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Synthesis of cationic allyl- and dienecarbonyl complexes of group VI–VIII metals in the presence of strong protonic acid

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Abstract

Cationic allylcarbonyl complexes of Cr, Mo, W, Mn, Re, Fe, Co, Rh and Ir are synthesized by reaction of a carbonyl-containing compound with allyl alcohol or conjugated diene in the presence of strong protonic acid. This reaction is promoted by an increase in basicity of the initial complex and an increase in acidity of the medium; the nature of the organic substrate is also important for synthesis of this type of carbonyl complex. Cationic diene complexes have been formed by the action of dienes and acid on compounds with a metal–metal bond or on neutral allyl complexes.

Introduction

Cationic organometallic complexes of transition metals appear to be of interest as reagents and catalysts in organic synthesis. At the same time, they exhibit a higher catalytic activity than the analogous neutral compounds [1–5]. Their high reactivity with respect to nucleophilic reagents is especially attractive [6,7]. However, no simple or sufficiently general method of synthesis for these complexes has been developed so far.

In organic chemistry, the method of synthesis of cationic particles in strong protonic acids is widely employed [8]. However, application of the latter for such purposes in organometallic chemistry is only of limited importance. Wide application of this method in organometallic chemistry has seemed to be restricted by the prejudice based on the idea of the intermediately formed products of protonation, particularly carbonyl derivatives of metals, being unstable [9].

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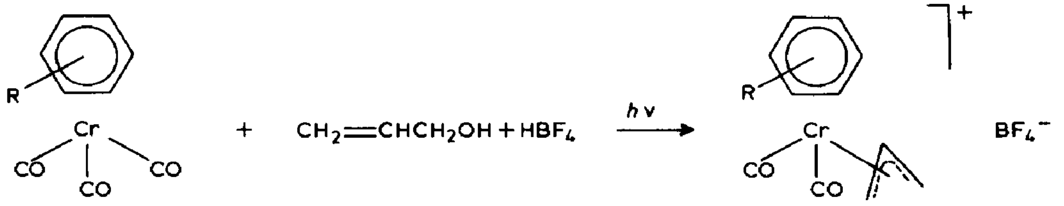
In the present paper, we propose to use strong protonic acids for the synthesis of cationic allyl, diene and ethylene complexes by means of ligand exchange *. This simple one-step synthesis is based on the carbonyl ligands exchange in metal carbonyls. By the use of a low oxidation state metal carbonyls the oxidation of the metal atom take place simultaneously with the substitution of the CO-group resulting in the formation of a stable cationic 18-electron complexes.

Results and discussion

Previously, we found that upon the simultaneous action of hydrofluoroboric acid and UV irradiation on a solution of arene–tricarbonylchromium complexes with allyl alcohol in ether, cationic allyl complexes I were smoothly formed [11,12].



In the present work we have made an attempt to determine the limits of application of this reaction. We have shown that it is of quite broad significance and thus that it could be extended to the carbonyl compounds of other metals and to other unsaturated substrates.

It turned out that even iron, molybdenum and tungsten carbonyls react with allyl alcohol and $HBF_4 \cdot Et_2O$ under UV irradiation to yield cationic allyl complexes II–IV [13].

$$M(CO)_n + CH_2{=}CHCH_2OH + HBF_4 \cdot Et_2O \xrightarrow{h\nu} \underset{\text{(II–IV)}}{[M(CO)_{n-1}(\eta^3\text{-}C_3H_5)]^+ BF_4^-}$$

(II: M = Fe, $n = 5$; III: M = W, $n = 6$; IV: M = Mo, $n = 6$)

In this case, iron and tungsten complexes are obtained rather smoothly in ether solution, while the molybdenum complex requires a less basic solvent (benzene). Similarly, no chromium compound was obtained, even under these conditions. Such a difference in the behaviour of the carbonyls of Group VI can be explained possibly by the decrease in basicity of identical compounds in the order W > Mo > Cr [14].

Complexes of iron(II) and tungsten(III) were found to be rather stable compounds; the molybdenum analogue readily decomposes and, therefore, it was characterized only by IR spectroscopy and elemental analysis. An increase in basicity of the initial compound due to the substitution of one CO group in

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* See the review on the synthesis of cationic arene complexes by this method, developed by one of us, in ref. 10.

