of **12**, while the $Fe(CO)_5$-promoted addition of $CBrCl_3$ to **12** smoothly led to formation of **13**. These observations show again the difference between the mechanism of the

Scheme III



free-radical chain addition and that of the catalyzed addition.

(5) The addition of CCl_4 to alkyl-substituted conjugated dienes promoted by iron carbonyls gave rise to the formation of trichloromethyl-substituted diene iron tricarbonyl complexes (Table III).

(6) The reaction between $Fe(CO)_5$ (and also $Fe_2(CO)_9$) and $CBrCl_3$ was shown to afford $Fe(CO)_4Br_2$; conceivably the reactions of $Me_3NFe(CO)_4$ and $CBrCl_3$ and of $Fe_2(CO)_9$ and CCl_4 afforded unstable species of the type FeL_mX_n (L = CO, Me_3N; X = Cl, Br; *m* and *n* unknown) which were observed by IR spectroscopy. By analogy, a similar complex (although not observed by IR measurements) is assumed to be involved in the decomposition of $Me_3NFe(CO)_4$ in CCl_4 solution. Also some organic derivatives of iron carbonyls, viz., **17** and **18**, proved to decompose in $CBrCl_3$ solution to afford $CBrCl_3$-incorporated products and $Fe(CO)_4Br_2$; complex **18** also decomposed in CCl_4 solution to provide the corresponding CCl_4 adducts. We will first discuss these reactions between iron carbonyls and perhalomethanes because they are intimately related to the iron carbonyl catalyzed additions of perhalomethanes to carbon–carbon double bonds.

(B) Reactions between Iron Carbonyls and Perhalomethanes. The initial step of the catalyzed additions of perhalomethanes to carbon–carbon double bonds is supposed to be the reaction between perhalomethanes and iron carbonyls to generate species of the type $Fe(CO)_3(L)X$ (L = CO, Me_3N; X = Cl, Br) and trichloromethyl radicals. The involvement of trichloromethyl radicals is strongly suggested by the observed formation of C_2Cl_6. Furthermore, the generation of $COCl_2$ as observed by IR measurements most likely originates from an oxidation of trichloromethyl radicals by traces of oxygen present in the solution rather than from an iron carbonyl CO group.[38]

The formation of $Fe(CO)_4Br_2$ from $Fe(CO)_5$[39] (or $Fe_2(CO)_9$[41]) and $CBrCl_3$ can be rationalized by assuming a subsequent reaction of $Fe(CO)_4Br$ with $CBrCl_3$ (Scheme III). The possibility of $Fe(CO)_4Br$ and CCl_3 being in equilibrium with $Cl_3CFe(CO)_4Br$ is certainly not excluded

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[35] D. I. Davies and L. T. Parfitt, *J. Chem. Soc. C*, 2691 (1967).

[36] W. A. Pryor, "Free Radicals", McGraw-Hill, New York, 1966, Chapter 21.

[37] Reference 10, pp 166–167.

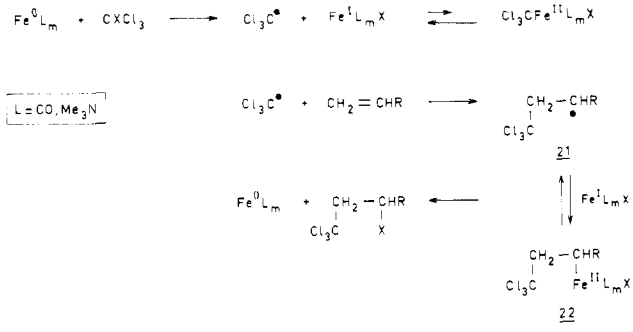
[38] A. Agapiou and E. McNelis, *J. Organomet. Chem.*, **99**, C47 (1975); R. B. Silverman, and R. A. Olofson, *J. Chem. Soc., Chem. Commun.*, 1313 (1968).

[39] The initial step of the reaction between $Fe(CO)_5$ and $CBrCl_3$ is not fully understood. A preliminary dissociation of $Fe(CO)_5$ into $Fe(CO)_4$ and CO followed by a reaction of the highly reactive species $Fe(CO)_4$ with $CBrCl_3$ is unlikely since it has been reported that CO does not exchange with $Fe(CO)_5$ at ambient temperature.[40] Possibly $Fe(CO)_5$ and $CBrCl_3$ form an activated complex, e.g., a charge-transfer complex of the type $[Fe(CO)_5{}^{+}\cdot CBrCl_3{}^{-}\cdot]$ from which $Fe(CO)_4Br$ and a trichloromethyl radical derive. In this context it is of interest to note that in some cases the initial step in the oxidative addition of organic halides to metal(0) complexes was found to be formation of a charge-transfer complex (see, for a recent review concerning this subject, ref 10, chapter 17).

[40] A. N. Webbs and J. J. Mitchell, *J. Phys. Chem.*, **63**, 1878 (1959); K. Noack and M. Ruch, *J. Organomet. Chem.*, **17**, 309 (1969).

[41] The formation of $Fe(CO)_4Br_2$ from $Fe_2(CO)_9$ involves the intermediacy of the highly reactive species $Fe(CO)_4$, which has been observed spectroscopically at very low temperature. M. Poliakoff, *Chem. Soc. Rev.*, **7**, 527 (1978).

Scheme IV



in view of the fact that $Fe(CO)_5$ and perfluoroalkyl iodides are known[42] to afford stable complexes of the type $R_FFe(CO)_4I$, e.g., $F_3CFe(CO)_4I$ in the case of CF_3I. The difference in stability between $F_3CFe(CO)_4I$ and $Cl_3CFe(CO)_4Br$ can be attributed to the weaker iron carbon σ bond in $Cl_3CFe(CO)_4Br$ due to a less efficient $d_\pi-\sigma^*$ back-donation from the metal to the trihalomethyl ligand,[43] chlorine substituents being less strongly electron withdrawing than fluorine substituents. Similar trichloromethyl-substituted transition-metal complexes were indeed found to be sensitive toward homolysis of the metal–carbon σ bond.[44] The reactions of $Me_3NFe(CO)_4$ with $CBrCl_3$ and CCl_4 and of $Fe_2(CO)_9$ with CCl_4 can be explained analogously to the case of the reaction of $Fe_2(CO)_9$ and $CBrCl_3$.

(C) Mechanism of the Catalyzed Additions. A conceivable mechanism of the iron carbonyl catalyzed additions of CCl_4 and $CBrCl_3$ to carbon–carbon double bonds is represented in Scheme IV. It accounts for the evidence given above and implies addition of the (possibly complexed) trichloromethyl radical, generated by the reaction between iron carbonyl and perhalomethane (Discussion, section B), to the double bond to provide radical **21** and the species FeL_mX, probably in equilibrium with σ complex **22**. Abstraction of an atom X from FeL_mX either via **21** or **22** then yields the α,α,α,γ-tetrahalo-substituted derivative and the species FeL_m which reenters the catalytic cycle.[45] Such a process involving consecutive oxidations and reductions of iron shares features with that proposed for the iron and copper chloride[11] catalyzed as well as the $Ru(PPh_3)_4Cl_2$[17]-catalyzed additions of CCl_4 to alkenes; the catalysis of this type of additions by redox systems has recently been reviewed.[10] It remains uncertain, however, whether intrinsically free radicals **21** or metal coordinated radicals, viz., σ complexes **22**, are involved in the catalytic process. In section D evidence will be presented for the intermediacy of σ complexes **22**, trapped as stable π complexes in the case of the addition of CCl_4 to alkyl-substituted conjugated dienes.

The proposed mechanism implying initial attack of a (possibly complexed) trichloromethyl radical to give radical **21** is consistent with the finding that in the case of the catalyzed additions of CCl_4 and $CBrCl_3$ to strained carbon–carbon double bonds, viz., to bicyclobutane-bridged enone **1** and diene **2** (and also norbornadiene), no α,α,α,γ-tetrahalo derivatives are obtained, but instead rearranged products result. The same products are also produced in the free-radical addition of CCl_4 and $CBrCl_3$, indicative of the occurrence in both processes of bicyclobutylcarbinyl radical **19** (possibly complexed to iron in the catalyzed reaction).

Especially high yields of CCl_4 adducts were obtained in the cases of the strained ring systems of norbornadiene and bicyclobutane bridged compounds **1** and **2**. A reasonable explanation is that, for instance, in the case of compounds **1** and **2**, rearrangement of the initially generated radicals **19** to give radicals **20a** and **20b** is energetically favorable due to relief of ring strain, which may contribute to a fast and efficient addition.[22] Independent of the addition reaction, irreversible decomposition of the iron carbonyl catalyst or other iron carbonyl intermediates ultimately into $FeCl_2$ occurs; so, when the addition reaction is not efficient, lower yields of addition products are obtained as is the case with simple and especially more sterically hindered alkenes (see Table I).

