Organic Chemistry

Addition of CCl_4 to unsaturated compounds catalyzed by $M_3(CO)_{12}$ (M = Fe, Ru, Os)

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The addition of CCl_4 to hex-1-ene and to the methyl ester of *N*-(*trans*-cinnamoyl)-L-proline (**2**) catalyzed by $M_3(CO)_{12}$ or by the $M_3(CO)_{12}$+DMF system (M = Fe, Ru, Os) was studied. The use of ruthenium and osmium dodecacarbonyls in combination with DMF increases the yields of adducts $CCl_3CH_2CHClC_4H_9$ (**4**) and $PhCHClCH(CCl_3)C(O)R'$ (**3**) over those obtained in reactions catalyzed by the same carbonyls without DMF. In addition to adduct **3**, salts $[M(CO_3)Cl_3]^-[Me_2NH_2]^+$ were isolated from the products of the reaction between CCl_4 and **1** in the presence of $M_3(CO)_{12}$+DMF (M = Ru, Os). These salts do not catalyze this reaction and apparently result from chain termination. Experimental results in favor of a coordination mechanism of the addition of CCl_4 to olefins in the presence of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ were obtained.

Key words: addition reactions, catalysis, transition metal carbonyls; coordination mechanism.

Carbonyls and salts of transition metals have been used widely and successfully for many years as catalysts of the addition of halogen-containing compounds to unsaturated compounds.[1—7] The catalytic activity of transition metal carbonyls in various processes involving homolysis of the C—Hal bond increases when they are used together with nucleophilic co-catalysts (alcohols, amines, amides, *etc.*).[1,3] The most pronounced increase in the activity has been observed in the addition and telomerization reactions of α-olefins with chlorine-containing telogens catalyzed by the $Fe(CO)_5$+DMF system.[1] In some studies published previously,[3,8] the activating role of DMF in these processes was attributed to the promotional effect of this additive on the formation of metal-carbonyl radical cations, which generate free radicals by abstracting the halogen atom from R—Hal:

$$[M(CO)_n]^{\cdot+} + R\text{—}Hal \longrightarrow [M(CO)_n]Hal + R^{\cdot}$$

In the opinion of other researchers,[9] DMF activates the process by dissolving salts of iron, which are known[10] to be formed already in the early steps of these processes through the decomposition of iron carbonyls in the halogen-containing medium.

In this work, we studied for the first time the addition of CCl_4 to hex-1-ene (**1**) catalyzed by $M_3(CO)_{12}$ (M = Ru, Os) and by their systems containing DMF and, for comparison, a similar reaction catalyzed by $Fe_3(CO)_{12}$ and $Fe(CO)_5$. The results were compared with published data.[11,12] Ruthenium and osmium dodecacarbonyls have not been used previously as catalysts in addition reactions and, therefore, it was also important to attempt to isolate any metal-containing

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complexes arising during the process. Previously, in studies of reactions catalyzed by complexes of other transition metals, no attempts of this sort have been made,[10] although data on the structures and activities of these complexes would make it possible to elucidate the mechanism of the process as a whole. We also studied the addition of CCl_4 to the methyl ester of *N*-(*trans*-cinnamoyl)-L-proline (**2**) catalyzed by ruthenium and osmium carbonyls in order to investigate the regio- and stereoselectivity of this process and to identify the preferred reaction mechanism.

Experimental

IR spectra were measured in the 4000—50 cm^{-1} range on Bruker IFS-25 and IFS-113 instruments for solutions in CH_2Cl_2, pellets with KBr, and suspensions in vaseline oil. ^1H NMR spectra were recorded on a Bruker AMX-400 spectrometer in $(CD_3)_2CO$. The yield of the adduct $PhCHClCH(CCl_3)C(O)R'$ (**3**) and the ratio of its diastereomers (from here on, R′ is the methyl L-prolinate residue) were determined from the intensity of the signals corresponding to the PhCHCl group (δ 5.59 and 5.54, J = 10.11 Hz).