$Mo(CO)_6$ for $P(OMe)_3$ made it possible to obtain a stable complex (V), even in ether.

$$(MeO)_3PMo(CO)_5 + CH_2{=}CHCH_2OH + HBF_4 \cdot Et_2O \xrightarrow{h\nu} \underset{(V)}{[(MeO)_3PMo(CO)_4(\eta\text{-}C_3H_5)]^+\ BF_4^-}$$

In the case of $Cr(CO)_6$, only the substitution of two carbonyl ligands for $P(OMe)_3$ results in the formation of an unstable cationic complex, the presence of which is assumed only on the basis of IR spectra.

Conjugated dienes form allylcarbonyl cationic complexes less easily than does allyl alcohol. Thus, the neutral butadiene–tricarbonyliron complex (VII) is formed upon UV irradiation of an ether solution of $Fe(CO)_5$ in the presence of $HBF_4 \cdot Et_2O$ and butadiene, instead of the cationic allyl complex VIII as in the case of allyl alcohol.

$$\begin{tikzcd}
Fe(CO)_5 + C_4H_6 + HBF_4 \cdot Et_2O \arrow[r, "h\nu"] & \underset{(VI)}{(CO)_4Fe(\eta^2\text{-}C_4H_6)} \arrow[r] \arrow[d, "\times" marking] & \underset{(VII)}{(CO)_3Fe(\eta^4\text{-}C_4H_6)} \\
 & \underset{(VIII)}{[(CO)_4Fe(\eta^3\text{-}C_4H_7)]^+\ BF_4^-} &
\end{tikzcd}$$

Complex VI formed in the first stage upon UV irradiation appears to turn into complex VII considerably faster (intramolecular reaction) than it is attacked by a proton, followed by the formation of complex VIII. Though it is well known that η^4-diene complexes of this type can be protonated readily, yielding cationic allyl complexes [15,16], the acidity of the medium appears to be insufficient in our case.

When $Fe_2(CO)_9$ is used as an initial compound in the absence of UV irradiation, precipitation of complex VIII from the reaction mixture takes place, but its yield is low (18%). At the same time, the solution contains a considerable amount of neutral η^2-complex VI, according to the IR spectral data.

$$Fe_2(CO)_9 + C_4H_6 + HBF_4 \cdot Et_2O \rightarrow \underset{(VI)}{(CO)_4Fe(\eta^2\text{-}C_4H_6)} + \underset{(VIII)}{[(CO)_4Fe(\eta^3\text{-}C_4H_7)]^+\ BF_4^-}$$

An increase in the acid concentration by evaporation of the solvent results in a higher yield of complex VIII (up to 78%). It should be noted that when allyl alcohol was used in this reaction, allyl complex II was obtained in 92% yield, without concentration of the solution *.

In the case of $W(CO)_6$, η^2-butadiene complex IX is also formed at the first stage, cationic crotyl complex X being formed only upon evaporating the reaction mixture,

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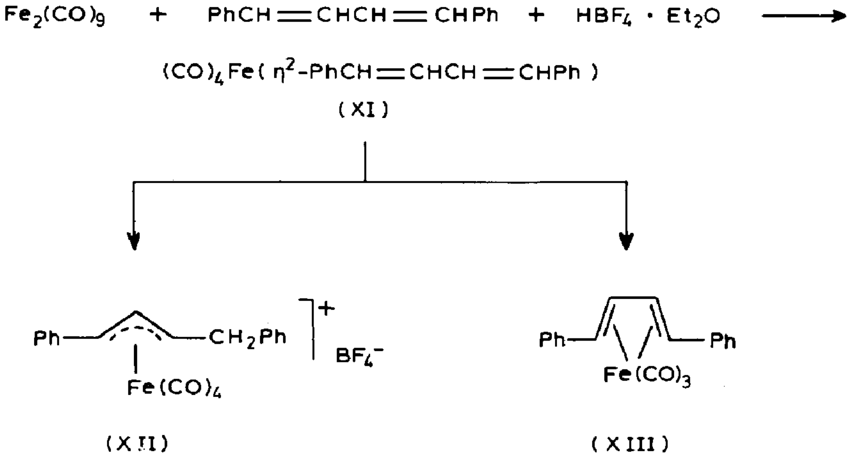
* Previously, this complex was obtained by Nicholas and co-workers [17]; however, addition of acid only after the formation of η^2-complex requires a CO atmosphere and thus complicates the reaction.

