

THE NAPHTHALENECHROMIUM TRICARBONYL-CATALYZED ADDITION OF CARBON TETRACHLORIDE TO OLEFINS AT AMBIENT TEMPERATURES

O. Gandolfi* and Michael Cais**

Department of Chemistry, Technion-Israel Institute of Technology, Haifa, Israel

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Summary

Naphthalenechromium tricarbonyl is an effective catalyst for the addition reaction of carbon tetrachloride to olefins to form 1,1,1,3-tetrachloroalkanes. Mechanistic aspects of this reaction are discussed.

Introduction

The catalytic effectiveness of naphthalenechromium tricarbonyl in the regio-selective and stereospecific hydrogenation of dienes at ambient temperatures has been recently demonstrated [1,2]. The scope of this and similar hydrogenation reactions [3] and additional mechanistic studies [4] will be presented in separate communications. The observation in the course of previous studies [5,6] that the chromium catalytic species involved in the hydrogenation reactions with dienes appears capable of activating not only the hydrogen molecule, but also the carbon-hydrogen bond in the cyclohexane molecule, thereby providing a source of hydrogen atoms for hydrogenation, prompted us to investigate the possibility of catalytically activating carbon-halogen bonds with arenechromium tricarbonyl complexes. The initial reaction of choice for these studies was the addition of carbon tetrachloride

* Permanent address: Dipartimento di Chimica - Università della Calabria
Armeria di Rende (CS) - 87030 ITALY

to olefinic systems. The catalysis of this reaction by mononuclear metal carbonyl complexes [7] such as $\text{Fe}(\text{CO})_5$, $\text{Mo}(\text{CO})_6$ and $\text{Cr}(\text{CO})_6$ as well as dinuclear metal carbonyls [8] such as $\text{Co}_2(\text{CO})_8$, $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ and $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ has been reported to require relatively high temperatures ($>150^\circ$) and long reaction times (> 15 hr) leading to conversion yields of up to 70%.

The use of ruthenium(II)triphenylphosphine complexes as catalysts in the addition of CCl_4 to olefins, in a sealed tube, has been found [9] to give good conversion yields at lower temperatures (80°) and shorter reaction times (~ 4 hr).

We were hopeful that the high catalytic activity of the naphthalenechromium tricarbonyl/tetrahydrofuran system as exhibited in the hydrogenation of dienes [1-4] might manifest itself also in the CCl_4 addition to olefins and that milder reaction conditions could be achieved. Some of the results of our investigation on this reaction are presented in this communication.

Experimental

Apparatus - NMR spectra were determined on a Varian T-60 spectrometer in CCl_4 solution with tetramethylsilane as internal standard and are expressed in δ -values. Infrared spectra were taken on a Perkin-Elmer Model 257 grating spectrophotometer. G.l.c. analyses were performed on a Packard Model 805 (series 7300) instrument fitted with a flame ionization detector and disc integrator; (calibratic with standard samples indicated an accuracy of $\pm 1\%$). G.l.c. separation of reactor products on a Varian Aerograph Model 920 or 90-P afforded the collection of samples mass spectra measurements. The latter were carried out with a high-resolution MAT-711 (Varian) or an ATLAS-CH4 mass spectrometer (with direct inlet at 70 eV).

Materials - All reagent grade olefins were distilled and freed from peroxides by passage through an active alumina (basic) column. Carbon tetrachloride was purified by distillation and tetrahydrofuran was distilled over calcium hydride under nitrogen immediately prior to use in reactions. All solvents and reactants were degassed prior to reactions and transfers were carried out under nitrogen with syringe technique. The arenechromium tricarbonyl derivatives were

$\text{trans-Cr(CO)}_4\{\text{P(C}_6\text{H}_5)_3\}_2$ were synthesized and purified as described in the literature.

All reactions were routinely performed at room temperature under dry, oxygen-free nitrogen in 10 ml Erlenmeyer flasks carefully protected from light and fitted with rubber sealing caps and magnetic stirrers.