General procedure. Experiments on the addition of CCl_4 to unsaturated compounds **1** and **2** were carried out in glass cylindrical 1.5-mL tubes, except for the addition of CCl_4 to **2** catalyzed by $Ru_3(CO)_{12}$, which was carried out in 8-mL tubes. CCl_4 (0.5 mL, 5.17 mmol), compound **1** (0.3 mL, 2.4 mmol), DMF (0.04 g, 0.514 mmol), and a metal carbonyl ($1.56 \cdot 10^{-2}$ mmol), ($[\mathbf{2}]_0$ = 0.613 mol L^{-1}) were placed in the tubes. Compound **1** and CCl_4 were distilled in an argon atmosphere immediately prior to the reaction, and DMF was dried over K_2CO_3 and distilled *in vacuo*. The experiments without DMF were carried out under the same reaction conditions. The initial concentrations of Me_2NH were 0.25 and 0.5 mol L^{-1}. The sealed tubes were placed in metallic jackets and heated at 95 °C.

The yield of the adduct $CCl_3CH_2CHClC_4H_9$ (**4**) was determined by GLC analysis of reaction mixtures on a LKhM-8M-5 chromatograph (katharometer, helium as the carrier gas, a 2000×3 mm column, 15% SE-30 on Chromaton N-AW (0.16—0.20 mesh); the temperature of the detector was 210 °C, that of the evaporating chamber was 200 °C, and the temperature of the thermostat was 150 °C). 1,1,1-Trichlorohexane was used as the external standard.

Reaction in the presence of dodecacarbonyltriiron. A dark green mixture of CCl_4, **1**, and $Fe_3(CO)_{12}$ became colorless after heating for 4 h, and a precipitate of $FeCl_2$, whose IR spectrum exhibited no absorption bands due to metal-carbonyl groups, was formed. The dependence of the yield of adduct **4** on the duration of heating is shown in Fig. 1 (curve *1*). The reaction mixture became dark after heating for 40 h.

Reaction in the presence of $Fe_3(CO)_{12}$+DMF. In the presence of DMF, discoloration of the solutions occurred sooner. In this case, the precipitate that formed contained C, H, Fe, Cl, and N (80, 7, 8, 5, and 0.3%, respectively), which can apparently be due to the fact that, along with iron salts, it contained oligomers. The time variation of the yield of adduct **4** is illustrated in Fig. 1 (curve *2*).

Reaction in the presence of dodecacarbonyltriruthenium. By the end of the experiment (20 h), the yellow color of the solution had virtually disappeared. According to IR spectroscopy, along with the small amounts of unreacted $Ru_3(CO)_{12}$, the precipitate mostly contained ruthenium carbonyls as indicated by absorption frequencies of 2140, 2124, and 2078 typical of vibrations of C=O and by the absorption bands in the region of Ru—Cl vibrations (327, 300, 294, and 267 cm^{-1}). Apparently, a mixture of chloro-derivatives of ruthenium carbonyls was formed.[13] The variation of the yield of adduct **4** with time is shown in Fig. 1 (curve *3*).

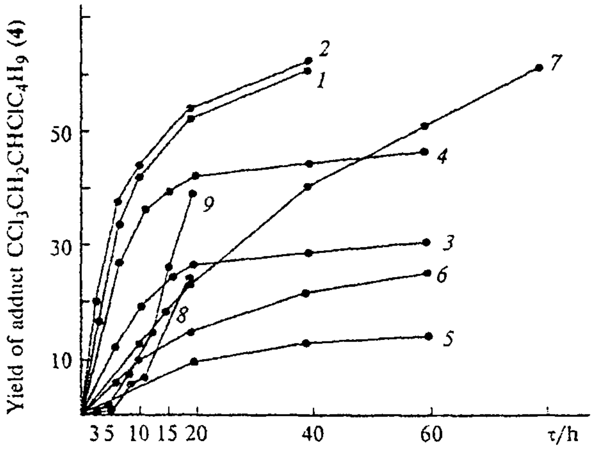


Fig. 1. Dependence of the yield of the product of the addition of CCl_4 to CH_2=CHC_4H_9 on time and on the catalyst or the catalytic system: $Fe_3(CO)_{12}$ (*1*); $Fe_3(CO)_{12}$+DMF (*2*); $Ru_3(CO)_{12}$ (*3*); $Ru_3(CO)_{12}$+DMF (*4*); $Os_3(CO)_{12}$ (*5*); $Os_3(CO)_{12}$+DMF (*6*) and (*7*); $Fe(CO)_5$ (*8*); $Fe(CO)_5$+DMF (*9*).