apparently due to a lower basicity of complex IX in comparison with its iron analogue VI.

$$W(CO)_6 + C_4H_6 + HBF_4 \cdot Et_2O \rightarrow \underset{(IX)}{(CO)_5W(\eta^2\text{-}C_4H_6)} \rightarrow \underset{(X)}{[(CO)_4W(\eta^3\text{-}C_4H_7)]^+ BF_4^-}$$

The presence of aryl substituents in the diene molecule results in a decreased tendency to form cationic allyl complexes. For example, only neutral complex XI is formed as a result of the interaction of $Fe_2(CO)_9$ with 1,4-diphenylbuta-1,3-diene and $HBF_4 \cdot Et_2O$ in ether, yielding upon evaporation of the reaction mixture cationic allyl complex XII with only a 2% yield. The main reaction product in this case is η^4-diene complex XIII.



When the reaction is performed in benzene, the increase in acidity of the medium results in a higher yield of XII (up to 28%). The corresponding complex of tungsten is not formed, even under these conditions.

The data obtained made it possible to assume that η^2-diene complexes were the intermediate products during the formation of cationic allylcarbonyl complexes; it was verified by means of IR spectroscopy in a number of cases. In the case of allyl alcohol, η^2-complexes are probably also formed first of all.

Half-sandwich derivatives of chromium, molybdenum, manganese and rhenium form stable cationic complexes, even in the presence of 48% aqueous HBF_4, due to the higher basicity of these derivatives as compared with carbonyls; in addition, the nature of the organic substrate does not noticeably affect the synthesis of these compounds * [11,12,18,19].

$$LM(CO)_3 + CH_2{=}CHCH_2OH + HBF_4 \xrightarrow{h\nu} \underset{(XIV\text{–}XVII)}{[LM(CO)_2(\eta^3\text{-}C_3H_5)]^+ BF_4^-}$$

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* Previously, a relative manganese complex was obtained in a low yield via several steps [20].

(XIV: $L = 1,3,5\text{-}(CH_3)_3C_6H_3$, $M = Cr$; XV; $L = 1,3,5\text{-}(CH_3)_3C_6H_3$, $M = Mo$;
XVI: $L = C_5H_5$, $M = Mn$; XVII: $L = C_5H_5$, $M = Re$)

$$LM(CO)_3 + \text{diene} + HBF_4 \xrightarrow{h\nu} [LM(CO)_2(\eta^3\text{-allyl})]^+\ BF_4^-$$
$$\text{(XVIII–XXV)}$$

It is necessary to use UV irradiation for the synthesis of cationic complexes (XIV–XXV), as in the reaction of mononuclear carbonyls with allyl alcohol or dienes. It should be noted that the UV irradiation time considerably increases upon transition downwards in a subgroup. Thus, the reaction time for molybdenum and rhenium complexes is 3–4 times longer than for the corresponding chromium and manganese derivatives, while tungsten complex hardly reacts with allyl alcohol under these conditions.

One can suppose that for the half-sandwich derivatives of Group VI and VII metals there is primary formation of η^2-complexes and subsequent protonation. This proposal is supported by the isomeric composition of cationic compounds obtained from conjugated dienes; this will be discussed in detail in a later paper [21].

Cyclopentadienyldicarbonyl complexes of cobalt and rhodium also react with allyl alcohol or diene in the presence of HBF_4 under UV irradiation to form the corresponding allyl complexes [22].

$$C_5H_5M(CO)_2 + CH_2{=}CHCH_2OH + HBF_4 \rightarrow [C_5H_5(CO)(\eta\text{-}C_3H_5)]^+\ BF_4^-$$
$$\text{(XXVI, } M = Co\text{; XXVII, } M = Rh\text{)}$$

$$C_5H_5M(CO)_2 + C_4H_6 + HBF_4 \rightarrow [C_5H_5M(CO)(syn\text{-}C_4H_7)]^+\ BF_4^-$$
$$\text{(XXVIIIa, } M = Co\text{; XXIXa, } M = Rh\text{)}$$
$$+ C_5H_5M(CO)(anti\text{-}C_4H_7)^+\ BF_4^-$$
$$\text{(XXVIIIb, } M = Co\text{; XXIXb, } M = Rh\text{)}$$

