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Investigation of the stereochemistry of transition metal allyl cationic complexes

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Abstract

Stereochemistry of transition metal-allyl cationic complexes synthesized by reaction of the corresponding metal carbonyls with allyl alcohol or a conjugated diene in the presence of a strong protonic acid has been investigated by means of NMR and IR spectroscopy. The number of isomers, as well as the position of substituents in the allyl ligands of complexes of the group 6 and 7 metals and iron, is determined by the formation of η^2-diene complexes in the transoid conformation in which the diene is coordinated via a substituted or non-substituted double bond. The protonation products formed in the initial stage of the reactions of $CpM(CO)_2$ (where M = Co, Rh, Ir) with acids lead to the mixtures of *syn*- and *anti*-crotyl isomers in their subsequent reactions with butadiene, the *anti*-isomers being transformed into *syn*-complexes on heating. The study of conformational isomerism of the half-sandwich allyl complexes has shown that the Cr, Mo, W, Mn and Re compounds of $[LM(CO)_2(allyl)]^+ BF_4^-$ (where L = arene, cyclopentadienyl) exist in the form of equilibrium mixtures of *exo*- and *endo*-conformers, the *endo*-conformer prevailing in the case of Mo, W and Re; for $[CpM(CO)(allyl)]^+ BF_4^-$ (where M = Co, Rh, Ir), disappearance of the *endo*-isomer on heating has been observed.

Introduction

The positive charge in the cationic allyl complexes of transition metals is responsible for their reactions with a variety of nucleophilic agents, thus making it possible for the complexes to be used as allylating agents in preparative organic synthesis. In some cases the addition of nucleophilic agents occurs regioselectively, thus allowing the structure of the products of stoichiometric as well as of catalytic reactions to be controlled [1a–1d]. Regioselectivity of these reactions depends on the structure of the cationic allyl complexes, including their isomerism [1c–1e]. Therefore, the study of isomerism of cationic complexes and the reasons behind the

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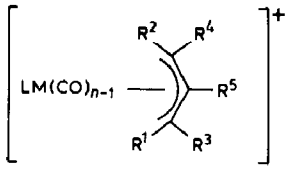
Table 1

IR and NMR data for BF_4^- salts of cationic allyl complexes of type



Complex	ν(CO) (cm^{-1})	Chemical shifts (ppm) and coupling constants (Hz)					
		R^1	R^2	R^3	R^4	R^5	L
IV	2140, 2058, 2018, 1939	3.59d, J_{15} 12.0	4.85dq, J_{25} 12.0, J_{24} 6.5	4.69d, J_{35} 6.5	2.50d(Me), J_{24} 6.5	5.50td [c], J_{15} J_{25} 12.0, J_{35} 6.5	–
V	2155, 2090	3.00d, J_{15} 12.0	4.44dq, J_{25} 12.0, J_{24} 6.0	4.04d, J_{35} 6.5	2.16d(Me), J_{24} 6.5	5.41m [c]	–
IXa	2152, 2090	2.117s(Me)	3.540dd, J_{25} 11.8, J_{24} 3.3	2.530s(Me)	4.434dd, J_{45} 7.3, J_{24} 3.3,	5.780dd [c] J_{25} 11.8, J_{45} 7.3	–
XIIIa	2152, 2090	4.462dq, J_{15} 11.6 J_{13} 6.3	4.462dq, J_{25} 11.6, J_{24} 6.3	2.394d(Me), J_{13} 6.3	2.394d(Me), J_{24} 6.3	5.693t [c] J_{15}, J_{25} 11.6	–
		3.755dd, J_{15} 12.2, J_{13} 3.1	4.793ddd, J_{26} 15.1, J_{25} 12.2, J_{27} 3.0	4.343dd, J_{35} 7.2, J_{13} 3.1,	2.012t(Me) J(Me–H^6), J(Me–H^7) 7.4 2.588ddq (H^6) J_{62} 15.1, J(Me–H^6) 7.4, J_{67} 7.4, 2.768ddq (H_7), J(Me–H^7) 7.4, J_{67} 7.4, J_{72} 3.0	6.038td J_{15}, J_{25} 12.2, J_{35} 7.2	–