Reaction in the presence of $Ru_3(CO)_{12}$+DMF. The rate of the formation of adduct **4** (see Fig. 1, curve *4*) markedly decreased after the reaction mixtures were heated for 20 h. Although we did not optimize the process, its chain index was ~70. Upon cooling to ~20 °C, a precipitate was formed. Evaporation of **1**, CCl_4, DMF, and **4** *in vacuo* and washing of the residue with hexane gave the salt $[Ru(CO)_3Cl_3]^-[Me_2NH_2]^+$ as a pale yellow precipitate in ~70% yield based on the initial $Ru_3(CO)_{12}$. Single crystals suitable for X-ray diffraction were grown from CH_2Cl_2. The structure of the salt is shown in Fig. 2, and the characteristic frequencies observed in its IR spectrum are listed in Table 1.

Reaction in the presence of dodecacarbonyltriosmium. The starting lemon color did not change even when the reaction mixture was heated for 80 h. Cooling afforded the initial $Os_3(CO)_{12}$ as a yellow precipitate. The variation of the yield of **4** with time is shown in Fig. 1 (curve *5*).

Reaction in the presence of $Os_3(CO)_{12}$+DMF. The precipitate obtained contained, in addition to the initial $Os_3(CO)_{12}$, the colorless salt $[Os(CO)_3Cl_3]^-[Me_2NH_2]^+$, which precipitated due to its poor solubility in CH_2Cl_2. Table 1 presents the IR frequencies for this salt, which coincide with the corresponding frequencies for the salt $[Ru(CO)_3Cl_3]^-[Me_2NH_2]^+$ and the salt $[Os(CO)_3Cl_3]^-Cs^+$ described previously.[13] It is noteworthy that a change in the concentration of DMF has a marked effect on the rate of formation of **4** (*cf.* Fig. 1, curves *6* and *7*).

Addition of CCl_4 to compound 1 in the presence of the $[M(CO)_3Cl_3]^-[Me_2NH_2]^+$ salt. Heating reaction mixtures consisting of CCl_4, **1**, DMF, and $1.5 \cdot 10^{-2}$ mmol of $[M(CO)_3Cl_3]^-[Me_2NH_2]^+$ (M = Ru, Os) for 40 and 60 h under the conditions described in the general procedure afforded adduct **4** in a yield of 2—3%, *i.e.*, the yield was as low as that obtained when CCl_4 is heated with **1** in DMF in the absence of metal carbonyls.

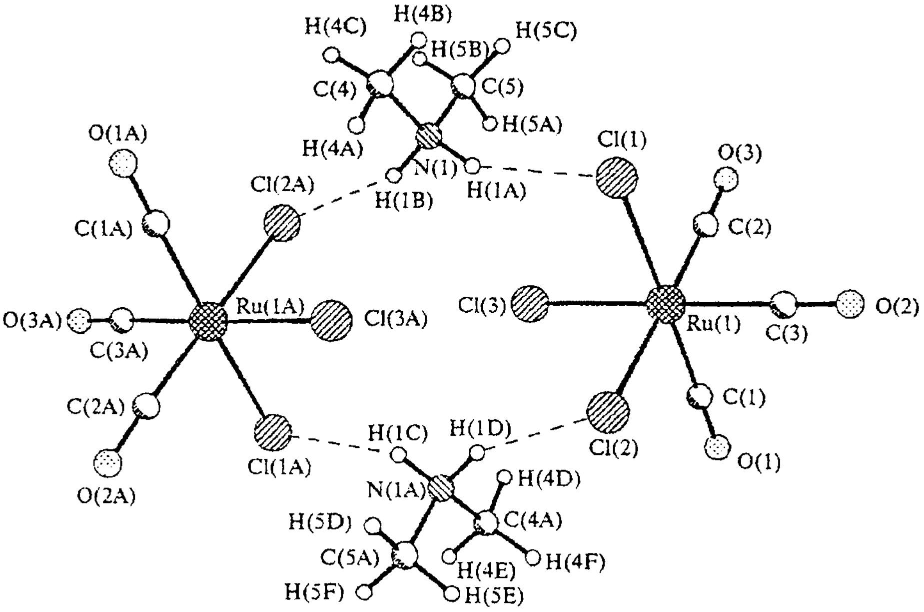


Fig. 2. Fragment of the crystal structure of $[Ru(CO)_3Cl_3]^-[Me_2NH_2]^+$.