However, in the case of cobalt and rhodium UV irradiation is not necessarily required, unlike the other organometallic compounds used, and reaction time and yield depend on the acidity of the medium, which becomes maximal when $HBF_4 \cdot Et_2O$ and weakly basic solvents (benzene, nitromethane) are used. At the same time, the formation of anti-isomers (XXVIIIb, XXIXb, XXXb) typical for conjugated diene incorporation into the M–H bond of hydride complexes [23] allows us to propose a different reaction scheme, consisting of primary protonation of the metal atom in the initial complex with subsequent addition of the cationic metal hydride to the substrate. It is confirmed by IR spectroscopy identification of those products with an M–H bond (ν(CO) (nitromethane) 2115 and 2076 cm^{-1} in the case of $CpCo(CO)_2$) in the reaction mixture. In the case of the iridium complex, the protonation product (ν(CO) (nitromethane) 2136, 2096 cm^{-1}) is formed first and then a slow reaction with allyl alcohol starts, as demonstrated by special experiment.

$$C_5H_5Ir(CO)_2 + CH_2{=}CHCH_2OH + HBF_4 \cdot Et_2O \rightarrow [C_5H_5Ir(CO)_2H]^+\ BF_4^- \rightarrow$$
$$[C_5H_5Ir(CO)(C_3H_5)]^+\ BF_4^-$$
$$\text{(XXXI)}$$

The reaction with conjugated dienes is the most convincing example of how the π-electron system of the ligand easily adapts to the electron requirements of the metal upon the formation of the 18-electron complex. In the cases described above, the dienes produced the cationic allyl complexes. When binuclear carbonyl complexes such as $Co_2(CO)_8$ and $[CpMo(CO)_3]_2$ were used, cationic η^4-diene complexes were obtained from dienes under the same conditions.

The reaction of $Co_2(CO)_8$ with an excess of butadiene does not stop at the stage of complex XXXII previously obtained by Pauson and co-workers within two stages [24], but results in a mixture of mono- and previously unknown bis-butadiene complexes XXXIII [25]. The latter can be obtained individually by the action of butadiene on a solution of this mixture in nitromethane.

$$Co_2(CO)_8 + C_4H_6 + HBF_4 \cdot Et_2O \rightarrow \underset{\text{(XXXII)}}{[(C_4H_6)Co(CO)_3]^+\ BF_4^-}$$

$$+ \underset{\text{(XXXIII)}}{\left[(\eta^4\text{-}C_4H_6)_2Co(CO)\right]^+\ BF_4^-}$$

$$\text{XXXII} + \text{XXXIII} + C_4H_6 \rightarrow \underset{\text{(XXXIII)}}{\left[(\eta^4\text{-}C_4H_6)_2Co(CO)\right]^+\ BF_4^-}$$

The molybdenum dimer behaves similarly, though substitution of the CO-ligand proceeds less smoothly. Application of UV irradiation considerably reduces the reaction time and increases the yield of complex XXXV [26].

$$[C_5H_5Mo(CO)_3]_2 + \text{diene} + HBF_4 \cdot Et_2O \rightarrow \underset{\text{(XXXVa, b)}}{\left[C_5H_5Mo(CO_2)(\eta^4\text{-diene})\right]^+\ BF_4^-}$$

(diene = (a) butadiene, (b) isoprene)

It should be noted that complexes of this type with indenyl ligand were obtained previously [27] by a two-step synthesis using silver salts.

Cationic complexes from dimers $[C_5H_5Fe(CO)_2]_2$, $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ were also obtained from ethylene. Though the yields in this case are not high (20–25%), the reaction is performed at the atmospheric pressure of ethylene and is an easier reaction than that using carbonylhalide dimers [26].

$$[C_5H_5Fe(CO)_2]_2 + C_2H_4 + HBF_4 \cdot Et_2O \rightarrow \underset{\text{(XXXVI)}}{[C_5H_5Fe(CO)_2(\eta\text{-}C_2H_4)]^+\ BF_4^-}$$

$$M_2(CO)_{10} + C_2H_4 + HBF_4 \cdot Et_2O \rightarrow \underset{\substack{\text{(XXXVII, M = Mn;} \\ \text{XXXVIII, M = Re)}}}{[M(CO)_5(\eta\text{-}C_2H_4)]^+\ BF_4^-}$$

Previously, complex XXXVI was obtained from $[C_5H_5Fe(CO)_2]_2$ in acid medium [28–30] on addition of quinone or O_2, which were considered to be oxidants in this reaction. We have found that the formation of cationic complexes from dimers occurred in an inert atmosphere and therefore the protonating acid must play the role of oxidant.