The mechanism which accounts for the addition of $CXCl_3$ to compounds **5**, **6**, and **12**, promoted by iron carbonyls, is shown in Scheme V. This reaction involves (possibly complexed) allyl radicals **23**, which display a homallylic rearrangement[46] to give radicals **24** (probably in equilibrium with σ complexes **25**).[47] In the case of X = Cl, compound **7** is obtained by Cl abstraction from FeL_mCl. In a competitive reaction compound **8** is formed either from **24** (X = Cl) by direct β-H elimination or from **25** via (π-alkene)iron hydrochloride complex **26**.[48] The latter step implies loss of HCl, which was shown to be evolved during the reaction. There are indications in the literature that in β-H elimination,[49] a well-known reaction of σ-bonded alkyliron complexes,[50] radicals can be involved.[51] The formation of **8** from **7** by iron carbonyl promoted dehydrochlorination was excluded because

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[42] T. A. Manuel, S. L. Stafford, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 249 (1961); R. B. King, S. L. Stafford, P. M. Treichel, and F. G. A. Stone, *ibid.*, **83**, 3604 (1961); E. Pitcher and F. G. A. Stone, *Spectrochim. Acta*, 18, 585 (1962).

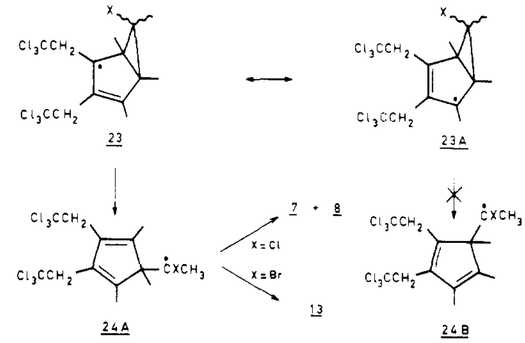
[43] F. A. Cotton and J. A. McCleverty, *J. Organomet. Chem.*, 4, 490 (1965); M. R. Churchill, *Inorg. Chem.*, 6, 185 (1967).

[44] W. A. Nugent and J. K. Kochi, *J. Organomet. Chem.*, 124, 371 (1977).

[45] It cannot be derived unambiguously from the present results whether the trimethylamino group is maintained at iron during the $Me_3NFe(CO)_4$-catalyzed process. However, both the observed reaction of $CBrCl_3$ with $Me_3NFe(CO)_4$ as shown by IR spectroscopy and certain differences observed between the $Fe_2(CO)_9$- and $Me_3NFe(CO)_4$-catalyzed additions of CCl_4 (Table I, entries 4, 5, and 9–11) indicate that the trimethylamino moiety plays an important role and possibly remains at iron during the overall process.

[46] R. Sustmann and F. Lübbe, *Chem. Ber.*, **112**, 42 (1979); P. K. Freeman, F. A. Raymond, J. C. Sutton, and W. R. Kindley, *J. Org. Chem.*, 33, 1448 (1968).

[47] A referee has pointed out that it is difficult to explain why ring opening from localized allyl radical **23** to **24A** is strongly preferred over ring opening from the alternative localized radical **23A** to **24B** unless it is assumed that **23** does not occur intrinsically free but is rather complexed to iron. It should be noted, however, that the presence of small amounts of products derived from **24B** in the reaction mixture obtained cannot be excluded.



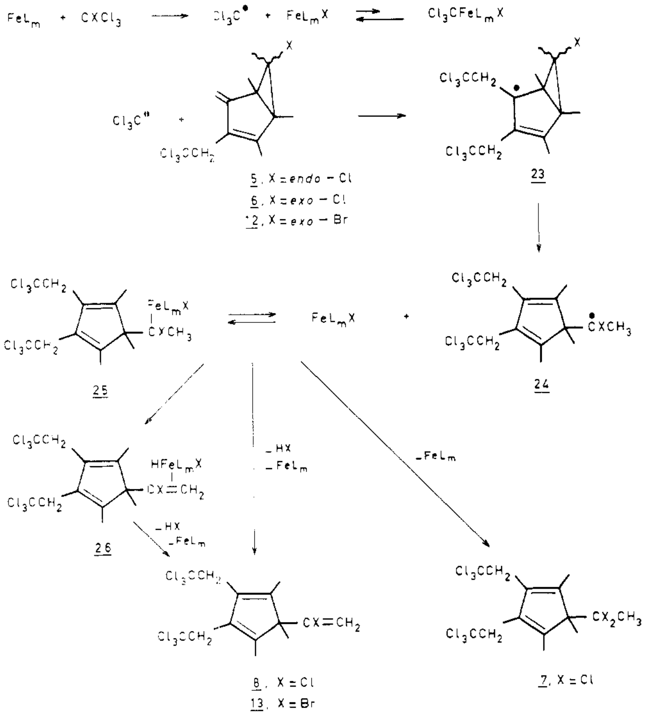
[48] Similar hydrochloride complexes of palladium are proposed as intermediates in the Pd-catalyzed vinylation of conjugated dienes. B. A. Patel, L. C. Kao, N. A. Cortese, J. V. Minkiewicz, and R. F. Heck, *J. Org. Chem.*, **44**, 918 (1979).

[49] P. J. Davidson, M. F. Lappert, and R. Pearce, *Chem. Rev.*, **76**, 219 (1976).

[50] D. L. Reger and E. C. Culbertson, *J. Am. Chem. Soc.*, **98**, 2789 (1976).

[51] S. M. Florio and K. M. Nicholas, *J. Organomet. Chem.*, **144**, 321 (1978).

Scheme V



compounds 7 and 8 proved to be stable under the reaction conditions toward $Me_3NFe(CO)_4$ and $Fe_2(CO)_9$ in CCl_4 solution. In the case of X = Br only the dehydrobromination pathway seems to be followed since only compound **13** could be isolated.

(D) Mechanism of the Additions to Alkyl-Substituted Conjugated Dienes. The mechanism of the $Fe_2(CO)_9$-promoted additions of CCl_4 to certain alkyl-substituted conjugated dienes (Table III) is assumed to occur according to Scheme VI. The (possibly complexed) trichloromethyl radical adds to a double bond of the diene system to afford (possibly complexed) allyl radical **27**. Because CCl_4 adducts **31** and/or **32** were not isolated as products in this reaction,[52] **27** does not abstract a chlorine atom from $Fe^I(CO)_4Cl$ but, in this particular case, forms the π-allyl complex **28**. Complex **28** readily loses HCl under the present reaction conditions to yield ultimately **14** or **15**, respectively, possibly via complex **30**[48] involving β-hydride elimination.[49-51] The driving force for the process will be provided by the formation of a stable diene iron tricarbonyl complex which, of course, is not possible in the case of the addition of CCl_4 to simple alkenes (Table I), while in the case of the addition of CCl_4 to diene **2**, rearrangement of the initially generated allyl radical **19** (Scheme II) is the more favorable process. Attempts to observe complex **28** by monitoring the reaction with IR spectroscopy were unsuccessful under the present conditions; it might have been, however, that the IR absorptions of **28**, expected [23] to be observed at about 2090, 2040, and 2000 cm^{-1}, were hidden by the overwhelmingly intense signals of $Fe(CO)_5$. Although (π-allyl)iron tricarbonyl chloride complexes are often quite stable compounds,[54] some methyl substituted (π-allyl)iron tricarbonyl chloride complexes (analogous to **28**) were found to decompose into the corresponding diene iron tricarbonyl complexes within hours.[55,56]

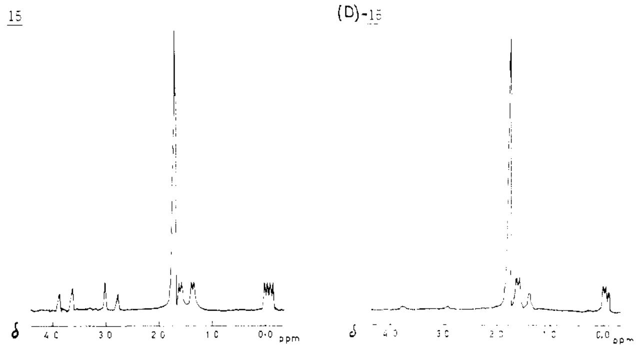


Figure 2. ^1H NMR spectra of complexes **15** and (D)-**15** (C_6D_6 solution).