Table 1. IR vibration frequencies (ν/cm^{-1}) for the $[M(CO)_3Cl_3]^-[Me_2NH_2]^+$ complexes (M = Ru (**5**), Os (**6**))

Complex	ν(C=O)	ν(M—Cl)	ν(M—C)	δ(M—CO)	δ(ClMCl)	ν(N—H)
5	2131(2137)	322(315)	480(475)		174	3090 s, br
	2060(2061)	285(282)	474(472)	580(575)		3036 m, br
	2042(2047)					2966
						2830
						2782
6	2126(2125)	321(314)		624(624)	180	3090 s, br
	2036(2046)	286(281)	505(505)	604(598)		3036 m, br
	2014(2014)		(501)			2966
						2830
						2786

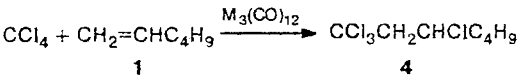
Note. The corresponding frequencies for $[M(CO)_3Cl_3]^-Cs^+$ (M = Ru, Os) are given in parentheses.[13]

X-ray diffraction study of $[Ru(CO)_3Cl_3]^-[Me_2NH_2]^+$. The crystals of $[Ru(CO)_3Cl_3]^-[Me_2NH_2]^+$ are monoclinic; at 20 °C a = 11.646(2) Å, b = 9.838(2) Å, c = 11.639(2) Å, β = 119.27(3)°, V = 1163.4 Å^3, d_{calc} = 1.927 g cm^{-3}, Z = 4, space group $P2_1/C$. The unit cell parameters and the intensities of 3332 independent reflections were measured on a CAD-4 Enraf-Nonius automatic diffractometer (20 °C, Mo-Kα-radiation, graphite monochromator, θ—5/3θ-scanning, θ ≤ 30°).

The structure was solved by the direct method and refined by the full-matrix least squares method in the anisotropic approximation. The hydrogen atoms were arranged geometrically and included in the refinement according to the "rider" model. The final residual factors were: R_1 = 0.0556 (over F for 2161 observed reflections with $I \geq 2\sigma(I)$), wR_2 = 0.1969 (over F^2 for all of the 3327 independent reflections used in the refinement). All the calculations were carried out using the SHELXTL PLUS 5 program (gamma-version) on an IBM PC. The coordinates of atoms are listed in Table 2.

Results and Discussion

As a result of this study, we established (see Fig. 1) the dependence of the yield of the product resulting from the addition of CCl_4 to compound **1** (adduct **4**), catalyzed by $M_3(CO)_{12}$ (M = Fe, Ru, Os) and by systems based on these carbonyls and containing DMF, on the duration of heating.



$$\underset{\textbf{1}}{CCl_4 + CH_2{=}CHC_4H_9} \xrightarrow{M_3(CO)_{12}} \underset{\textbf{4}}{CCl_3CH_2CHClC_4H_9}$$

Of the $M_3(CO)_{12}$ used in this reaction, $Fe_3(CO)_{12}$ proved to be the most active catalyst, while $Os_3(CO)_{12}$ was the least active. However, the addition of DMF to $Os_3(CO)_{12}$ promotes the formation of adduct **4** to a

Table 2. Coordinates of atoms (×10^4) and equivalent isotropic heat parameters (×10^3) in the structure of $[RuCl_3(CO)_3]^-[NH_2Me_2]^+$