In a typical reaction, a solution of norbornadiene (180 mg, 1.9 mmoles) in 2.5 ml of a mixture of THF/ CCl_4 (7:3) was added with a syringe to a degassed erlenmeyer flask containing naphthalenechromium tricarbonyl (10 mg, 0.038 mmoles). The reaction mixture, protected from light, was magnetically stirred for about 20 hr. Aliquots were removed at fixed time intervals and analyzed for products by g.l.c. with a 15% DEGS column on chromosorb W. In some experiments the aliquots were also used for measuring the infrared spectral changes in the 2000 cm^{-1} metal carbonyl region (vide infra).

In a preparative experiment, cyclooctene (2.5g, 22.8 mmoles) and NCT (0.2g, 0.76 mmoles) in 15 ml THF/ CCl_4 (1:1) were magnetically stirred at room temperature overnight. After removing the solvent and unreacted olefin by distillation, the reaction product was passed over alumina (basic) and eluted with THF, to yield 4.4g of 1-trichloromethyl-2-chloro-cyclooctane, corresponding to a 76% conversion yield.

Results

The reaction of CCl_4 with norbornadiene (NBD) in the presence of naphthalenechromium tricarbonyl (NCT) was first investigated. When the reaction was carried out with 3.8 mmoles of NBD and 0.38 mmoles catalyst, all the olefin was consumed after 2 hr. G.l.c. analysis showed the formation of three saturated products, I_A , I_B and I_C in a ratio of 8:14:1 respectively. Separation by preparative g.l.c. and mass spectra measurements showed that the two major products I_A (31%) and I_B (55%) were isomeric $\text{NBD}\cdot\text{CCl}_4$ adducts ($\text{C}_8\text{H}_8\text{Cl}_4$). The minor product I_C (4%) had the composition $\text{C}_9\text{H}_8\text{Cl}_6$ corresponding to the addition of two CCl_3 groups to NBD. Under similar reaction conditions, but using only 2 mole % NCT catalyst (relative to NBD), a 95% conversion to $\text{NBD}\cdot\text{CCl}_4$ adducts was reached after

catalyst promoted only a 23% conversion of NBD to the CCl_4 -adducts. Similarly, bipyridyl $\text{Cr}(\text{CO})_4$ led to a conversion of 8.3%; and *trans*- $\text{Cr}(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2$ yielded a conversion of 11.1%. With mesitylene $\text{Cr}(\text{CO})_3$, dimethylterephthalate $\text{Cr}(\text{CO})_3$ or triphenylphosphine [12] as catalysts, no NBD- CCl_4 adducts were formed at all and after 5.5 hr of reaction time unchanged NBD was recovered quantitatively.

The effect of the THF/ CCl_4 ratio on the % conversion of NBD to NBD- CCl_4 adducts after 5 hr reaction time is shown in Fig.1. The results indicate that optimal conversions should occur with 30%-50% CCl_4 in the solvent mixture. The effects of reaction time on olefin conversion with various THF/ CCl_4 solvent mixture are illustrated in Fig.2. A reaction time of 4-5 hr would be required for maximum conversion with a 2 mole % catalyst (relative to olefin). For comparison, a hydrogenation experiment carried out with NBD and NCT (1 mole %) in THF at ambient