It can be concluded that in the β-hydride elimination step, viz., **29** → **30**, a hydrogen atom is more easily removed from the methyl group than from the CH_2CCl_3 moiety since only complex **14** or **15**, respectively, was obtained, no formation of **33** being observed. Similar behavior is displayed in the addition to 1,3-cyclohexadiene, since only the 5-trichloromethyl derivative **16**, and not its 1-trichloromethyl isomer, was formed. It is of interest to note that the addition to 1,3-cyclohexadiene occurs in a stereospecific fashion because only one geometric isomer of **16** was obtained; the mutual orientation of the trichloromethyl and iron tricarbonyl moieties (being either syn or anti) could not be elucidated from the spectroscopic data, however.

According to the mechanism of the addition reaction, as shown in Scheme VI, one of the methylene units of 2-methylbutadiene or of 2,3-dimethylbutadiene is transformed into a CH_2CCl_3 group and a methyl group into a new olefinic methylene unit in **14** and **15**, respectively. To verify this assumption, it was decided to perform the $Fe_2(CO)_9$-promoted addition of CCl_4 with the labeled diene 2,3-dimethylbutadiene-*1,1,4,4*-d_4, which was prepared by the sequence of reactions shown in Scheme VII. The deuteration of the methylene groups of **34** was accomplished[56,57] by treatment with a large excess of CF_3CO_2D to afford deuterated **34** [(D)-**34**] in 75% yield, the methylene groups containing 90 ± 3% D (70 ± 3% tetra-

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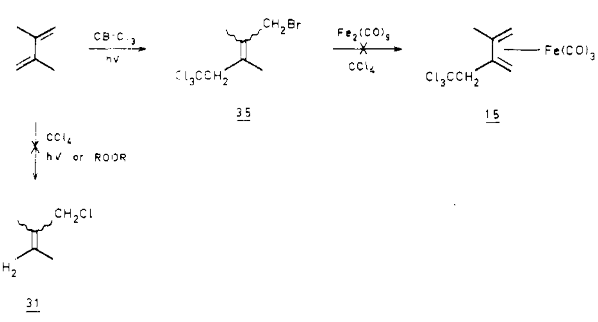
(52) An alternative explanation for the $Fe_2(CO)_9$-promoted addition of CCl_4 to, e.g., 2,3-dimethylbutadiene would be the initial $Fe_2(CO)_9$-catalyzed formation of the CCl_4 adduct **31** and/or **32** followed by a reaction with excess $Fe_2(CO)_9$ to yield the diene iron tricarbonyl complex **15**. This possibility was ruled out, however, because **35** prepared from 2,3-dimethylbutadiene and $CBrCl_3$[53] (attempts to prepare the corresponding chlorine derivative **31** by performing a free-radical addition of CCl_4 to 2,3-dimethylbutadiene gave rise to formation of unidentified products, no monoadducts being isolated) did not furnish **15** upon treatment with $Fe_2(CO)_9$ in CCl_4 but was recovered unchanged.



(53) C. S. Hsia Chen and E. F. Hosterman, *J. Org. Chem.*, **28**, 1585 (1963).

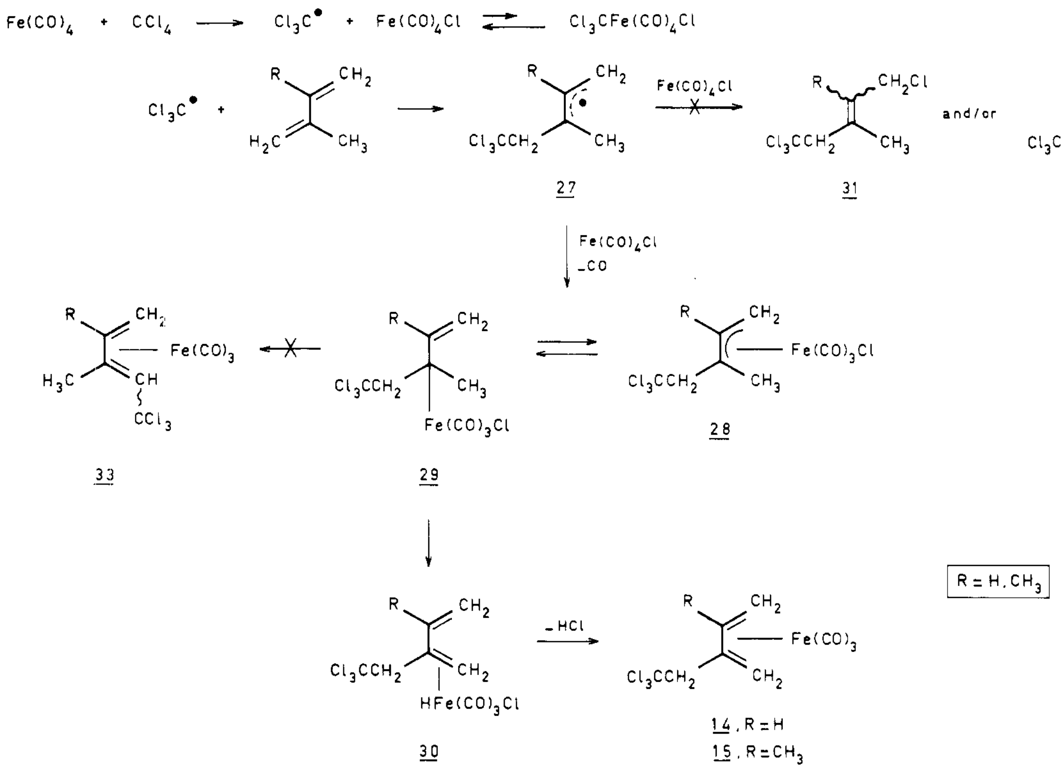
(54) A. N. Nesmeyanov and I. I. Kritskaya, *J. Organomet. Chem.*, **14**, 387 (1968).

(55) F. J. Impastato and K. G. Ihrman, *J. Am. Chem. Soc.*, **83**, 3726 (1961).

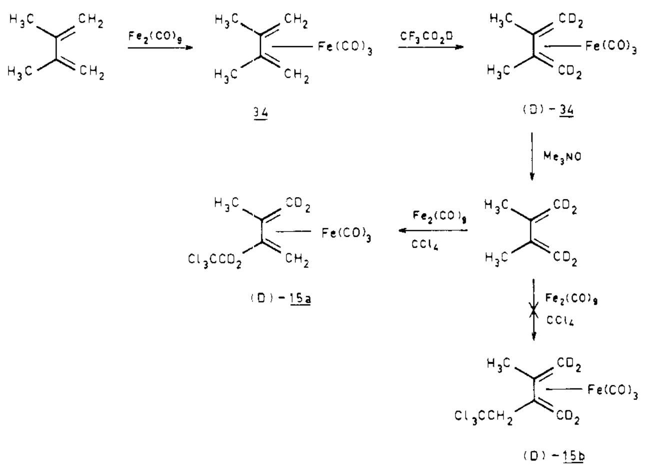
(56) T. H. Whitesides and R. W. Arhart, *J. Am. Chem. Soc.*, **93**, 5296 (1971).

(57) A. J. Birch and I. D. Jenkins in "Transition Metal Organometallics in Organic Synthesis", Vol. I, H. Alper, Ed., Academic Press, New York, 1976, p 46.

Scheme VI

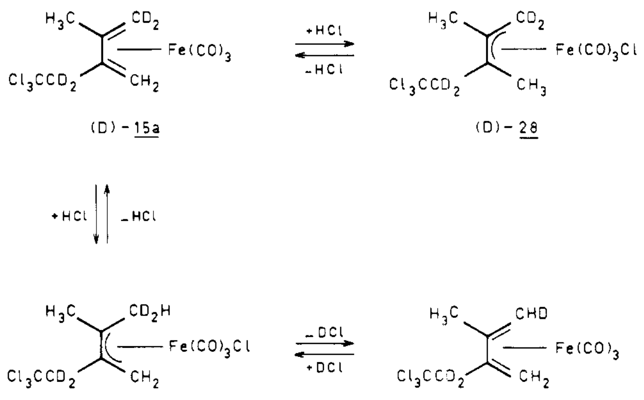


Scheme VII



deuterated and 30 ± 3% trideuterated). Decomplexation[58] of (D)-**34** afforded the corresponding diene which upon treatment with $Fe_2(CO)_9$ in CCl_4 provided after chromatography deuterated **15** [(D)-**15**] in 15% yield which was 60 ± 3% tetradeuterated and 30 ± 3% trideuterated. A comparison of the ^1H NMR spectra of (D)-**15** and its undeuterated counterpart, depicted in Figure 2, shows that in (D)-**15** the AB absorptions at δ 3.75 and 2.90 due to the CH_2CCl_3 group[59] are present to an extent of 10 ± 3% and the doublets at δ 1.38 and −0.14 due to one syn and one anti olefinic hydrogen atom to an extent of 20 ± 3%; the doublets at δ 1.60 and −0.03 due to the remaining syn and anti olefinic hydrogen atoms as well as the methyl singlet at δ 1.75 are present in (D)-**15** with an intensity equal to that in undeuterated **15**. These results prove unambiguously that the complex has structure (D)-**15a** and reject the alternative structure (D)-**15b**. It should be noted that

Scheme VIII



the slight difference (10 ± 3%) in deuterium contents of the deuterated olefinic methylene group and the CD_2CCl_3 group of (D)-**15a** is explained by the reversibility of the dehydrochlorination step, thus causing besides loss of HCl also loss of some DCl (Scheme VIII). Besides the ^1H NMR data, the ^{13}C NMR data (see Experimental Section) are also consistent with structure (D)-**15a** and not with (D)-**15b**. The formation of (D)-**15a** is in agreement with the mechanism as depicted in Scheme VII.