XXII	1980, 1927 [b]	1.37d, J_{15} 12.0	1.37d, J_{25} 12.0	3.82d, J_{35} 8.0	3.82d, J_{45} 8.0	4.78–5.22m	2.44s(9H,3Me) [d], 6.52s(3H)
VI	1977, 1923 [b]	1.376dd, J_{15} 10.8, J_{13} 2.0	2.205dq, J_{25} 10.8, J_{24} 6.0	3.654dd, J_{35} 7.0, J_{13} 2.0	2.152d(Me), J_{24} 6.0	4.745td J_{15}, J_{52} 10.8 J_{35} 7.0	2.442s(9H,3Me) [d], 6.459s(3H)
Xa	1977, 1927 [b]	0.853s(Me)	1.966dd, J_{25} 11.4, J_{24} 3.5	2.189c(Me)	3.737dd, J_{45} 7.0, J_{24} 3.5	4.578dd, J_{25} 11.4, J_{45} 7.0	2.189s(9H,3Me) [d] 6.409s(3H)
Xb	1998, 1952	2.476s	3.467q, J_{24} 6.5	3.842s	2.165d(Me), J_{24} 6.5	1.355s(Me)	2.372s(9H,3Me), 6.362s(3H)
XIVa	1976, 1923 [b]	1.805dq, J_{15} 10.4, J_{13} 6.7	1.805dq, J_{25} 10.4, J_{24} 6.7	2.179d(Me), J_{13} 6.7	2.179d(Me), J_{24} 6.7	4.753t, J_{15}, J_{25} 10.4	2.498s(9H,3Me) [d], 6.301s(3H)
XIVb		1.353dd, J_{15} 10.8, J_{13} 2.2	1.952ddd, J_{25} 10.8, J_{26} 10.2, J_{27} 4.4	3.664dd, J_{35} 7.0, J_{13} 2.2	1.273t(Me), J(Me–H^6) J(Me–H^7) 7.8 2.10–2.60m (H^u6,H^7)	4.682dt, J_{15}, J_{25} 10.8, J_{35} 7.0	2.498s(9H,3Me), 6.415s(3H)
XIVc		1.034d(Me), J 6.4					2.355s(9H,3Me), 6.394s(3H)
XXIII-*endo*	2010, 1967 [b]	2.045d, J_{15} 10.5	2.045d, J_{25} 10.5	3.461d, J_{35} 5.6	3.461d, J_{45} 5.6	4.200tt, J_{15}, J_{25} 10.5, J_{35},J_{45} 5.6	2.328s(9H,3Me) [e], 6.489s(3H)
XXIII-*exo*	1992, 1924	1.700d, J_{15} 11.3	1.700d, J_{25} 11.3	–	–	4.200m	2.359s(9H,3Me), 6.609s(3H)
XXI-*endo*	2041, 2002 [b]	3.656d, J_{15} 11.2	3.656d, J_{25} 11.2	4.736d, J_{35} 6.9	4.736d, J_{45} 6.9	5.886tt, J_{15}, J_{25} 11.2, J_{35}, J_{45} 6.9	5.886s(5H) [d]
XXI-*exo*		2.416d, J_{15} 11.4	2.416d, J_{25} 11.4	4.503d, J_{35} 7.0	4.503d, J_{45} 7.0	5.974tt J_{15}, J_{25} 11.4 J_{35}, J_{45} 7.0	5.840s(5H)

Table 1 (continued)

Complex	ν(CO) (cm^{-1})	Chemical shifts (ppm) and coupling constants (Hz)					
		R^1	R^2	R^3	R^4	R^5	L
XII	2043, 2000 [b]	2.161d, J_{15} 12.2	3.362dq, J_{25}, 12.2, J_{24} 6.5	4.325d, J_{35}, 6.8	2.178d(Me), J_{24} 6.5	5.852dt, J_{15}, J_{25} 12.2, J_{35} 6.8	5.793s(5H) [d]
XIa	2036, 1982 [b]	1.365s(Me)	2.747dd, J_{25} 11.6, J_{24} 2.4	2.311s(Me)	4.491dd, J_{45} 7.1, J_{24} 2.4	5.645dd, J_{25} 11.6, J_{45} 7.1	5.751s(5H) [d]
XIb	2045, 2002 [b]	3.381s	4.588q, J_{24} 6.8	4.309s	2.270d(Me), J_{24} 6.8	1.794s(Me)	5.800s(5H)
XVa	2041, 2000 [b]	3.074dq J_{15} 10.7, J_{13} 6.5	3.074dq, J_{25} 10.7, J_{24} 6.5	2.184d(Me), J_{13} 6.5	2.184d(Me), J_{24} 6.5	5.883t, J_{15}, J_{25} 10.7	5.775s(5H) [d]
XVb	2043, 2001 [b]	2.164dd J_{15} 11.2 J_{13} 1.0	3.302ddd, J_{23} 11.2, J_{26} 8.8, J_{27} 5.5	4.342dd, J_{35} 6.6, J_{13} 1.0	1.306t(Me), J(Me–H^6), J(Me–H^7) 7.4, 2.353ddq (H^6) J_{26} 8.8, $J_{6\text{-Me}}$ 7.4, J_{67} 7.2 2.474ddq (H_7), $J_{7\text{-Me}}$ 7.4, J_{67} 7.2, J_{72} 5.5	5.836dt, J_{15}, J_{25} 11.2, J_{35} 6.6	5.782s(5H) [d]
XXII-*endo*	2060, 2004 [a]	3.466d, J_{15} 10.4	3.466d, J_{25} 10.4	3.843d, J_{35} 6.1	3.843d, J_{45} 6.1	4.960tt, J_{15}, J_{25} 10.4, J_{35}, J_{45} 6.1	6.352s(5H) [d]
XXII-*exo*	2047, 1982 [a]	2.715d, J_{15} 10.7	2.715d, J_{25} 10.7	4.140d, J_{35} 7.0	4.140d, J_{45} 7.0	5.328tt, J_{15}, J_{25} 10.7, J_{35}, J_{45} 7.0	6.379s(5H)