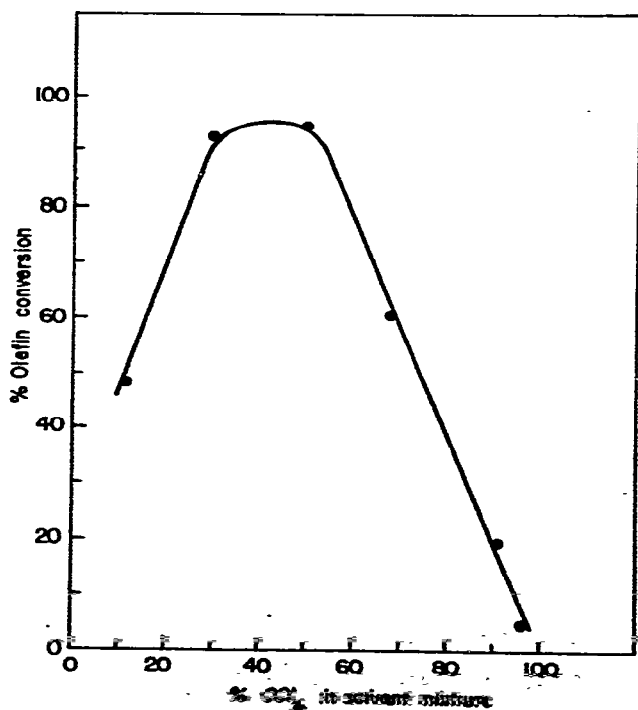


Fig. 1: The effect of THF/ CCl_4 ratio on % conversion of norbornadiene into the CCl_4 -adducts. Reaction conditions: norbornadiene

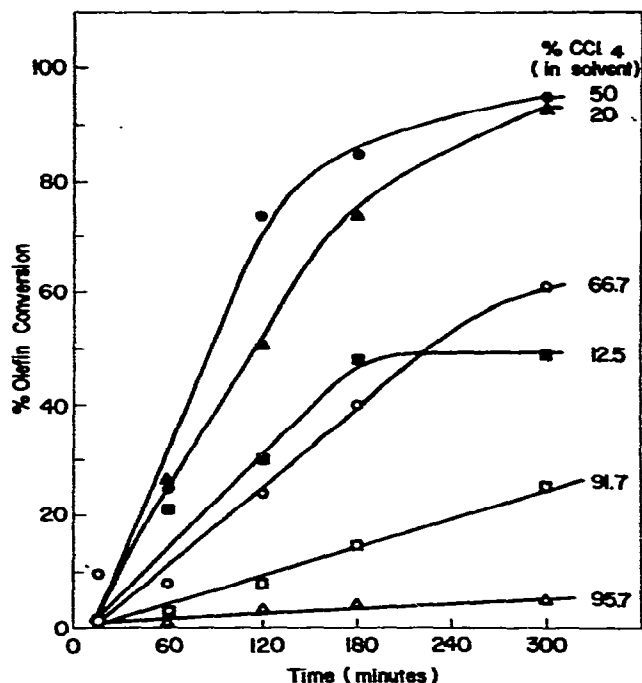


Fig.2: The effect of reaction time on % conversion of norbornadiene into the CCl_4 -adducts for various THF/ CCl_4 solvent mixtures. Reaction conditions: as in Fig.1.

temperature, under conditions described elsewhere [4], yielded after 30 min. a 54% conversion to the hydrogenated products, nortricyclene (~70%) and norbornene (~30%). For further comparison with the hydrogenation reaction, the catalyst (NCT) was first dissolved in THF and allowed to equilibrate at room temperature for 15 min in order to obtain a significant concentration of $(\text{THF})_3\text{Cr}(\text{CO})_3$ which has been shown [2] to be the active catalytic species in hydrogenation. An appropriate solution of NBD in CCl_4 was then charged to the THF-catalyst system. In a parallel, and simultaneous experiment, all the reactants (in identical amounts as in the first experiment) were added together from the start (i.e. omitting the equilibration step). The progress of the reaction, as monitored by g.i.c., was initially rather similar in both experiments, leading to approximately 50% conversion of NBD at the end of about one hour. The reaction in which all the reactants had been added