Conclusions

It has been demonstrated that iron carbonyls are capable of catalyzing the additions of CCl_4 and $CBrCl_3$ to carbon–carbon double bonds at ambient temperature. The initial step of the addition is considered to be a reaction between perhalomethane and iron carbonyl with the generation of (possibly complexed) trichloromethyl radicals. The catalytic process is explained in terms of a redox chain mechanism, in which iron passes through the oxidation states II, I, and 0. It is without doubt that organic radicals occurring either as free radicals or as metal-coordinated species are intermediates in the addition reactions. By analogy, the results presented here suggest an analogous reaction mechanism be applied[60] for the addition of po-

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[58] Y. Shvo and E. Hazum, *J. Chem. Soc., Chem. Commun.*, 336 (1974).

[59] The CH_2CCl_3 hydrogen atoms are diasterotopic due to the asymmetry of the complex caused by the $Fe(CO)_3$ moiety.

lyhalomethanes to alkenes catalyzed by similar transition-metal complexes, e.g., (naphthalene)chromium tricarbonyl[15] at room temperature and $(CpFe(CO)_2)_2$[13] and $Fe(CO)_5$[16] at high temperature. Furthermore, the results discussed in this publication support the idea[10,61,62] that radicals, either free or coordinated to the metal, play an important role in certain processes of organometallic chemistry, e.g., oxidative additions.

Experimental Section

General Methods. CCl_4, $CBrCl_3$, and the alkenes were purified by distillation; $Fe(CO)_5$, 1,3-cyclohexadiene and tetramethylethylene were commercially available and used without further purification; enone **1**,[63] diene **2**,[64] the iron carbonyl complexes **17**[31] and **18**,[33] and $Fe_2(CO)_9$[65] were prepared according to published methods. Elemental analyses were performed in the Microanalytical Department of this laboratory by Mr. H. Draayer, Mr. J. Ebels, Mr. J. E. Vos, and Mr. A. F. Hamminga. Melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 237 spectrophotometer and calibrated with polystyrene. Mass spectra were measured on an AEI MS-902 apparatus by Mr. A. Kiewiet. ^1H NMR spectra were determined with a Hitachi Perkin-Elmer R24B using Me_4Si as internal standard. ^{13}C NMR spectra were recorded with a Varian XL-100 spectrometer operating at 25.2 MHz. Analytical and preparative-scale separations by means of high-pressure liquid chromatography were carried out with a Waters high-pressure LC apparatus, ALC/GPC, equipped with a differential refractometer and a Schoeffel Spectraflow SF 770 monitor. Irradiations were performed with a Hanau Q-81 high-pressure mercury arc, if not otherwise indicated. All manipulations involving the use of iron carbonyls, e.g., the catalyzed additions of CCl_4 and $CBrCl_3$, were conducted in a dry nitrogen atmosphere.

Dehydration of Trimethylamine Oxide Dihydrate. A 7.0-g (63 mmol) sample of $Me_3NO{\cdot}2H_2O$ was dehydrated in a drying pistol (Alderhelden vacuum drying apparatus supplied with an oven) containing P_2O_5 as the drying agent by heating the apparatus in vacuo (~30 mmHg pressure) to 80–90 °C, where melting of $Me_3NO{\cdot}2H_2O$ occurred. Slow dehydration took place at this temperature, and after several hours Me_3NO (mp 208 °C) crystallized. The temperature was subsequently elevated to 160 °C, where Me_3NO sublimed as white needles in the cold part of the drying pistol (yield 4.0 g, 90%). Me_3NO, being highly hygroscopic, was kept in a desiccator in vacuo over P_2O_5 as a drying agent.

Synthesis of (Trimethylamino)iron Tetracarbonyl ($Me_3NFe(CO)_4$). A solution of 3.9 g (20 mmol) of $Fe(CO)_5$ in 25 mL of tetrahydrofuran was added dropwise to a mechanically stirred suspension of 3.0 g (40 mmol) of Me_3NO (dried as described above) in 50 mL of tetrahydrofuran, while the temperature of the reaction mixture was maintained below -30 °C. Upon the addition of the $Fe(CO)_5$ solution the reaction mixture instantaneously turned red and CO_2 evolved which was identified as $BaCO_3$. Stirring was continued for another 2 h while the temperature was allowed to rise to room temperature. Evaporation of the solvent yielded a red-brown residue, which was extracted with pentane; the pentane solution was washed with water and dried over Na_2SO_4. Removal of the solvent gave 2.0 g (9.0 mmol, 45% yield) of $Me_3NFe(CO)_4$, obtained as an orange-red solid which was unstable at room temperature in the crystalline state but moderately stable when stored in a frozen benzene solution at -20 °C.

A sample of solid $Me_3NFe(CO)_4$ was heated to 50 °C; rapid decomposition occurred with the evolution of Me_3N (identified by its characteristic odor) leaving a brown residue of inorganic material.

The synthesis of $Me_3NFe(CO)_4$ was also carried out by using $Me_3NO{\cdot}2H_2O$ instead of anhydrous Me_3NO; only a 10% yield of $Me_3NFe(CO)_4$ was obtained: mass spectrum for $C_7H_9FeNO_4$, calcd *m/e* 226.988 (M^+), found *m/e* 226.991, 199, 171, 143, 115 (successive loss of four CO groups); IR (CCl_4) 2050, 1960, 1940–1920 (CO) cm^{-1}; ^1H NMR (C_6D_6, 35 °C) δ 1.87 (s); ^{13}C NMR (C_6D_6, 10 °C) δ 217.5, 61.4 (q, J_{CH} = 137 Hz).

Addition of CCl_4 to Alkenes Catalyzed by $Me_3NFe(CO)_4$. General Procedure. A solution of 2.0 mmol of the appropriate substrate in 10 mL of CCl_4 was added to 45 mg (0.2 mmol) of $Me_3NFe(CO)_4$. The initially clear red solution slowly turned brown, while insoluble material deposited on the wall of the flask. The reaction mixture was stirred overnight (in some cases 3 h, see Table I), after which complete decomposition of $Me_3NFe(CO)_4$ had occurred as indicated by the IR spectrum. The amounts of alkene consumed and adduct formed were determined by ^1H NMR spectroscopic measurement of the reaction mixture with an appropriate amount of benzene as standard. (Results, see Table I).

The excess of alkene and CCl_4 were removed in vacuo, and the residue was extracted with pentane. Further purification of the product was performed by passing the pentane layer over a short silica gel column which afforded the adducts as colorless oils, being greater than 90% pure according to the ^1H NMR spectrum.

Characterization in the cases of the known adducts (entries 1–3, Table I) was carried out by comparison of their ^1H NMR and mass spectral data with those reported in ref 15, in the case of the CCl_4 adducts of norbornadiene (entry 6) by comparison with an authentic sample prepared according to ref 35, and in the case of adducts **3–6** (entries 7, 8) by comparison with authentic samples prepared according to ref 22; for the new products see below.

Addition of CCl_4 to Alkenes Catalyzed by $Fe_2(CO)_9$. General Procedure. To a solution of 2.0 mmol of the appropriate substrate in 10 mL of CCl_4 was added 73 mg (0.2 mmol) of $Fe_2(CO)_9$ with stirring. Slowly $Fe_2(CO)_9$ dissolved, initially turning the solution orange and later on brown, while insoluble material deposited on the wall of the flask. Stirring was continued overnight, after which the reaction mixture was filtered. The amounts of alkene consumed and adduct formed were determined as described above; the workup procedure was the same as that described above for the addition of CCl_4 catalyzed by $Me_3NFe(CO)_4$.