Atom	$-x$	y	z	U_{eq}/Å^2
Ru(1)	8259(1)	6244(1)	−1369(1)	29(1)
Cl(1)	8396(2)	3784(2)	−1538(2)	45(1)
Cl(2)	7119(2)	6092(2)	1003(2)	47(1)
Cl(3)	6183(2)	6212(2)	−1348(2)	43(1)
O(1)	8020(7)	9297(7)	−1079(8)	68(2)
O(2)	9654(8)	6373(8)	−4354(6)	69(2)
O(3)	10803(6)	6130(7)	−1247(7)	59(2)
N(1)	5863(6)	1988(7)	3136(7)	46(2)
C(1)	8115(7)	8171(9)	−1183(7)	40(2)
C(2)	9134(7)	6352(8)	−3241(8)	42(1)
C(3)	9922(6)	6192(8)	−1302(7)	38(1)
C(4)	5654(11)	3402(10)	3553(13)	69(3)
C(5)	6436(10)	1802(12)	1716(9)	61(2)

greater extent, while its addition to $Fe_3(CO)_{12}$ promotes the reaction to a smaller extent. Evidently, all these distinctions are due to the increase in the strength of the M—M bond length on going from top to bottom in the subgroup. In fact, the strength of the Fe—Fe bond, equal to 19.2 kcal mol^{-1}, is substantially lower than those of the Ru—Ru (27.9 kcal mol^{-1}) and Os—Os (31.1 kcal mol^{-1}) bonds.[14] Therefore, our results suggest that the M—M bonds are cleaved to give catalytically active mononuclear species. The minor effect of DMF on the catalytic activity of $Fe_3(CO)_{12}$ and the ability of the $FeCl_2$ resulting from decomposition of $Fe_3(CO)_{12}$ in a medium of chloro-derivatives to act as a catalyst in the same reactions (which follows from published data[7,10]) suggests that the mechanism of the catalysis by $Fe_3(CO)_{12}$ differs from those for $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$.

It is believed that in the case of iron carbonyls, an increase in the rate of initiation is favored by an increase in the rate of formation of iron chlorides (see, for example, Ref. 10), which are known[7] to catalyze the addition of CCl_4 to unsaturated compounds by a redox catalysis mechanism (Scheme 1).

Scheme 1

$$FeCl_2 + CCl_4 \longrightarrow FeCl_3 + Cl_3C^{\cdot}$$

$$Cl_3C^{\cdot} + CH_2{=}CHC_4H_9 \longrightarrow CCl_3CH_2C^{\cdot}HC_4H_9$$

$$CCl_3CH_2C^{\cdot}HC_4H_9 + FeCl_3 \longrightarrow CCl_3CH_2CHClC_4H_9 + FeCl_2$$

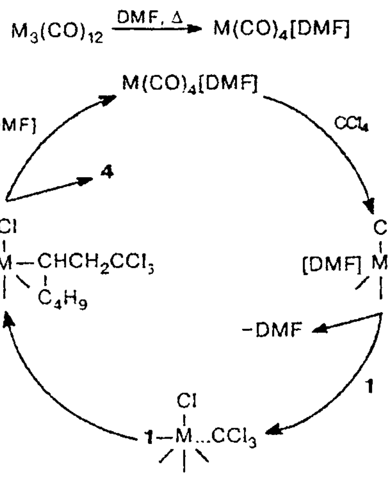
While discussing the catalytic effect of $Fe_3(CO)_{12}$, it is important to compare its activity with the behavior of $Fe(CO)_5$ in the same reaction. Therefore, we carried out experiments with $Fe(CO)_5$ without a promoter (see Fig. 1, curve *8*) and in combination with DMF (curve *9*) under similar conditions. It follows from a comparison of these curves that the role of DMF in $Fe(CO)_5$ is quite substantial compared to that in the case of $Fe_3(CO)_{12}$ (see Fig. 1, curves *1* and *2*). It becomes obvious that the action of DMF in catalysis by $Fe(CO)_5$ consists mostly in the replacement of the carbonyl group. Since the strength of the Fe—CO bond (27.9 kcal mol^{-1})[14] is much larger than that of the Fe—Fe bond, it is no wonder that the reaction catalyzed by $Fe(CO)_5$ occurs at a lower rate than that catalyzed by $Fe_3(CO)_{12}$.

As noted above, the catalytic activity of $Os_3(CO)_{12}$ in the reaction in question is lower (see Fig. 1, curve *5*) than the activities of other metal dodecacarbonyls. However, in the presence of DMF, its activity increases to a markedly greater extent (curve *7*) than those of $Fe_3(CO)_{12}$ (curves *1* and *2*) and $Ru_3(CO)_{12}$ (curves *3* and *4*).