It is known that $[C_5H_5Fe(CO)_2]_2$ produces a stable protonation product [9]. This product was obtained by us in the free state and when used in the reaction with ethylene yielded complex XXXVI, which confirms the participation of the dimer protonated form in the reaction. The protonated form of dimer is likely to degradate also in other cases, with the formation of a coordinatively unsaturated cationic particle. A similar scheme was proposed for nitrosyl derivatives of Group VI metals [31].

Thus, this reaction must be influenced by the basicity of the initial compound. Furthermore, the synthesis of cationic complexes from dimers must depend largely on the strength of the metal–metal bond in the protonation product. This assumption explains the fact that the ethylene complex of manganese (XXXVII) is formed under milder conditions than a similar compound of rhenium (XXXVIII) [26], though it is known that the basicity of analogous compounds of rhenium is higher than that of manganese compounds [32].

Synthesis of cationic complexes in strong protonic acids can be carried out also by means of exchange of ligands other than carbonyls. Thus, we managed to obtain cationic diene complexes of molybdenum by the action of dienes on neutral allyl complexes in the presence of $HBF_4 \cdot Et_2O$ [33], the use of 48% aqueous HBF_4 also being possible under UV irradiation.

$$C_5H_5Mo(CO)_2(\eta^3\text{-}C_3H_5) + \text{diene} + HBF_4 \cdot Et_2O \rightarrow$$

$$[C_5H_5Mo(CO)_2(\eta^4\text{-diene})]^+ BF_4^-$$

(XXXVa–XXXVd)

(diene = (a) butadiene, (b) isoprene, (c) cyclohexadiene, (d) cyclooctadiene)

It should be noted that Markham and co-workers have studied the behaviour of $C_5H_5Mo(CO)_2(C_3H_5)$ in acidic medium and have recently shown that a 14-electron cationic particle was formed in the process [34]. We have obtained similar cobalt complexes also from $(\eta\text{-}C_4H_7)Co(CO)_2P(OMe)_3$, though allyltricarbonylcobalt does not enter this reaction, probably due to low basicity * [33].

$$(\eta^3\text{-}C_4H_7)Co(CO)_2P(OMe)_3 + \text{diene} + HBF_4 \cdot Et_2O \rightarrow$$

$$[(\eta^4\text{-diene})Co(CO)_2P(OMe)_3]^+ BF_4^-$$

(XXXIXa, XXXIXb)

(diene = (a) isoprene, (b) cyclohexadiene)

Thus, we have developed a wide one-step method of synthesizing cationic complexes of transition metals by ligand exchange in strong protonic acid.

Experimental

All of the procedures for synthesizing cationic complexes were performed in an argon atmosphere, using absolute solvents. UV irradiation was performed using a PRK-7 lamp (1000 W). The structures of the complexes obtained were established by the methods of IR and ^1H NMR spectroscopy, such data being given in refs. 11, 13, 18, 19, 21, 22, 25, 26, 33.

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[*] Previously, Muetterties et al. obtained "quasidiene" cationic cobalt complexes by substitution of allyl in strongly basic cobalt complexes in acidic medium [35].