VIII-*endo*	2054, 2001 [b]	3.206dd, J_{15} 12.1, J_{13} 1.4	4.353dq, J_{25} 10.5, J_{24} 6.1	3.609dd, J_{35} 6.1, J_{13} 1.4	2.146d(Me), J_{42} 6.1	4.860ddd, J_{15} 12.1, J_{25} 10.5, J_{35} 6.1	6.298s(5H) [d]
VIII-*exo*	2043, 1981 [b]	2.341dd, J_{15} 11.1, J_{13} 1.8	3.648dq, J_{25} 11.1, J_{24} 6.4	3.840dd, J_{35} 6.9, J_{13} 1.8	2.145d(Me), J_{24} 6.4	5.312ddd, J_{15}, J_{25} 11.1, J_{35} 6.9	6.364s(5H)
XIIa	2050, 1995 [b]	1.865s(Me)	2.763dd, J_{25} 10.4, J_{24} 3.4	2.262s(Me)	3.964dd, J_{45} 6.9, J_{24} 3.4	5.377dd, J_{25} 10.4, J_{45} 6.9	6.375s(5H) [d]
XIIb	2033, 1973 [b]	3.334d, J_{13} 1.5	4.419q, J_{24} 6.2	3.807d, J_{13} 1.5	2.130d(Me), j_{24} 6.2	2.618s(Me)	6.232s(5H)
XVIII	2086 [b]	2.856d, J_{15} 12.4	2.856d, J_{25} 12.4	4.773d, J_{35} 7.1	4.773d, J_{45} 7.1	5.782tt, J_{15}, J_{25} 12.4, J_{35}, J_{45} 7.1	6.176s(5H) [d]
XVIa	2079 [b]	2.504dd, J_{15} 12.0, J_{13} 0.9	3.846dq, J_{25} 12.0, J_{24} 6.4	4.488dd, J_{35} 7.1, J_{13} 0.9	1.958d(Me), J_{24} 6.4	5.781dt, J_{15}, J_{25} 12.0, J_{35} 7.1	6.031s(5H) [d]
XVIb		3.331dd, J_{15} 13.1, J_{13} 1.5	1.204d(Me), J_{24} 7.1	4.873dd, J_{35} 7.3, J_{13} 1.5	5.9–6.1m	5.623dt, J_{15} 13.1, J_{35}, J_{45} 7.3	6.063s(5H)
XIX-*endo*	2093 [b]	3.806d, J_{15} 12.6	3.806d, J_{25} 12.6	4.534d, J_{35} 7.0	4.534d, J_{45} 7.0	–	6.339d(5H) [d] J(HRh) 1.0
XIX-*exo*		3.185dd, J_{15} 11.8, J_{13} 1.0	3.185dd, J_{25} 11.8, J_{24} 1.0	4.645dd, J_{35} 6.8, J_{13} 1.0	4.645dd, J_{45} 6.8, J_{24} 1.0	5.684ttd, J_{15}, J_{25} 11.8, J_{35}, J_{45} 6.8, (H-Rh) 1.0	6.256d(5H), J(HRh) 1.0
XVII-*endo*	2084 [b]	3.343d, J_{15} 12.0	4.779dq, J_{25} 12.0, J_{24} 6.9	4.051d, J_{35} 6.8	2.068d(Me), J_{24} 6.3	5.102tdd, J_{15}, J_{25} 12.0, J_{35} 6.9, J(HRh) 1.1	5.997s(5H) [c]
XVII-*exo*		2.719dd, J_{15} 11.6, J_{13} 1.5	4.081dq, J_{25} 12.4, J_{24} 6.3	4.220dd, J_{35} 6.9, J_{13} 1.5	1.984d(Me), J_{24} 6.3	5.450dddd, J_{15} 11.6, J_{25} 12.4, J_{35} 6.9, J(HRh) 1.5	5.889s(5H)