of 5 hr (total reaction time). On the other hand, the reaction with the prior equilibrating step, reached a maximum olefin consumption of 60% at the end of about 1.5 hr total reaction time and no further change occurred for another 3.5 hrs. This behaviour was quite different from that which had been observed in hydrogenation experiments under analogous conditions [2] and provided a strong indication that different active catalytic species could be involved in the two reactions: hydrogenation of dienes and CCl_4 addition to olefins (see Discussion). Additional support for this possible conclusion became available when we attempted to obtain direct spectroscopic evidence on the identity of the catalytic species in the olefin- CCl_4 addition reaction by a method which had proven helpful in the investigations on the hydrogenation reaction [1,2]. NCT in THF exhibits initially typical ν_{CO} absorptions in the infrared spectrum at 1970(s), 1900(s) and 1890(s) cm^{-1} . Solvolysis by THF leads to the species $(\text{THF})_3\text{Cr}(\text{CO})_3$, identified by ν_{CO} at 1920 and 1773 cm^{-1} , which in approximately 40 min at room temperature constitutes about 55% of the equilibrated mixture [2]. NCT in CCl_4 exhibited ν_{CO} bands at 1980, 1920 and 1905 cm^{-1} which retained unchanged intensity even after 24 hr. A solution of NCT in a mixture of THF/ CCl_4 (7:3) protected from light exhibited a new band ν_{CO} at 1940 cm^{-1} which grew in intensity at the expense of the 1890 cm^{-1} band. The 1940 cm^{-1} band reached maximum intensity after about 2 hr and remained constant for another hour whilst the bands at 1900 and 1890 cm^{-1} continued to decrease. At the same time, two new absorptions at 2030 and 1980 cm^{-1} began to appear, the 1980 cm^{-1} band growing stronger at the expense of all the other bands. After 20 hr the absorption pattern in the ν_{CO} region was as follows: 2030(w), 1980(s), 1940(w) 1890(m) cm^{-1} . The light-protection was then removed and after 30 min of exposure to daylight the solution changed colour from brown to violet and the infrared spectrum exhibited absorptions at ν_{CO} 2030(w) and 1980(s) cm^{-1} , characteristic of $\text{Cr}(\text{CO})_6$ in this solvent mixture. Work up of the violet solution led to the isolation of $(\text{THF})_3\text{CrCl}_3$ (~50% yield) identified by comparison with an authentic sample [13]. It is important to note the absence, in this THF/ CCl_4 medium, of the bands typical of the hydrogenation catalytic species [2] $(\text{THF})_3\text{Cr}(\text{CO})_3$ (vide supra). In the presence of NBD, the same infrared pattern as described above was

in the presence and absence of CCl_4 in the solvent mixture. This latter band belongs to the stable $(\text{NBD})\text{Cr}(\text{CO})_4$ complex. A similar band was not observed with other olefins studied in this work.

The next step was to investigate the NCT-catalyzed addition of CCl_4 to other dienes, known to undergo selective hydrogenation with arene $\text{Cr}(\text{CO})_3$ catalysts [1-4]. Conjugated dienes, such as 2,4-hexadiene, methyl 2,4-hexadienoate (methyl sorbate) and cycloheptatriene subjected to the same reaction conditions as NBD, were recovered unchanged and no chlorinated products could be detected. Interestingly, the presence of these dienes in the NCT/THF/ CCl_4 system did not interfere with the evolution of the same infrared absorption pattern as described above.

On the other hand, linear non-conjugated dienes and monoolefins, incorporating a terminal carbon-carbon double bond formed CCl_4 -adducts under catalysis with NCT in the THF/ CCl_4 system at ambient temperatures. Monoolefins with non-terminal double bonds such as 2-hexene and 3-hexene were recovered unchanged. However, cyclic monoenes and non-conjugated cyclodienes were also converted to CCl_4 -adducts in this reaction. The results are summarized in Table 1, which also includes data for the chlorine-containing mass-spectrum fragments observed for the CCl_4 -adducts. Table 2 presents the NMR data for the reaction products. Unexpectedly, non-conjugated linear dienes, in which both double bonds were in the terminal position e.g. 2-methyl-hexa-1,5-diene formed only the two isomeric mono(olefin- CCl_4) adducts, the remaining double bond being left unreacted. A similar result was obtained with cyclo-octa-1,5-diene, where only a 1:1 adduct was obtained, but the remaining double-bond was not present in the product, probably due to an intramolecular cyclization reaction, as observed in the case of NBD.