Synthesis of 1,1,1,3-Tetrachloro-2,2,3-trimethylbutane ($C_7H_{12}Cl_4$) and of 4,4,4-Trichloro-2,3,3-trimethyl-1-butene ($C_7H_{11}Cl_3$). A solution of 2.0 g (23 mmol) of tetramethylethylene in 50 mL of CCl_4 was added to 2.27 g (10 mmol) of $Me_3NFe(CO)_4$. After being stirred overnight at room temperature, the dark brown reaction mixture was filtered and evaporated. The residue was extracted with pentane, leaving, after removal of pentane in vacuo, 3.2 g of a green oil which contained $C_7H_{12}Cl_4$ and $C_7H_{11}Cl_3$ (ratio of 5:1, according to the NMR spectrum) in an overall yield of 90% (based on the intake of $Me_3NFe(CO)_4$). The mixture was chromatographed (5-cm silica gel column, eluent pentane) to remove the green contamination (probably $Fe_3(CO)_{12}$), providing 2.5 g of a slightly greenish half-crystalline residue containing $C_7H_{12}Cl_4$ and $C_7H_{11}Cl_3$ in a ratio of 3:1, respectively; if a larger column was used the ratio changed in favor of the latter compound due to dehydrochlorination. Crystallization from methanol at -40 °C afforded about 1.0 g of $C_7H_{12}Cl_4$ (90% pure, yield 40%, based on the intake of $Me_3NFe(CO)_4$). Repeated crystallization from methanol at 0 °C and room temperature furnished an analytically

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(60) In agreement with this suggestion is the fact that $(CpFe(CO)_2)_2$ was found to catalyze the addition of CCl_4 to enone **1** at ambient temperature to furnish a mixture of **3** and **4**.

(61) Some recent reviews emphasizing the role of radicals in organometallic chemistry: ref 10; M. F. Lappert and P. W. Lednor, *Adv. Organomet. Chem.*, 14, 345 (1976); J. Halpern, *Pure Appl. Chem.*, **51**, 217 (1979).

(62) T. Y. Luh, C. H. Lai, K. L. Lei, and S. W. Tam, *J. Org. Chem.*, **44**, 641 (1979); M. D. Johnson, *Acc. Chem. Res.*, **11**, 57 (1978); J. San Filippo, J. Silbermann, and P. J. Fagan, *J. Am. Chem. Soc.*, **100**, 4834 (1978); H. Felkin, P. J. Knowles, and B. Meunier, *J. Organomet. Chem.*, **146**, 151, 169 (1978); K. J. Klabunde and J. S. Roberts, *ibid.*, **137**, 113 (1977); H. B. Abrahamson and M. S. Wrighton, *J. Am. Chem. Soc.*, **99**, 5510 (1977); A. N. Nesmeyanov, N. A. Volkenau, and V. A. Petrokova, *J. Organomet. Chem.*, **136**, 363 (1977); H. C. Clark and C. S. Wong, *J. Am. Chem. Soc.*, **99**, 7073 (1977); G. A. Russell and D. W. Lamson, *J. Organomet. Chem.*, **156**, 17 (1978); W. L. Waltz, O. Hackelberg, L. M. Dorfman, and A. Wojcicki, *J. Am. Chem. Soc.*, **100**, 7259 (1978); R. J. Kinney, W. D. Jones, and R. G. Bergman, *ibid.*, **100**, 7902 (1978); J. D. Cotton, *J. Organomet. Chem.*, **159**, 465 (1978); N. G. Connally, M. D. Kitchen, R. F. D. Stansfield, S. M. Whiting, and P. Woodward, *J. Organomet. Chem.*, **155**, C34 (1978); M. J. S. Gynane, M. F. Lappert, S. J. Miles, and P. P. Power, *J. Chem. Soc., Chem. Commun.*, 192 (1978).

(63) R. F. Heldeweg, H. Hogeveen, and E. P. Schudde, *J. Org. Chem.*, **43**, 1912 (1978).

(64) H. Hogeveen and P. W. Kwant, *J. Org. Chem.*, **39**, 2624 (1974).

(65) E. Speyer and H. Wolf, *Chem. Ber.*, **60**, 1424 (1927).

pure sample of $C_7H_{12}Cl_4$ as white crystals, mp 101–103 °C; the product proved to be highly volatile in vacuo (~10 mmHg pressure).

Spectroscopic data of 1,1,1,3-tetrachloro-2,2,3-trimethylbutane ($C_7H_{12}Cl_4$): mass spectrum for $C_7H_{12}{}^{35}Cl_4$, *m/e* 201 ($M^+ - {}^{35}Cl$); ^1H NMR (CCl_4) δ 1.94 (s, 6 H), 1.62 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 108.4, 77.4, 58.9, 32.3 (q, J_{CH} = 125 Hz), 24.3 (q, J_{CH} = 125 Hz).

Anal. Calcd for $C_7H_{12}Cl_4$: C, 35.33; H, 5.08; Cl, 59.59. Found: C, 35.77; H, 5.15; Cl, 59.23.

A pentane solution of $C_7H_{12}Cl_4$ was passed over a neutral alumina column (20 cm), and complete dehydrochlorination occurred to afford $C_7H_{11}Cl_3$ as a colorless oil in 70% yield.

Spectroscopic data of 4,4,4-trichloro-2,3,3-trimethylbutene ($C_7H_{11}Cl_3$): mass spectrum[66] for $C_7H_{11}{}^{35}Cl_3$, *m/e* 200 (M^+); IR (CCl_4) 1625 (C=C) cm^{-1}; ^1H NMR (CCl_4) δ 5.22 (m, 2 H), 2.02 (br s, 3 H), 1.53 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 145.0, 119.4, (t, J_{CH} = 160 Hz), 109.6, 57.3, 25.3 (q, J_{CH} = 125 Hz), 23.0 (q, J_{CH} = 125 Hz).

Synthesis of 5-(1,1-Dichloroethyl)-2,3-bis(2,2,2-trichloroethyl)-1,4,5-trimethyl-1,3-cyclopentadiene (7). A solution of 160 mg (1.0 mmol) of diene **2** in 20 mL of CCl_4 was added to 272 mg (1.2 mmol) of $Me_3NFe(CO)_4$; stirring was conducted overnight at room temperature. The evolution of an acidic gas (HCl) during the reaction was shown with universal indicator paper (pH 2). The reaction mixture was filtered and evaporated to dryness; subsequently the black residue was extracted with pentane, leaving, after evaporation of the pentane, 480 mg of a slightly yellow oil that consisted of **7** and **8** in a ratio of 65:35 (overall yield 70%) as determined by NMR spectroscopic integration with benzene as standard. Attempts to separate the mixture of **7** and **8** by preparative TLC were in vain; 15 mg of compound **7** could be obtained by applying analytical high-pressure LC (isooctane, silica gel) as a white solid: mp 115–120 °C; mass spectrum for $C_{14}H_{16}{}^{35}Cl_8$, calcd *m/e* 463.876 (M^+), found *m/e* 463.872; ^1H NMR (CCl_4) δ 3.95 (AB system, *J* = 15 Hz, 4 H), 2.18 (s, 6 H), 1.91 (s, 3 H), 1.52 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 149.4, 134.4, 100.2, 94.0, 60.7, 50.4 (t, J_{CH} = 130 Hz), 33.7 (q, J_{CH} = 130 Hz), 18.7 (q, J_{CH} = 125 Hz), 16.5 (q, J_{CH} = 125 Hz). Although compound **8** could also be obtained by separating a mixture of **7** and **8** using high-pressure LC, larger scale preparations were performed as described below.

Synthesis of 5-(1-Chlorovinyl)-2,3-bis(2,2,2-trichloroethyl)-1,4,5-trimethyl-1,3-cyclopentadiene (8). To a benzene solution of 450 mg of a mixture of **7** and **8** (containing 0.55 mmol of **7** and 0.30 mmol of **8**, obtained as described above) was added 207 mg (1.0 mmol) of silver perchlorate. The solution, which rapidly turned black, was stirred overnight. Evaporation of solvent and extraction of the black residue with pentane afforded, after evaporation of the pentane, 400 mg of a slightly yellow oil, which contained 0.79 mmol of **8** (yield 80%, determined by NMR spectroscopic integration with benzene as standard). Further purification was achieved by chromatography (silica gel, eluent pentane) to afford 300 mg (0.70 mmol) of **8** as a white crystalline solid. Repeated crystallization from methanol afforded an analytical pure sample of **8** as white crystals: mp 69–70 °C; mass spectrum for $C_{14}H_{15}{}^{35}Cl_7$, *m/e* 428 (M^+); IR (CCl_4) 1620 ($CCl{=}CH_2$) cm^{-1}; ^1H NMR (C_6D_6) δ 5.20 (d, *J* = 2 Hz, 1 H), 4.95 (d, *J* = 2 Hz, 1 H), 3.80 (s, 4 H), 1.70 (s, 6 H), 0.90 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 149.3, 142.9, 132.6, 114.0 (dd, J_{CH} = 158, 160 Hz), 100.5, 64.2, 50.7 (t, J_{CH} = 132 Hz), 19.4 (q, J_{CH} = 125 Hz), 12.6 (q, J_{CH} = 125 Hz).