Table 1

Analytical data and reaction conditions for cationic allyl complexes

Complex	Method of synthesis	Organic substrate	Acid	Reaction time (h)	Yield (%)	Analytical data (Found (calcd.) (%)) C	H
$(CO)_5Mo(C_3H_5)BF_4$ (IV)	1	$CH_2{=}CHCH_2OH$	$HBF_4 \cdot Et_2O$	8	48	25.91 (26.41)	1.66 (1.38)
$(CO)_5W(C_3H_5)BF_4$ (III)	1	$CH_2{=}CHCH_2OH$	$HBF_4 \cdot Et_2O$	9	37	21.39 (21.27)	1.20 (1.12)
$(CO)_4Fe(C_3H_5)BF_4$ (II)	1	$CH_2{=}CHCH_2OH$	$HBF_4 \cdot Et_2O$	8	88	–	–
II	4	$CH_2{=}CHCH_2OH$	$HBF_4 \cdot Et_2O$	6	90	–	–
$(MeO)_3PMo(CO)_4(C_3H_5)BF_4$	1	$CH_2{=}CHCH_2OH$	$HBF_4 \cdot Et_2O$	8	54	–	–
$Me_3C_6H_3Cr(CO)_2(C_3H_5)BF_4$ (XIV)	1	$CH_2{=}CHCH_2OH$	48% HBF_4	3	78	47.22 (47.22)	4.81 (4.81)
$Me_3C_6H_3Mo(CO)_2(C_3H_5)BF_4$ (XV)	1	$CH_2{=}CHCH_2OH$	48% HBF_4	16	28	42.03 (41.31)	4.28 (4.31)
$CpMn(CO)_2(C_3H_5)BF_4$ (XVI)	1	$CH_2{=}CHCH_2OH$	48% HBF_4	5	55	39.99 (39.50)	3.41 (3.30)
$CpRe(CO)_2(C_3H_5)BF_4$ (XVII)	1	$CH_2{=}CHCH_2OH$	$HBF_4 \cdot Et_2O$	16	46	27.53 (27.60)	2.61 (2.32)
$CpCo(CO)(C_3H_5)BF_4$ (XXVI)	1	$CH_2{=}CHCH_2OH$	48% HBF_4	5	54	–	–
XXVI	2	$CH_2{=}CHCH_2OH$	$HBF_4 \cdot Et_2O$	0.5	82	–	–
$Me_3C_6H_3Cr(CO)_2(1,1\text{-}Me_2C_3H_3)BF_4$ (XXIa)	1	$CH_2{=}C(CH_3)CH{=}CH_2$	48% HBF_4	4	42	49.44 (50.03)	5.45 (5.51)
$Me_3C_6H_3Cr(CO)_2($*syn*$\text{-}1,2\text{-}Me_2C_3H_3)BF_4$ (XXIb)							
$CpMn(CO)_2(1,1\text{-}Me_2C_3H_3)BF_4$ (XXIIa)	1	$CH_2{=}C(CH_3)CH{=}CH_2$	48% HBF_4	5	20	34.40 (35.54)	3.16 (3.58)
$CpMn(CO)_2($*syn*$\text{-}1,2\text{-}Me_2C_3H_3)BF_4$ (XXIIb)							
$CpRe(CO)_2(1,1\text{-}Me_2C_3H_3)BF_4$ (XXIIIa)	1	$CH_2{=}C(CH_3)CH{=}CH_2$	$HBF_4 \cdot Et_2O$	16	28	–	–
$CpRe(CO)_2($*syn*$\text{-}1,2\text{-}Me_2C_3H_3)BF_4$ (XXIIIb)							