Discussion

Any attempts to discuss the addition of CCl_4 to olefins under catalysis by the NCT (naphthalenechromium tricarbonyl)/THF system, must take into account the known [2] formation of several intermediate species as a result of reaction between the coordinating solvent and the arenemetal carbonyl complex. The stepwise displacement of the arene moiety by THF, as illustrated in equation (i),

TABLE 1
REACTION OF CARBON TETRACHLORIDE WITH OLEFINS IN THE PRESENCE OF NAPHTHALENE-Cr(CO)₃^a

Olefin	Conversion ^b ([catalyst]/[olefin])	Product (% yield) ^c	Chlorine containing ions in mass spectrum of adducts (m/e) ^d
Methylcyclohexadiene	95(1:50); 100(1:10)	I _A . C ₈ H ₈ Cl ₄ (31)	209(M-Cl) ⁺ ; 173(M-2Cl) ⁺
		I _B . C ₈ H ₈ Cl ₄ (55)	209(M-Cl) ⁺ ; 173(M-2Cl) ⁺
		I _C . C ₉ H ₈ Cl ₆ (4)	326(M) ⁺ ; 290(M-Cl) ⁺ ; 256(M-2Cl) ⁺
1,5-Cyclooctadiene	22(1:50); 50(1:20)	II _A . C ₉ H ₁₂ Cl ₄ (100)	260(M) ⁺ ; 225(M-Cl) ⁺ ; 224(M-HCl) ⁺ ; 189(M-2Cl-H) ⁺
1,4-Pentadiene	8(1:50); 16(1:20)	III _A . CCl ₃ CH ₂ CHClCH ₂ CH=CH ₂ (60)	185(M-Cl) ⁺ ; 149(M-2Cl-H) ⁺
		III _B . Unidentified product(40)	
1,5-Hexadiene	40(1:50); 75(1:10)	IV _A . CCl ₃ CH ₂ CHCl(CH ₂) ₂ CH=CH ₂ (100)	234(M) ⁺ ; 199(M-Cl) ⁺ ; 163(M-2Cl-H) ⁺
1,5-Heptadiene	35(1:50)	V _A . CCl ₃ CH ₂ CHCl(CH ₂) ₂ CH=CHCH ₂ (100)	248(M) ⁺ ; 213(M-Cl) ⁺ ; 212(M-HCl) ⁺ ; 178(M-2Cl) ⁺
1,2,5-Dimethyl-1,5-hexadiene	15(1:20)	VI _A . CCl ₃ CH ₂ C(CH ₃)ClCH ₂ C(CH ₃)=CH ₂ (90)	262(M) ⁺ ; 227(M-Cl) ⁺ ; 191(M-2Cl-H) ⁺
1,3-Methyl-1,5-hexadiene	15(1:50)	VII _A . CCl ₃ CH ₂ C(CH ₃)Cl(CH ₂) ₂ CH=CH ₂ (80)	248(M) ⁺ ; 213(M-Cl) ⁺ ; 212(M-HCl) ⁺ ; 177(M-2Cl-H) ⁺
		VII _B . CCl ₃ CH ₂ CHCl(CH ₂) ₂ C(CH ₃)=CH ₂ (20)	
1,3-Methyl-1,5-hexadiene	26(1:20)	VIII _A . CCl ₃ CH ₂ CHClCH(CH ₃)CH ₂ CH=CH ₂ (68)	248(M) ⁺ ; 213(M-Cl) ⁺ ; 177(M-2Cl-H) ⁺
		VIII _B . CCl ₃ CH ₂ CHClCH ₂ CH(CH ₃)CH=CH ₂ (32)	
1,3-Methyl-1,5-heptadiene	33(1:20); 43(1:11)	IX _A . CCl ₃ CH ₂ CHClCH(CH ₃)CH ₂ CH=CHCH ₂ (88)	262(M) ⁺ ; 91(M-2Cl-H) ⁺