Anal. Calcd for $C_{14}H_{15}Cl_7$: C, 38.97; H, 3.51; Cl, 57.52. Found: C, 38.87; H, 3.53; Cl, 57.26.

Catalyzed Additions of $CBrCl_3$. General Procedure. (A) Catalyzed by $Me_3NFe(CO)_4$ and $Fe_2(CO)_9$. These reactions were performed analogously to the $Fe_2(CO)_9$- and $Me_3NFe(CO)_4$-catalyzed additions of CCl_4 by using $CBrCl_3$ instead of CCl_4. The results are listed in Table II.

(B) Catalyzed by $Fe(CO)_5$. To a solution of 2.0 mmol of the appropriate substrate in 10 mL of $CBrCl_3$ in a Pyrex vessel was added 40 mg (0.2 mmol) of $Fe(CO)_5$. The initially orange solution slowly turned brown, while insoluble material deposited on the wall of the flask. The reaction mixture was stirred for 3 h. The yield of adduct was determined by NMR spectroscopic integration with benzene as standard (see Results and Table II). $CBrCl_3$ was removed in vacuo, leaving a residue which was extracted with pentane, affording, after evaporation of the pentane, the adducts as colorless or slightly yellow oils. Characterization of compounds **9–12** was accomplished by comparison with authentic samples.[22]

Synthesis of 5-(1-Bromovinyl)-2,3-bis(2,2,2-trichloroethyl)-1,4,5-trimethyl-1,3-cyclopentadiene (13). Method I. To a solution of 240 mg (1.5 mmol) of diene **2** in 10 mL of $CBrCl_3$ was added 330 mg (1.7 mmol) of $Fe(CO)_5$. After the mixture was stirred overnight, $CBrCl_3$ was removed in vacuo, leaving a black residue, which was extracted with pentane, affording, after evaporation of the pentane, 680 mg of a yellow viscous oil (containing **11** and **13** in a ratio of 4:1, overall yield 60% as determined by NMR spectroscopic integration with benzene as standard). Column chromatography (silica gel, eluent pentane) afforded 70 mg (0.15 mmol) of **13** as a colorless oil (10% yield). Attempts to crystallize **13** were unsuccessful: mass spectrum[66] for $C_{14}H_{15}{}^{79}Br^{35}Cl_6$, *m/e* 472 ($M^+$); IR ($CCl_4$) 1620 ($CBr{=}CH_2$) cm^{-1}; ^1H NMR (CCl_4) δ 5.78 (d, *J* = 2 Hz, 1 H), 5.63 (d, *J* = 2 Hz, 1 H), 3.89 (s, 4 H), 1.91 (s, 6 H), 1.22 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 149.7, 134.3, 132.6, 118.8 (dd, J_{CH} = 158, 160 Hz), 100.4, 65.1, 50.7 (t, J_{CH} = 130 Hz), 19.4 (q, J_{CH} = 125 Hz), 12.6 (q, J_{CH} = 125 Hz).

Method II. To 20 mg (0.06 mmol) of **12** in 10 mL of $CBrCl_3$ solution was added 14 mg (0.07 mmol) of $Fe(CO)_5$. Stirring was conducted overnight, after which $CBrCl_3$ was removed in vacuo, leaving a residue which was extracted with pentane. The pentane layer was evaporated, affording 20 mg of **13** as a colorless oil (yield 70%).

Synthesis of (5,5,5-Trichloro-2-methyl-3-methylene-1-pentene)iron Tricarbonyl (15). Method I. With $Fe_2(CO)_9$. To a solution of 250 mg (3.3 mmol) of 2,3-dimethylbutadiene in 40 mL of CCl_4 was added 1.28 g (3.2 mmol) of $Fe_2(CO)_9$. The reaction mixture was vigorously stirred overnight. During the reaction, the evolution of an acidic gas (HCl) was shown with universal indicator paper (pH 2). The solvent was removed in vacuo, and the residue was extracted with pentane which after evaporation gave 350 mg of a slightly yellow oil that contained, according to the ^1H NMR spectrum, besides **15**, unidentified products (probably telomeric or polymeric material, because the ^1H NMR spectrum of these side products showed no well-resolved absorptions). Further purification was accomplished by repeated preparative TLC (alumina, eluent pentane), affording 150 mg (yield 15%) of **15** as a yellow oil: mass spectrum for $C_{10}H_9{}^{35}Cl_3FeO_3$, calcd *m/e* 337.897, found *m/e* 337.894 (M^+), 310 (M^+ – CO), 282 (M^+ – 2 CO), 275 ($M^+ - CO - {}^{35}Cl$), 264 (M^+ – 3 CO); IR (CCl_4) 2060, 1990, 1970 (CO) cm^{-1}; ^1H NMR (C_6D_6) δ 3.75/2.90 (AB system, *J* = 14 Hz, 2 H), 1.75 (s, 3 H), 1.60 (d, *J* = 3.3 Hz, 1 H), 1.38 (d, *J* = 2.3 Hz, 1 H), –0.03 (d, *J* = 3.3 Hz, 1 H), –0.14 (d, *J* = 2.3 Hz, 1 H); ^{13}C NMR (C_6D_6) δ 211.1, 103.8, 99.2, 95.0, 58.4 (t, J_{CH} = 135 Hz), 44.3 (t, J_{CH} = 160 Hz), 43.6 (t, J_{CH} = 160 Hz), 21.0 (q, J_{CH} = 130 Hz).

Method II. With $Me_3NFe(CO)_4$. A solution of 840 mg (10 mmol) of 2,3-dimethylbutadiene in 25 mL of CCl_4 was added to 230 mg (1 mmol) of $Me_3NFe(CO)_4$. The solution was stirred overnight and the solvent removed in vacuo. The residue was extracted with pentane, leaving, after evaporation 190 mg of an oily residue, which contained, besides **15**, other products which could not be isolated due to their instability. Preparative TLC afforded 15 mg of complex **15** (yield 5%).

Method III. Irradiation in the Presence of $Fe(CO)_5$. A solution of 150 mg (1.8 mmol) of 2,3-dimethylbutadiene and 350 mg (1.8 mmol) of $Fe(CO)_5$ in 30 mL of CCl_4 was irradiated in a Pyrex vessel for 3 h. After the workup as described above, 130 mg of a yellow oil was obtained that contained compound **15** together with unidentified products (probably telomeric or polymeric material). Preparative TLC afforded 65 mg of compound **15** (yield 10%) as a yellow oil.

Synthesis of (5,5,5-Trichloro-3-methylene-1-pentene)iron Tricarbonyl (14). Compound **14**, prepared analogously to compound **15** (method I) by starting from 10 mmol of 2-methylbutadiene, was obtained as a yellow oil: yield 15%; mass spectrum for $C_9H_7{}^{35}Cl_3FeO_3$, calcd *m/e* 323.881, found *m/e* 323.881 (M^+), 296 (M^+ – CO), 268 (M^+ – 2 CO), 261 ($M^+ - CO - {}^{35}Cl$), 240 (M^+ – 3 CO); IR (CCl_4) 2060, 1985, 1975 (CO) cm^{-1}; ^1H NMR (C_6D_6) δ 4.95 (m, 1 H), 3.25/3.05 (AB system, *J* = 14 Hz, 2 H),

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[66] The intensity of the parent peak was too low to allow an exact mass determination.

1.65 (dd, J = 1.5, 3.0 Hz, 1 H), 1.42 (dd, J = 2.2, 7.0 Hz, 1 H), 0.13 (d, J = 3.0 Hz, 1 H), −0.15 (dd, J = 2.2, 9.0 Hz, 1 H); ^{13}C NMR (C_6D_6) δ 211.0, 98.4, 96.9, 89.2 (d, J_{CH} = 174 Hz), 61.9 (t, J_{CH} = 135 Hz), 45.1 (t, J_{CH} = 160 Hz), 39.5 (t, J_{CH} = 160 Hz).