The activating role of DMF in the case of $Ru_3(CO)_{12}$ is not as significant as in the case of $Os_3(CO)_{12}$. As in the latter case, the reaction yielded the $[Ru(CO)_3Cl_3]^-[Me_2NH_2]^+$ salt, whose structure was established in an X-ray diffraction experiment (see Fig. 2). The fact that the M—CO and M—Cl absorption bands for the osmium-containing salt coincide with the corresponding bands for the ruthenium-containing salt and for the known cesium salts $[M(CO)_3Cl_3]^-Cs^+$ (M = Ru, Os)[13] indicates that the anions in these compounds have similar structures. The $[Ru(CO)_3Cl_3]^-[PPN]^+$ salt is known to be an active catalyst of the addition of methyl formate to ethylene.[15] Therefore, we attempted to use the isolated salts $[M(CO)_3Cl_3]^-[Me_2NH_2]^+$ (M = Ru, Os) as catalysts of the addition of CCl_4 to compound **1**. We found that neither the ruthenium salt nor the osmium salt catalyzes the addition of CCl_4 to **1**; hence, it can be assumed that they result from chain termination. Therefore, the metal-carbonyl complexes isolated for the first time from the reaction under consideration can provide indirect evidence concerning the composition and structure of the catalytically active species. The results indicate that the reaction is catalyzed by a metal-carbonyl species, and, thus, the catalysis can be described in terms of the coordination mechanism[8] that was described in detail in a previous publication.[16] Taking into account the role of DMF, the following scheme for the addition of CCl_4 to **1** in the presence of $M_3(CO)_{12}$ (M = Ru, Os) can be proposed (Scheme 2).

According to this scheme, DMF is assumed to act as a π-donor facilitating cleavage of the M—M bond and promoting the oxidative addition of CCl_4. It is not inconceivable that the catalytically active species is not only capable of being π-coordinated to compound **1** but also partially abstracts CO from the coordinated DMF molecule thus enabling the coordination of Me_2NH to the metal. Generally, amines are stronger π-donors than DMF, and, apparently, this species can serve as a species responsible for chain termination, while the Me_2NH displaced from the coordination sphere is converted into the $Me_2NH_2^+$ cation. The data available at this point are not yet sufficient to describe the pathway yielding the $[M(CO)_3Cl_3]^-[Me_2NH_2]^+$ salts; however the fact that the initial $Ru_3(CO)_{12}$ is converted almost completely into this salt is evidence supporting the assumption that the salt results from chain termination. At the same time, when the reaction is catalyzed by $Os_3(CO)_{12}$, the mixture of reaction products does contain the initial