Table 1 (continued)

Complex	ν(CO) (cm^{-1})	Chemical shifts (ppm) and coupling constants (Hz)					
		R^1	R^2	R^3	R^4	R^5	L
XVIIb-*endo*		–	1.807d(Me), J_{25} 6.1	–	–	–	5.877s(5H)
XVIIb-*exo*		3.462d, J_{15} 12.5	1.574d(Me), J_{25} 6.9	4.565d, J_{35} 7.4	5.670dq, J_{45} 7.4, J_{35} 6.9	5.378dt, J_{15} 12.5, J_{35}, J_{45} 7.4	5.920s(5H)
XX-*endo*	2069 [b]	3.592dd, J_{15} 11.5, J_{13} 0.8	3.592dd, J_{25} 11.5, J_{24} 0.8	4.298dd, J_{35} 6.7, J_{13} 0.8	4.298dd, J_{45} 6.7, J_{24} 0.8	5.176tt, J_{15}, J_{25} 11.5, J_{35}, J_{45} 6.7	6.473s(5H) [d]
XX-*exo*		3.000dd, J_{15} 10.9, J_{13} 1.2	3.000dd, J_{25} 10.9, J_{23} 1.2	4.372dd, J_{35} 6.7, J_{13} 1.2	4.372dd, J_{45} 6.7, J_{24} 1.2	5.365tt, J_{15}, J_{25} 10.9, J_{35}, J_{45} 6.7	6.402s(5H)
XXIV	2012,1960 (*endo*), 1995, 1935 [a] (*exo*)	1.924d, J_{15} 10.6	1.924d, J_{25} 10.6	3.240d, J_{35} 6.1	3.240d, J_{45} 6.1	4.447tt, J_{15}, J_{35} 10.6, J_{25}, J_{45} 6.1	2.410c(9H,3Me) [e], 6.431c(3H)
(η^5-C_9H_7)-$Re(CO)_2C_3H_5$	2063, 2007 (*endo*)	0.310d, J_{15} 10.6	0.310d, J_{25} 6.2	4.447d, J_{35} 6.2	4.447d, J_{45} 6.2	4.666tt, J_{15}, J_{25} 10.6, J_{35}, J_{45} 6.2	6.295t(1H, J 2.6) [f], 6.770d(2H, J 2.6), 7.42–7.68m(4H)
	2059, 1986 (*exo*)	2.625dd, J_{15} 10.8, J_{13} 0.9	2.625dd, J_{25} 10.8, J_{24} 0.9	3.364dd, J_{35} 7.0, J_{13} 0.9	3.364dd, J_{45} 7.0, J_{24} 0.9	1.668tt, J_{15}, J_{25} 10.8, J_{35}, J_{45} 0.9	6.295t(1H, J 2.6) 6.808d(2H, J 2.6) 7.42–7.68m(4H)

[a] In CH_3NO_2. [b] In $(CH_3)_2CO$. [c] In CF_3COOD. [d] In $(CD_3)_2CO$. [e] In CD_3NO_2 at −25°C. [f] In CD_3NO_2.

different types has acquired special interest. At the same time, in the absence of a general route for the synthesis of allyl complexes a systematic study of isomerism in these compounds has not yet been performed.

Results and discussion

We have already developed a general one-stage synthetic route to allylcarbonyl cationic complexes, based on the interaction of an organometallic compound with allyl alcohol or a conjugated diene in the presence of a strong protonic acid [2a–2f].

A wide range of allyl derivatives of the group 6 and 7 metals (including earlier unknown compounds) has been obtained by this method. The present paper is concerned with their stereochemistry, studied by means of IR and NMR spectroscopy.

In general, the NMR spectra of the allyl ligands (Table 1) are analogous to those of the neutral compounds; however, all of the proton signals are shifted downfield, due to the positive charge of the complexes. The chemical shifts of *anti*-protons at terminal and substituted carbon atoms lie in the ranges 2.0–3.5 and 3.5–4.5 ppm, respectively. The chemical shifts of *syn*-protons at terminal and substituted carbon atoms lie in the ranges 3.5–5.0 and 4.5–6.0 ppm, respectively. The range 5.0–6.0 is characteristic of the signals of central protons. Coupling constants are typical of the allyl complexes and their values vary as follows: J_{anti} 10–14 Hz; J_{syn} 6.0–8.0 Hz; J_{gem} 1.0–4.0 Hz. The *anti*-, *syn*- and central methyl group signals lie in the ranges 0.8–1.7, 1.4–2.6 and 2.2–2.5 ppm, respectively.