CpCo(CO)(1,1-$Me_2C_3H_3$)BF_4 (XXXa)	3	CH_2=C(CH_3)CH=CH_2	$HBF_4 \cdot Et_2O$	24	22	–	–
CpCo(CO)(*anti*-1,2-$Me_2C_3H_3$)BF_4 (XXXb)							
$Me_3C_6H_3Cr(CO)_2$(*syn*-1-EtC_3H_4)BF_4 (XXIVa)	1	CH_2=CHCH=$CHCH_3$	48% HBF_4	4	47	50.12 (50.03)	5.55 (5.51)
$Me_3C_6H_3Cr(CO)_2$(*syn*,*syn*-1,3-$Me_2C_3H_3$)BF_4 (XXIVb)							
$CpMn(CO)_2$(*syn*-1-EtC_3H_4)BF_4 (XXVa)	1	CH_2=CHCH=$CHCH_3$	48% HBF_4	5	31	42.97 (43.41)	4.40 (4.25)
$CpMn(CO)_2$(*syn*,*syn*-1,3-$Me_2C_3H_3$)BF_4 (XXVb)							
$(CO)_4$Fe(*syn*-1-Ph,*syn*-3-CH_2Ph-C_3H_3)BF_4 (XIII)	4	PhCH=CHCH=CHPh	$HBF_4 \cdot Et_2O$	5	28	–	–
CpRh(CO)(C_3H_5)BF_4 (XXVII)	2	CH_2=$CHCH_2OH$	$HBF_4 \cdot Et_2O$	0.5	87	34.06 (33.38)	2.49 (3.11)
CpIr(CO)(C_3H_5)BF_4 (XXXI)	2	CH_2=$CHCH_2OH$	$HBF_4 \cdot Et_2O$	4	67	–	–
$(CO)_5$W(*syn*-MeC_3H_4)BF_4 (IX)	1	CH_2=CHCH=CH_2	$HBF_4 \cdot Et_2O$	7	25	–	–
$(CO)_4$Fe(*syn*-MeC_3H_4)BF_4 (VIII)	4	CH_2=CHCH=CH_2	$HBF_4 \cdot Et_2O$	5	78	–	–
$Me_3C_6H_3Cr(CO)_2$(*syn*-MeC_3H_4)BF_4 (XVIII)	1	CH_2=CHCH=CH_2	48% HBF_4	4	72	48.65 (48.68)	5.14 (5.17)
$CpMn(CO)_2$(*syn*-MeC_3H_4)BF_4 (XIX)	1	CH=CHCH=CH_2	48% HBF_4	5	35	40.90 (41.55)	3.74 (3.80)
$CpRe(CO)_2$(*syn*-MeC_3H_4)BF_4 (XX)	1	CH_2=CHCH=CH_2	$HBF_4 \cdot Et_2O$	16	20	29.64 (29.41)	2.60 (2.69)
CpCo(CO)(*syn*-MeC_3H_4)BF_4 (XXVIIa)	1	CH_2=CHCH=CH_2	$HBF_4 \cdot Et_2O$	8	65		
CpCo(CO)(*anti*-MeC_3H_4)BF_4 (XXVIIb)							
XXVIIa/XXVIIb	2	CH_2=CHCH=CH_2	$HBF_4 \cdot Et_2O$	24	18	–	–
CpRh(CO)(*syn*-MeC_3H_4)BF_4 (XXIXa)	2	CH_2=CHCH=CH_2	$HBF_4 \cdot Et_2O$	24	15		
CpRh(CO)(*anti*-MeC_3H_4)BF_4 (XXIXb)							

1. Synthesis of cationic allyl complexes under UV irradiation

A solution of the initial complex (1 mmol) in 70 ml of ether * was placed in a three-necked flask equipped with an inner condenser and an inlet for argon. Equimolecular amounts of allyl alcohol or conjugated diene and hydrofluoroboric acid were added. The precipitate obtained after irradiation of the reaction mixture was filtered off, washed with ether, dissolved in a minimum amount of nitromethane and precipitated with ether. The reaction conditions, yields and analytical data are listed in Table 1.

2. Synthesis of cationic cyclopentadienylallylcarbonyl complexes of cobalt and rhodium

Allyl alcohol (1 mmol) and the $HBF_4 \cdot Et_2O$ were added, with stirring, to a solution of $C_5H_5M(CO)_2$ (1 mmol) in 5 ml of nitromethane. The mixture obtained was stirred for 0.5 h and then 50 ml of ether were added. The precipitation formed was filtered off, washed with ether and dried. The yield of cobalt and rhodium complexes was 82 and 87%, respectively.

3. Synthesis of cyclopentadienylallylcarbonyl complexes of cobalt and rhodium from conjugated dienes

An excess of butadiene (isoprene) and $HBF_4 \cdot Et_2O$ (1 mmol) was added to a solution of $C_5H_5M(CO)_2$ (1 mmol) in 15 ml of ether and the mixture was stirred for 24 h. The precipitate formed was filtered off, washed with ether and dried in vacuo.

4. Synthesis of cationic allyl complexes of iron from nonacarbonyldiiron

Allyl alcohol or diene (1 mmol) and 1 mmol of $HBF_4 \cdot Et_2O$ were added to a suspension of 1 mmol of $Fe_2(CO)_9$ in 30 ml of solvent and stirred up to complete disappearance of $Fe_2(CO)_9$ (4–6 h). The precipitate formed was filtered off, washed with ether and reprecipitated from nitromethane.