Synthesis of [5-(Trichloromethyl)-1,3-cyclohexadiene]iron Tricarbonyl (16). Compound 16 prepared analogously to 15 (method I) by starting from 10 mmol of 1,3-cyclohexadiene was obtained as a yellow oil (yield 10%). Besides 16, (1,3-cyclohexadiene)iron tricarbonyl (yield 10%) was isolated by preparative TLC (alumina, eluent pentane); the latter complex was characterized by comparison with an authentic sample. Structural assignment of 16: mass spectrum[66] for $C_{10}H_7{}^{35}Cl_3FeO_3$, m/e 336 (M^+), 308 ($M^+ - CO$), 252 ($M^+ - 3\ CO$); IR (CCl_4) 2055, 1980–1960 (CO) cm^{-1}; ^{1}H NMR (C_6D_6) δ 4.9–4.5 (m, 2 H), 3.2–2.8 (m, 2 H), 2.5–2.3 (m, 1 H), 2.0–1.5 (m, 2 H); ^{13}C NMR (C_6D_6) δ 211.2, 103.7, 86.4 (d, J_{CH} = 170 Hz), 85.7 (d, J_{CH} = 170 Hz), 59.9 (d, J_{CH} = 140 Hz), 57.6 (d, J_{CH} = 160 Hz), 57.0 (d, J_{CH} = 160 Hz), 29.5 (t, J_{CH} = 130 Hz).

IR Measurements of the Reactions between Iron Carbonyls and Perhalomethanes. The IR spectra, discussed in the text, were recorded by using samples which were taken at appropriate intervals from the main solution and transferred into a 1-mm cell. The solutions were prepared as follows.

$Fe_2(CO)_9$ in $CBrCl_3$. A 50-mg (0.14 mmol) sample of $Fe_2(CO)_9$ was added to 5 mL of $CBrCl_3$ with vigorous stirring in a flask that was protected from light by wrapping it in black paper.

$Fe(CO)_5$ in $CBrCl_3$. A 10-mL sample of $CBrCl_3$ was added to 20 mg (0.10 mmol) of $Fe(CO)_5$. Protection of the solution from light had no effect on the IR measurements.

$Me_3NFe(CO)_4$ in $CBrCl_3$. A 10-mL sample of $CBrCl_3$ was added to 60 mg (0.26 mmol) of $Me_3NFe(CO)_4$. A vigorous reaction occurred (also when $CBrCl_3$ was added to $Me_3NFe(CO)_4$ in a flask wrapped with black paper) with the evolution of a gas which was shown to be CO. After the mixture was stirred overnight and the solvent evaporated, a residue was obtained which consisted mainly of $FeBr_2$ as shown by standard analytical techniques.

$Fe_2(CO)_9$ in CCl_4. A 50-mg (0.15 mmol) sample of $Fe_2(CO)_9$ was added to 6 mL of CCl_4 with vigorous stirring. After the mixture was stirred for 3 h and the solvent evaporated, a residue was left that consisted of $FeCl_2$ (as shown by standard analytical techniques) and C_2Cl_6 (identified by its melting point and mass spectrum).

$Me_3NFe(CO)_4$ in CCl_4. A 10-mL sample of CCl_4 was added to 35 mg (0.15 mmol) of $Me_3NFe(CO)_4$. After the mixture had been stirred overnight, the solvent was removed in vacuo, leaving a residue which was shown to contain $FeCl_2$ and C_2Cl_6.

Isolation of Dibromoiron Tetracarbonyl ($Fe(CO)_4Br_2$). A 20-mL sample of $CBrCl_3$ was added to 600 mg (3.1 mmol) of $Fe(CO)_5$ at room temperature. The solution rapidly turned orange and then brown, while insoluble material deposited on the wall of the flask. The reaction mixture was stirred for 2 h. After removal of the solvent in vacuo, the residue was extracted with pentane; the material which was insoluble in pentane was shown to consist mainly of $FeBr_2$. After evaporation of the pentane, 120 mg (0.8 mmol, yield 20%) of $Fe(CO)_4Br_2$ was obtained as an unstable orange solid. It was identified by comparing the CO absorptions in the IR spectrum at 2150, 2110, 2100, and 2075 cm^{-1} with those of an authentic sample prepared by the reaction between $Fe(CO)_5$ and Br_2.[24]

Attempts to Perform Free-Radical Additions of CCl_4 to 5 and 6. (1) A 20-mg (0.07 mmol) sample of a mixture of 5 and 6 (and in another experiment only 6) in CCl_4 solution was irradiated in an NMR tube for 2 h. No indications for the formation of diadducts 7 and/or 8 were obtained by ^{1}H NMR spectroscopy. Decomposition occurred upon longer irradiation. (2) A solution of 40 mg (0.14 mmol) of 6 and 10 mg (0.04 mmol) of dibenzoyl peroxide in 10 mL of CCl_4 was boiled for 16 h. No indications for the formation of diadducts 7 and/or 8 were obtained by ^{1}H NMR spectroscopy.

Attempt to Perform a Free-Radical Addition of $CBrCl_3$ to 12. A 20-mg (0.07 mmol) sample of 12 was irradiated in CCl_4 solution in a NMR tube for 2 h. No indications for the formation of 13 were obtained by ^{1}H NMR spectroscopy. Decomposition occurred upon longer irradiation.

Treatment of Enone Iron Tetracarbonyl Complex 18[33] with Perhalomethanes. (1) With $CBrCl_3$. A 5-mL sample of $CBrCl_3$ was added to 165 mg (0.5 mmol) of complex 18. IR spectra were recorded during the reaction. After the mixture was stirred overnight, the solvent was evaporated and the residue extracted with pentane to yield 165 mg of a slightly yellow oil, which was shown to contain only compounds 9 and 10 by ^{1}H NMR spectroscopy (ratio 78:22).

(2) With CCl_4. A 20-mL sample of CCl_4 was added to 165 mg (0.5 mmol) of complex 18. After the mixture was stirred overnight, the solvent was evaporated and the residue extracted with pentane. It was shown by ^{1}H NMR spectroscopy that a mixture of compound 18 and compounds 3 and 4 (ratio 85:15) was obtained.

Treatment of Diene Iron Tricarbonyl Complex 17[31] with Perhalomethanes. (1) With $CBrCl_3$. A 30-mg (0.1 mmol) sample of complex 17 was dissolved into 5 mL of $CBrCl_3$. After the mixture had been stirred for 2 h the solvent was evaporated. The residue was extracted with pentane to afford a yellow oil after evaporation of the pentane. It was shown by ^{1}H NMR and IR spectroscopy that complete decomposition of 17 had occurred to furnish a complicated reaction mixture which was shown by ^{1}H NMR spectroscopy to contain 11 and 13 and by IR spectroscopy to contain $Fe(CO)_4Br_2$.

(2) With CCl_4. Complex 17 was stable in CCl_4 solution for 2 days according to ^{1}H NMR and IR spectroscopy. Also in refluxing CCl_4 solution no decomposition of 17 had occurred after 6 h.

Iron Carbonyl Catalyzed Additions of CCl_4 to Diene 2 in the Presence of Hydroquinone (or *p*-Benzoquinone). To a solution of 100 mg (0.63 mmol) of diene 2, 66 mg (0.60 mmol) of hydroquinone, and 3 mL of tetrahydrofuran (necessary to dissolve the hydroquinone which is insoluble in CCl_4) in 10 mL of CCl_4 was added 22 mg (0.06 mmol) of $Fe_2(CO)_9$. A 2-mL portion was taken from the stirred reaction mixture after 1.5 h, and this portion was liberated from volatile material by evaporation. The residue was extracted with pentane, and removal of the pentane in vacuo left an oil which was shown by ^{1}H NMR spectroscopy to consist of 70 ± 10% of a mixture of 5 and 6 and 30 ± 10% of 2. After a reaction time of 3 h it was shown analogously that complete conversion of 2 into a mixture of 5 and 6 had occurred. The same result (70 ± 10% conversion of 2 into a mixture of 5 and 6 after 1.5-h reaction time and complete conversion after 3 h) was obtained in the blank experiment performed with omission of hydroquinone. The same result was also obtained when hydroquinone was replaced by *p*-benzoquinone.

The $Me_3NFe(CO)_4$-catalyzed addition of CCl_4 to diene 2 in the presence of 10 equiv of hydroquinone with respect to $Me_3NFe(CO)_4$ was conducted analogously. It was shown by ^{1}H NMR spectroscopy that a 60 ± 10% conversion of 2 into a mixture of 5 and 6 had occurred after 1 h and complete conversion after 3 h; the same result was obtained in the blank experiment with omission of hydroquinone.

Attempted $FeCl_2$-Catalyzed Addition of CCl_4 to Diene 2. To a solution of 50 mg (0.30 mmol) of diene 2 in 5 mL of CCl_4 was added 6.0 mg (0.03 mmol) of $FeCl_2{\cdot}4H_2O$. After the mixture had been stirred for 4 h at room temperature, the solvent was evaporated and the residue extracted with pentane to afford 50 mg of a colorless oil which was shown by ^{1}H NMR spectroscopy to contain only diene 2; no formation of 5 and 6 could be detected. In another experiment $FeCl_2$ (10% with respect to diene 2) was used, which was obtained from the reaction between $Fe_2(CO)_9$ and CCl_4. Diene 2 was recovered unchanged after stirring of the mixture overnight.