Scheme 2



carbonyl in addition to the salt $[Os(CO)_3Cl_3]^-[Me_2NH_2]^+$. In fact, after mixtures consisting of CCl_4, **1**, DMF, and $Os_3(CO)_{12}$ were heated for 40 h and compound **1**, CCl_4, DMF, and the resulting adduct **4** were isolated from the reaction mixture, 0.5 mL of CCl_4, 0.3 mL of **1**, and 0.04 g of DMF were again added to the solid residue (see Experimental). The new solutions were degassed and then heated for 20 and 40 h. The yields of adduct **4** were 18 and 32%, respectively (see Fig. 1, curve *7*). In addition, processing of the time dependence of the yield of adduct **4** using the integral method[17] indicates that the rate of the formation of **4** depends linearly on the concentration of CCl_4 (see Fig. 1, lines *6* and *7*). GLC of the reaction mixtures indicates that no other organic products that could result from transformations of CCl_4 are formed in noticeable amounts (more than 1%). Thus, the decrease in the rate of formation of adduct **4** with time is due to the decrease in the current concentration of CCl_4 rather than to the consumption of $Os_3(CO)_{12}$. These results imply that in this case, chain termination occurs at a lower rate than in the presence of $Ru_3(CO)_{12}$. It should be noted that the formation of the salts is not a consequence of direct participation of the Me_2NH arising through thermal decomposition of DMF in these processes. In fact, when some Me_2NH is added to the reaction mixture of the addition of CCl_4 to **1** in the presence of $M_3(CO)_{12}$ (M = Ru, Os), the yields of adduct **4** increase (33.7 and 31.8%); however, DMF is more efficient in this catalysis. It is significant that when the concentration of Me_2NH is larger than 0.3 mmol, the process is markedly inhibited but the $[M(CO)_3Cl_3]^-[Me_2NH_2]^+$ type salts are not formed. The IR spectra of the isolated precipitates do not contain absorption bands typical of these salts. These results suggest that $(Me_2NH)M(CO)_3Cl(CCl_3)$ formed intermediately in the presence of Me_2NH is less prone to react with electron-donating olefin **1** than its DMF-analog. As noted above, the formation of adduct **4** in the addition of CCl_4 to **1** in the presence of DMF and $M_3(CO)_{12}$ (M = Ru, Os) most likely follows a coordination mechanism (see Scheme 2). However, the role of DMF in this reaction might also consist in increasing the rate of the decomposition of the carbonyls to give $M(CO)_4$, *viz.*, the species responsible for the generation of radical adducts $CCl_3CH_2C^{\cdot}HC_4H_9$ and capable of abstracting chlorine from CCl_4. In this case, the addition of CCl_4 to **1** would be a free-radical chain process, because the metal-carbonyl species $[M(CO)_3Cl_3]^-[Me_2NH_2]^+$ do not catalyze this reaction. To decide between the two above schemes, we studied the addition of CCl_4 to the methyl ester of *N*-(*trans*-cinnamoyl)-L-proline (**2**) catalyzed by $M_3(CO)_{12}$ (M = Ru, Os) in the presence of DMF, because the $PhC^{\cdot}HCH(CCl_3)C(O)R'$ radical adducts resulting from the addition of CCl_3 to **2**, unlike the $CCl_3CH_2C^{\cdot}HAlk$ radical adducts, do not abstract chlorine from CCl_4.[18,19] We found that the reactions with compound **2** occur regio- and stereoselectively to give the diastereomers of adduct **3**, described previously,[18,19] which were identified using ^1H NMR spectroscopy. The yield of adduct **3** in the case of $Ru_3(CO)_{12}$ ($[CCl_4]_0 : [2]_0 = 230 : 1$) is 9% after 40 h, while that for $Os_3(CO)_{12}$ and $[CCl_4]_0 : [2]_0 = 16 : 1$ is 22% after 80 h. In the case of $Ru_3(CO)_{12}$ without DMF, adduct **3** was not formed under these experimental conditions. In the case of $Os_3(CO)_{12}$, its yield was 11%. According to ^1H NMR spectroscopy, the diastereomers were formed in a ratio of 1.5 : 1.

Thus, the use of $M_3(CO)_{12}$ (M = Ru, Os) in combination with DMF increases the catalytic activities of these carbonyls in the addition of CCl_4 to monomer **2**. The high stereoselectivity of the addition observed under the reaction conditions chosen suggests that the reaction follows a coordination mechanism.

The bond lengths and angles in the structure of the salt $[Ru(CO)_3Cl_3]^-[Me_2NH_2]^+$ are listed in Table 3.

The *rac*-isomer of the octahedral $[Ru(CO)_3Cl_3]^-$ anion has been structurally characterized in two complexes: $[Ru(CO)_3Cl_3]^-[H_5O_2]^+ \cdot SbCl_3$ [20] and $[Ru(CO)_3Cl_3]^-[S_5N_5]^+ \cdot 1/2\ CH_2Cl_2$.[21] The geometric parameters of the $[Ru(CO)_3Cl_3]^-$ anion are fairly close to those found before;[20,21] however, the crystal structure of the salt $[Ru(CO)_3Cl_3]^-[M_2NH_2]^+$ has some interesting peculiar features.

In the structure of this salt, centrosymmetrical dimers consisting of two $[Ru(CO)_3Cl_3]^-$ anions and two dimethylammonium cations (see Fig. 2) are formed through N—H...Cl hydrogen bonds. Both hydrogen atoms of the NH_2 group in the dimethylammonium cation (all the H atoms in the salt structure were arranged geometrically, see Experimental) participate in the formation of the hydrogen bonds with two Cl atoms of the neighboring anions: N(1)...Cl(1) is 3.24(1) Å (H(1a)...Cl(1) is 2.40 Å and the N(1)—H(1a)...Cl(1) angle is 157°); N(1)...Cl(2a) is 3.23(1) Å (H(1b)...Cl(2a) is 2.40 Å and N(1)—H(1b)...Cl(2a) is 154°). This dimer contains two more shortened contacts between the N atom and the Cl(3) atom (N(1)...Cl(3) is 3.23(1) Å and N(1)...Cl(3a) is 3.39(1) Å); however, taking into ac-