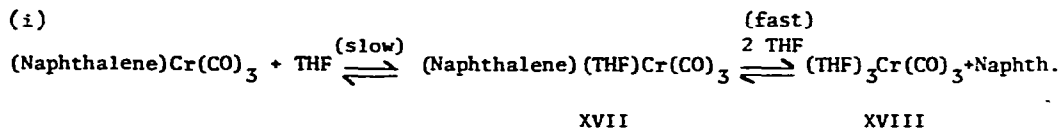
4,7-Octadiene	X _A ·	13(1:50); 31(1:20)	X _A ·	CCl ₃ CH ₂ CHCl(CH ₂) ₄ CH=CH ₂ (70)	262(M) ⁺ ; 227(M-Cl) ⁺ ;
	X _B ·		X _B ·	unidentified product(30)	191(M-2Cl-H) ⁺
4-Heptene	XI _A ·	39(1:20)	XI _A ·	CCl ₃ CH ₂ CHCl(CH ₂) ₄ CH ₃ (100)	221(M-C ₂ H ₅) ⁺ ; 185(M-C ₂ H ₅ -HCl) ⁺ ;
	XII _A ·	26(1:50)	XII _A ·	CCl ₃ CH(CH ₂) ₃ CHCl (100)	179(M-2Cl-H) ⁺
I. Cyclo-Pentene	XIII _A ·cis	15(1:50); 30(1:20)	XIII _A ·cis	CCl ₃ CH(CH ₂) ₄ CHCl (20)	185(M-Cl) ⁺ ; 150(M-2Cl) ⁺
	XIII _B ·trans		XIII _B ·trans	CCl ₃ CH(CH ₂) ₄ CHCl (20)	199(M-Cl) ⁺ ; 164(M-2Cl) ⁺
II. Cyclohexene	XIII _C ·		XIII _C ·	CCl ₃ CH(CH ₂) ₃ CH=CH (60)	199(M-Cl) ⁺ ; 163(M-2Cl-H) ⁺
	XIV _A ·	12(1:50); 16(1:30)	XIV _A ·	CCl ₃ CH(CH ₂) ₅ CHCl (70)	163(M-Cl) ⁺ ; 127(M-2Cl-H) ⁺
V. Cycloheptene	XV _A ·	25(1:100); 44(1:50); 76(1:30)	XV _A ·	CCl ₃ CH(CH ₂) ₄ CH=CH (30)	248(M) ⁺ ; 212(M-HCl) ⁺
	XVI _A ·		XVI _A ·	CCl ₃ CH(CH ₂) ₆ CHCl (100)	213(M) ⁺ ; 177(M-HCl) ⁺
I. Cyclododecene	XVI _A ·	11(1:100); 22(1:50)	XVI _A ·	CCl ₃ CH(CH ₂) ₁₀ CHCl (100)	226(M-HCl) ⁺ ; 191(M-2Cl-H) ⁺
	XVI _B ·		XVI _B ·	CCl ₃ CH(CH ₂) ₁₀ CHCl (100)	282(M-HCl) ⁺ ; 247(M-2Cl-H) ⁺

The reactions were carried out at room temperature with 25 ml of CCl₄/THF in 1:1 ration protected from light - conversion was determined by gic (based on olefin consumption) - (c) relative ratio determined by gic. - (d) the m/e values for the molecular ion of the adducts and the chlorine - containing fragment ions observed in the mass spectra these compounds were easily identified by the appearance of the expected isotopic chlorine distribution.

TABLE 2. NMR Data for Olefin - CCl₄ Adducts (a) δ (ppm)