5. Synthesis of cationic olefin complexes

Ethylene was bubbled through a solution of dimer (1 mmol) and $HBF_4 \cdot Et_2O$ (2 mmol) in 10 ml of nitromethane for 24 h. The reaction mixture was concentrated in vacuo to 5 ml and 30 ml of ether were added. The precipitate formed was filtered off, washed with ether and dried. Found: $[(CO)_5Mn(\eta\text{-}C_2H_4)]^+ BF_4^-$ 26%, IR: $\nu(CO)$ (CH_3NO_2) 2160, 2068 cm^{-1} [36], $[(CO)_5Re(\eta\text{-}C_2H_4)]^+ BF_4^-$ 22%, IR: $\nu(CO)$ (CH_3NO_2) 2170, 2073 cm^{-1} [36], $[CpFe(CO)_2(\eta\text{-}C_2H_4)]^+ BF_4^-$, IR: $\nu(CO)$ (CH_2Cl_2) 2073, 2028 cm^{-1}. ^1H NMR (acetone-d_6): 3.55s (4H); 5.70s (5H) [36].

6. Synthesis of cationic diene complexes from dimers

An excess of diene and $HBF_4 \cdot Et_2O$ (2 mmol) was added to a 1 mmol solution of $Co_2(CO)_8$ or $Cp_2Mo_2(CO)_6$. The precipitate formed was filtered off, washed with ether and reprecipitated from nitromethane.

A 22% yield of $[(CO)_3Co(\eta\text{-}C_4H_6)]^+ BF_4^-$ was obtained from $Co_2(CO)_8$ and butadiene at 0 °C for 24 h; 0.17 g of a mixture $[(CO)_3Co(\eta^4\text{-}C_4H_6)]^+ BF_4^-$ and $[(CO)Co(\eta^4\text{-}C_4H_6)_2]^+ BF_4^-$ in the ratio 3/1 according to ^1H NMR data was obtained from $Co_2(CO)_8$ (1 mmol at 25 °C for 24 h); 0.14 g (24%) of $[(CO)_3Co(\eta^4\text{-}C_5H_8)]^+ BF_4^-$ was obtained from $Co_2(CO)_8$ (1 mmol) and isoprene at 25 °C for 24

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* In the case of $Mo(CO)_6$, benzene was used instead of ether.

h; 0.10 g (13%) of $[CpMo(CO)_2(\eta^4\text{-}C_5H_8)]^+\ BF_4^-$ was obtained from $Cp_2Mo_2(CO)_6$ and isoprene at 25 °C for 85 h; 0.18 g (24%) of $[CpMo(CO)_2(\eta^4\text{-}C_5H_8)]^+\ BF_4^-$ was obtained upon UV irradiation of the same mixture.

7. Synthesis of cationic diene complexes from neutral allyl compounds

A 1 mmol solution of the initial complex, 1 mmol of $HBF_4 \cdot Et_2O$ and an excess of diene were stirred in 25 ml of ether for 24 h. The precipitate formed was filtered off, washed with ether and reprecipitated from nitromethane.

A 0.13 g (35%) yield of $[CpMo(CO)_2(\eta^4\text{-}C_5H_8)]^+\ BF_4^-$ was obtained from $CpMo(CO)_2(\eta\text{-}C_3H_5)$ and isoprene; 0.13 g (34%) of $[CpMo(CO)_2(\eta^4\text{-}C_6H_8)]^+\ BF_4^-$ was obtained from $CpMo(CO)_2(\eta\text{-}C_3H_5)$ and 1,3-cyclohexadiene; 0.06 g (15%) of $[CpMo(CO)_2(\eta^4\text{-}C_8H_{12})]^+\ BF_4^-$ was obtained from $CpMo(CO)_2(\eta\text{-}C_3H_5)$ and 1,5-cyclooctadiene. $[(CH_3O)_3PCo(CO)_2(\eta^4\text{-}C_5H_8)]^+\ BF_4^-$ and $[(CH_3O)_3PCo(CO)_2(\eta^4\text{-}C_6H_8)\}^+\ BF_4^-$ were obtained in the same way from $(CH_3O)_3PCo(CO)_2(\eta^3\text{-}C_4H_7)$ and isoprene or cyclohexadiene, respectively.

UV irradiation of an ether solution of 0.13 g of $CpMo(CO)_2(\eta^3\text{-}C_3H_5)$ (0.5 mmol), an excess of butadiene and 0.5 mmol of $HBF_4 \cdot Et_2O$ for 7 h resulted in the formation of 0.07 g (40%) of $[CpMo(CO)_2(\eta^4\text{-}C_4H_6)]^+\ BF_4^-$.

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