Table 3. Bond lengths (*d*) and angles (ω) in the structure of $[RuCl_3(CO)_3]^-[NH_2Me_2]^+$

Bond	*d*/Å	Bond	*d*/Å
Ru(1)—C(2)	1.904(8)	O(1)—C(1)	1.114(10)
Ru(1)—C(1)	1.906(9)	O(2)—C(2)	1.131(10)
Ru(1)—C(3)	1.977(7)	O(3)—C(3)	1.061(9)
Ru(1)—Cl(3)	2.406(2)	N(1)—C(4)	1.454(12)
Ru(1)—Cl(2)	2.413(2)	N(1)—C(5)	1.460(11)
Ru(1)—Cl(1)	2.428(2)		

Angle	ω/deg	Angle	ω/deg
C(2)—Ru(1)—C(1)	92.4(3)	C(2)—Ru(1)—Cl(1)	89.2(2)
C(2)—Ru(1)—C(3)	93.5(3)	C(1)—Ru(1)—Cl(1)	178.3(2)
C(1)—Ru(1)—C(3)	93.2(3)	C(3)—Ru(1)—Cl(1)	87.1(2)
C(2)—Ru(1)—Cl(3)	89.2(2)	Cl(3)—Ru(1)—Cl(1)	90.77(6)
C(1)—Ru(1)—Cl(3)	88.8(2)	Cl(2)—Ru(1)—Cl(1)	90.48(7)
C(3)—Ru(1)—Cl(3)	176.6(2)	C(4)—N(1)—C(5)	114.0(8)
C(2)—Ru(1)—Cl(2)	179.0(2)	O(1)—C(1)—Ru(1)	179.2(7)
C(1)—Ru(1)—Cl(2)	87.9(2)	O(2)—C(2)—Ru(1)	177.9(8)
C(3)—Ru(1)—Cl(2)	87.4(2)	O(3)—C(3)—Ru(1)	177.9(8)
Cl(3)—Ru(1)—Cl(2)	89.94(7)		

count the much larger distances, H(1a)...Cl(3), 2.78 Å, and H(1b)...Cl(3a), 2.87 Å, and the smaller angles, N(1)—H(1a)...Cl(3), 115°, and N(1)—H(1b)...Cl(3a), 119°, one can hardly speak of the existence of a bifurcated H-bond. This is indicated by the geometry of the anion, which is characterized by markedly inequivalent Ru—Cl distances. In fact, the Ru(1)—Cl(3) distance (2.406(2) Å) is somewhat shorter than the two other Ru—Cl distances (Ru(1)—Cl(1) is 2.428(2) Å and Ru(1)—Cl(2) is 2.413(2) Å), which can be explained by participation of the Cl(1) and Cl(2) atoms in hydrogen bonds. Dissimilar Ru—Cl distances have also been found in another study,[20] in which formation of a complex system of hydrogen bonds involving Cl atoms has also been observed. The fact that the Cl(3) does not participate in the H-bonds in the salt under consideration leads, apparently, to a substantial *trans*-influence of this atom. As a consequence, the Ru(1)—C(3) distance, equal to 1.977(7) Å, is much longer than the two other distances: Ru(1)—C(1), 1.906(9) Å, and Ru(1)—C(2), 1.904(8) Å, while the C(3)—O(3) distance, 1.061(9) Å, is correspondingly shorter than that of the C(1)—O(1) bond, 1.114(10) Å, or the C(2)—O(2) bond, 1.131(10) Å.

A further interesting feature of the geometry of the anion in the salt under consideration is that the C—Ru—C angles in the octahedron are slightly but regularly increased. Evidently, this results from the decrease in the C—Ru—Cl angles; the Cl—Ru—Cl angles retain values close to 90° (see Table 2). It is noteworthy that similar changes in the bond angles in the coordination octahedron of the Ru atom in the $[Ru(CO)_3Cl_3]^-$ anion have been described in earlier publications.[20,21]

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