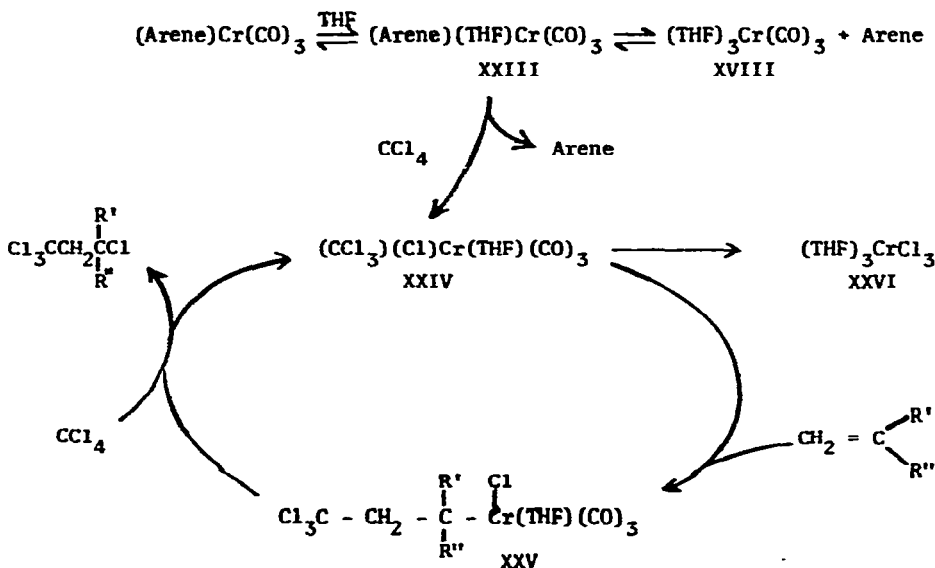
Adduct	HCCL	HCCI ₃	CH ₂	HCICH ₂	HC:CH	C:Cl ₂	C:CCl ₃	CH ₃ CCl	CH ₃ -C
III _A	4.30(m,1)	3.13(d,2)	2.2(m,2)	4.8-6.1(m,3)					
IV _A	4.28(m,1)	3.20(q,2)	2.0(m,4)	4.8-6.2(m,3)					
V _A	4.28(m,1)	3.18(q,2)	2.0(m,4)		5.47(m,2)	1.70(d,3)			
VI _A		3.40(s,2)	2.2(m,4)			4.73(m,2)	1.77(m,3)	1.90(s,3)	
VII _A		3.40(s,2)	2.23(m)	4.9-6.1(m,3)				1.87(s,3)	
VII _B	4.33(m,1)	3.23(q,2)				4.7(m,2)	1.70(s,3)		
VIII _A	4.33(m)	3.2(m)	1.6-2.3(m)	4.9-6.0(m)					1.07(d)
VIII _B									1.03(d)
IX _A	4.35(m,1)	3.15(d,2)	2.08(m,3)		5.47(m,2)	1.70(d,3)			1.03(m,3)
X _A	4.25(m,1)	3.17(q,2)	0.9-2.5(m,8)	4.8-6.1(m,3)					
XI _A	4.25(m,1)	3.18(q,2)	1.1-2.2(m,8)						0.9(t,3)
XII _A	4.47(m,1)	3.48(m,1)	1.5-2.5(m,6)						
XIII _A (b)	4.93(m,1)	2.6(m,1)	1.2-2.4(m)						
XIII _B (c)	4.53(m,1)	2.8(m,1)							
XIII _C		2.5(m)			5.57(m)				
XIV _A	4.70(m,1)	3.1(m)	1.2-2.6(m)						
XIV _B									
XV _A	4.22(m,1)	2.6(m,1)	1.9(m,12)						
XV _B	4.05(m,1)	2.45(m,1)	1.1-2.2(m,20)						

(a) Where more than one product was obtained, no separation of adducts was attempted for the NMR measurements except for removal of starting materials; (b) cis; (c) trans.