Attempted Addition of CCl_4 to Diene 2 Promoted by $Fe(CO)_5/NEt_3$. A solution of 160 mg (1 mmol) of diene 2, 200 mg (1 mmol) of $Fe(CO)_5$, and 100 mg (1 mmol) of Et_3N in 10 mL of CCl_4 was stirred overnight at room temperature. After evaporation of the solvent and extraction of the residue with pentane, diene 2 was recovered unchanged; no formation of 5 and/or 6 could be detected.

$Fe_2(CO)_9$-Promoted Addition of CCl_4 to 2,3-Dimethylbutadiene-*1,1,4,4-d₄*. (a) Synthesis of (2,3-Dimethylbutadiene-*1,1,4,4-d₄*)iron Tricarbonyl. The procedure used was slightly modified from the procedure of Whitesides and Arhart.[56] A solution of 400 mg (1.9 mmol) of (2,3-dimethylbutadiene)iron tricarbonyl in 20 mL of benzene was prepared in a flask provided with a septum. A 3-mL sample of CF_3CO_2D was added dropwise with a syringe within 10 min under vigorous

J. Org. Chem. 1980, 45, 3969-3974 3969

stirring which was continued for 0.5 h. The solvent and excess of $CF_3CO_2D(H)$ were removed in vacuo and the residue extracted with pentane, leaving, after evaporation of the pentane, a yellow oil, which was again treated with 3 mL of CF_3CO_2D as described above, furnishing 300 mg (1.35 mmol, yield 75%) of (2,3-dimethylbutadiene-*1,1,4,4-d_4*)iron tricarbonyl. It contained, according to mass spectroscopy, 70 ± 3% tetradeuterated, 30 ± 3% trideuterated, and less than 5% di- and undeuterated adducts as determined by measuring the respective M^+ peaks; it was shown by ^1H NMR spectroscopic integration with benzene as reference that the methylene groups contained 90 ± 3% D and the methyl groups less than 3% D.

(b) Decomplexation of (2,3-Dimethylbutadiene-*1,1,4,4-d_4*)iron Tricarbonyl. This was accomplished according to the method of Shvo and Hazum.[58] A mixture of 300 mg (1.35 mmol) of (2,3-dimethylbutadiene-*1,1,4,4-d_4*)iron tricarbonyl, as obtained above, and 1.0 g (13 mmol) of Me_3NO (dried according to the procedure described above) in 10 mL of benzene was stirred at 40 °C for 2 days. The reaction mixture was filtered, liberated from excess Me_3NO and Me_3N by extraction with water, and dried over Na_2SO_4. The IR spectrum showed the absence of carbonyl absorptions. Comparison of the ^1H NMR spectrum of a sample of the obtained benzene solution with that of a benzene solution of undeuterated 2,3-dimethylbutadiene showed the deuterium content of the methylene absorption to be larger than 90%.

(c) $Fe_2(CO)_9$-Promoted Addition of CCl_4 to 2,3-Dimethylbutadiene-*1,1,4,4-d_4*. The benzene solution of 2,3-dimethylbutadiene-*1,1,4,4-d_4*, obtained as described above, was added to 30 mL of CCl_4 followed by addition of 700 mg (2 mmol) of $Fe_2(CO)_9$, and the reaction mixture was stirred overnight. The workup procedure was identical with that described for complex **15** and yielded, after chromatography, 70 mg (yield 15%, based on the intake of (2,3-dimethylbutadiene)iron tricarbonyl) of (D)-**15a**. It consists of 60 ± 3% **15**-d_4, 30 ± 3% **15**-d_3 and 10 ± 3% **15**-d_{0-2} as determined by the respective M^+ peaks and as checked by ^1H NMR spectroscopy. Structural assignment of (D)-**15a** is based on the following spectroscopic data: mass spectrum for $C_{10}H_5D_4{}^{35}Cl_3FeO_3$, *m/e* 342 ($M^+$), 314 ($M^+$ - CO), 286 (M^+ - 2 CO), 279 (M^+ - CO - ^{35}Cl), 268 (M^+ - 3 CO); IR (CCl_4) 2060, 1990, 1970 (CO) cm^{-1}; ^1H NMR, see Figure 2; ^{13}C NMR (C_6D_6) δ 211.1, 103.8, 99.2, 95.0, 43.6 (t, J_{CH} = 160 Hz), 21.0 (q, J_{CH} = 130 Hz). The signals observed at δ 58.4 (CH_2CCl_3) and 44.3 ($=CH_2$) for undeuterated **15** were of too low intensity to be observed in the case of (D)-**15** due to the lower spin response of deuterium in comparison with hydrogen.

Registry No. 1, 56745-77-8; 2, 50590-86-8; 3, 70130-71-1; 4, 70190-91-9; 5, 70130-73-3; 6, 70190-93-1; 7, 74397-50-5; 8, 74397-51-6; 9, 70130-72-2; 10, 70190-92-0; 11, 70130-76-6; 12, 70130-75-5; 13, 74397-52-7; 14, 74397-73-2; 15, 74397-74-3; (D)-15a, 74397-75-4; 16, 74397-76-5; 17, 60970-94-7; 18, 64314-99-4; 1-heptene, 592-76-7; 1,1,1,3-tetrachlorooctane, 18088-13-6; 1,5-hexadiene, 592-42-7; 5,7,7,7-tetrachloro-1-heptene, 51287-99-1; cyclohexene, 110-83-8; 2,3-dimethyl-2-butene, 563-79-1; 1-chloro-2-(trichloromethyl)cyclohexane, 7484-12-0; 1,1,1,3-trichloro-2,2,3-trimethylbutane, 74397-53-8; 4,4,4-trichloro-2,3,3-trimethyl-1-butene, 74397-54-9, 121-46-0; (*exo,exo*)-3-chloro-5-(trichloromethyl)tricyclo[2.2.1.$0^{2,6}$]heptane, 62991-86-0; (*endo,exo*)-3-chloro-5-(trichloromethyl)tricyclo[2.2.1.$0^{2,6}$]heptane, 63039-08-7; 2,3-dimethylbutadiene, 513-81-5; 1,3-cyclohexadiene, 592-57-4; $Fe(CO)_5$, 13463-40-6; Me_3NO, 1184-78-7; $Me_3NFe(CO)_4$, 29863-43-2; $Fe(CO)_4Br_2$, 14878-20-7.

Utility of Purinyl Radicals in the Synthesis of Base-Modified Nucleosides and Alkylpurines: 6-Amino Group Replacement by H, Cl, Br, and I[1]

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When 9-substituted adenines are treated with *n*-pentyl nitrite in hydrogen atom donating solvents and the resulting reaction mixtures are warmed and photolyzed with visible light, the corresponding 9-substituted purines are isolated. The conversion apparently involves homolysis of the intermediate 6-diazonium salts or azo compounds to produce purinyl radical intermediates. These purinyl radicals can subsequently abstract hydrogen atoms from solvent molecules. We have utilized our deamination procedure for the direct synthesis of the antitumor antibiotic nebularine from adenosine. When the deaminations of 9-substituted adenines are conducted in dry CCl_4, $CHBr_3$, or CH_2I_2, the corresponding 6-chloro-, 6-bromo-, and 6-iodopurines are isolated in good yields. There appears to be no detectable hydrogen abstraction in competition with halogen abstraction in the cases of $CHBr_3$ and CH_2I_2 solvents. These transformations provide shortened preparative pathways to intermediates useful in the synthesis of other base-modified purines. Under appropriate reaction conditions, conversions to the 6–6′ dimers also may be possible. The type of transformation in this report represents one of the first examples of the use of neutral purinyl radicals in nucleic acid chemistry.

Modified nucleosides and nucleic acid bases have been extensively investigated due to their potential activity as antibiotics, enzyme inhibitors, and antitumor agents. For this reason, improved and abbreviated syntheses of such materials or their precursors are of considerable interest.

Recently we have communicated a new and direct synthesis for the adenosine deaminase inhibitor and nucleoside antibiotic nebularine (**1a**),[2,3] from readily available adenosine (**2a**), via the intermediacy of purinyl radicals.[4] These previously unreported purinyl radicals were generated in an anhydrous diazotization/deamination procedure using *n*-pentyl nitrite as the nitrosating agent. We now supply complete details for the synthesis of nebularine and 9-ethylpurine and extend the work to demonstrate the general utility of purinyl radical intermediates in the synthesis of 6-chloronebularine triacetate (**3b**), and its bromo and iodo congeners **4b** and **5b**, respectively, from triacetyladenosine (**2b**). From 9-ethyladenine (**6**), in addition to the deaminated compound **7**, 6-halo-9-ethyl-

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