hydrogenation reaction [2]. Intermediate XVII was detected by infrared spectroscopy only in the very early stages of the equilibration process before its characteristic absorption band ($\sim 1940 \text{ cm}^{-1}$) was swamped by that of the longer-lived (and hence more abundant) intermediate XVIII. However, even the latter was found [2] to undergo further transformations and disproportionations leading to $(\text{THF})_2\text{Cr(CO)}_4$, XIX; $(\text{THF})\text{Cr(CO)}_5$, XX; Cr(CO)_6 , XXI and Cr_2O_3 , XXII. In the presence of a sufficient concentration of CCl_4 ($\sim 30\%$) in the NCT/THF system the course of the equilibration reaction was changed and different intermediate species and/or disproportionation products could be observed. On monitoring the reaction course by infrared, as mentioned above, the appearance of species XVIII was completely suppressed in the presence of CCl_4 (as shown by the absence of the typical bands at 1920 and 1773 cm^{-1}). Therefore, we infer that interaction between CCl_4 and the coordinating sphere of the metal must take place after formation of species XVII and before formation of species XVIII. This conclusion agrees also with the established greater reactivity of $(\text{naphthalene})\text{Cr(CO)}_3$ relative to $(\text{phenanthrene})\text{Cr(CO)}_3$ and $(\text{mesitylene})\text{Cr(CO)}_3$ in the ligand exchange reaction whereby the THF partially displaces the arenemetal bonds [1,2]. If the amount of THF exceeds 70% in the THF/ CCl_3 mixture, the second step in the equilibrium (eq.i) becomes predominant leading to formation of species XVIII. Whereas this would be beneficial in the hydrogenation reaction, it is not so in the addition of CCl_4 to olefins. When NCT was allowed to equilibrate in THF in order to establish an optimal concentration of $(\text{THF})_3\text{Cr(CO)}_3$, XVIII, before addition of CCl_4 and NBD(I), a lower conversion of olefin to olefin- CCl_4 adduct resulted. Thus, formation of XVIII not only decreased the concentration of NCT (and/or of species XVII) at the time CCl_4 was added to the reaction, but also it provided an additional facile path for the side (disproportionation) reactions which hasten termination of the catalytic cycle. On the other hand, an increase in the $[\text{CCl}_4]/\text{THF}$ ratio might favour the side reaction between CCl_4 and the chromium species which leads to formation of the catalytically

inactive product $(\text{THF})_3\text{CrCl}_3$ and thus bring about the decrease in the yield of CCl_4 -adducts (see Fig. 1 and 2). Since conjugated dienes do not undergo the CCl_4 addition reaction, whereas terminal monoenes do so, we have to consider mechanistic pathways different from those postulated for the selective hydrogenation of dienes [2,4,6]. A possible mechanism is presented in Scheme 1. Oxidative addition



Scheme 1. Catalytic cycle for addition of CCl_4 to monoenes

of CCl_4 to the catalytic species XXIII, leading to the hexacoordinate Cr(II) species XXIV is followed by insertion of the olefin into the metal-trichloromethyl bond to form the 1-alkyl-3,3,3-trichloropropyl complex (XXV). Reaction of this complex with another molecule of CCl_4 yields the 1,1,1,3-tetrachloroalkane product and regenerates the chloro-trichloromethyl[Cr] complex (XXIV), to renew the catalytic cycle.

The possibility that species XXIII could react with CCl_4 to form free trichloromethyl radicals has been considered and excluded as a major reaction path. For a free-radical mechanism, in which CCl_3 radicals would be responsible for initiating the radical addition to olefins, one would have expected the formation of several other chlorinated products [14-16].

observed. Furthermore, augmenting the molar equivalent of naphthalenechromium tricarbonyl catalyst in these reactions resulted in a parallel increase in the yield of the 1:1 - CCl_4 /olefin adduct (Table 1). By analogy, we believe that the free radical mechanism proposed for the addition of CCl_4 to terminal olefins catalyzed by ruthenium (II) complexes [9] should be reconsidered and revised in the light of our findings.

The mechanism suggested in Scheme 1 differs only in the initial steps from that proposed [8] for the CCl_4 addition to olefins under catalysis by dinuclear metal carbonyls such as $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$. With these catalysts, CCl_4 is envisaged to react by forming two chlorinated intermediate species: $\text{CCl}_3\text{Mo}(\text{CO})_3(\text{C}_5\text{H}_5)$ and $\text{ClMo}(\text{CO})_3(\text{C}_5\text{H}_5)$. Insertion of the trichloromethylmetal complex into the olefin leads to the same type of complex as XXV in Scheme 1. The second chlorinated intermediate, $\text{ClMo}(\text{CO})_3(\text{C}_5\text{H}_5)$ is not considered to play any further role in the reaction mechanism.

Finally, just as for the hydrogenation reaction [1,2], the very mild reaction conditions which are sufficient for the addition of CCl_4 to olefins indicate a high catalytic activity for naphthalenechromium tricarbonyl in coordinating solvents.

The versatility and scope of this catalytic system is being further investigated.

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