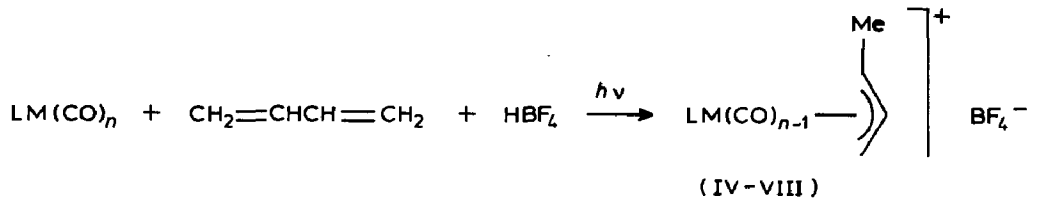
Several types of isomerism occur in allyl complexes: *syn*- and *anti*- (Ia,Ib) isomerism, caused by the different position of the substituent in the allyl ligand (IIa,IIb); and conformational isomerism (IIIa,IIIb) (Fig. 1).

The use of dienes allows cationic complexes to be formed which have substituted allyl ligands and exhibit all three types of isomerism, the formation of a particular isomer being largely dependent on the nature of the initial complex and diene.

The reaction of carbonyl derivatives with butadiene in the presence of tetrafluoroboric acid is stereospecific and leads to the formation of complexes IV–VIII with

(Ia) *syn* (Ib) *anti* (IIa) (IIb)

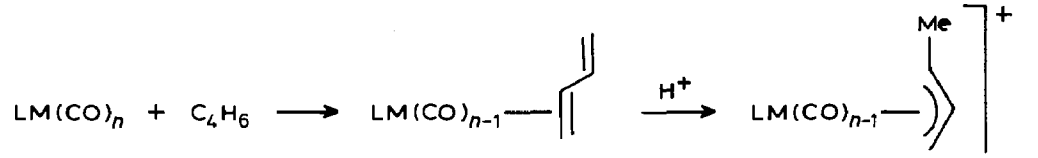
(IIIa) *endo* (IIIb) *exo*



(IV-VIII)

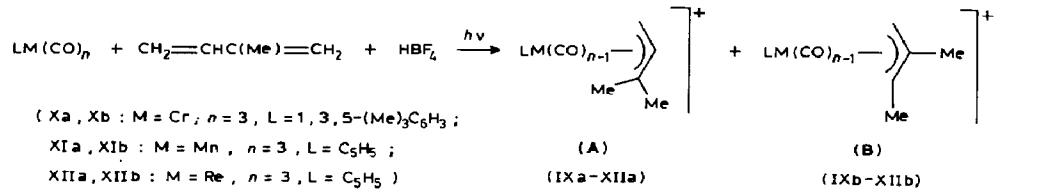
syn-crotyl ligands exclusively (IV): M = W, $n = 6$; V: M = Fe, $n = 5$; VI: M = Cr, $n = 3$, L = 1,3,5-$(CH_3)_3C_6H_3$; VII: M = Mn, $n = 3$, L = C_5H_5; VIII: M = Re, $n = 3$, L = C_5H_5).

The formation of intermediate η^2-diene complexes may be responsible for the stereospecificity of this reaction; in the case of $W(CO)_6$ and $Fe_2(CO)_9$ at low $HBF_4 \cdot Et_2O$ concentration, the existence of such complexes was proved by IR spectra [2e]. In good agreement with literature data [3,4], protonation of η^2-diene complexes in the transoid conformation * leads to *syn*-isomers.



It is noteworthy that according to ref. 6 protonation of η^4-diene complexes with a fixed cisoid conformation leads exclusively to *anti*-crotyl derivatives.

We have shown that when asymmetric dienes (isoprene, *Z*- and *E*-piperylenes) are used in the synthesis of cationic allyl complexes, a mixture of isomers is usually formed. Thus 1,1-dimethyl and 1,2-*syn*-dimethylallyl derivatives were obtained in reactions of $Fe_2(CO)_9$, 1,3,5-$(Me_3)_3C_6H_3Cr(CO)_3$ and $C_5H_5M(CO)_3$ (M = Mn, Re) with isoprene (**A** and **B**, Scheme 1) **.

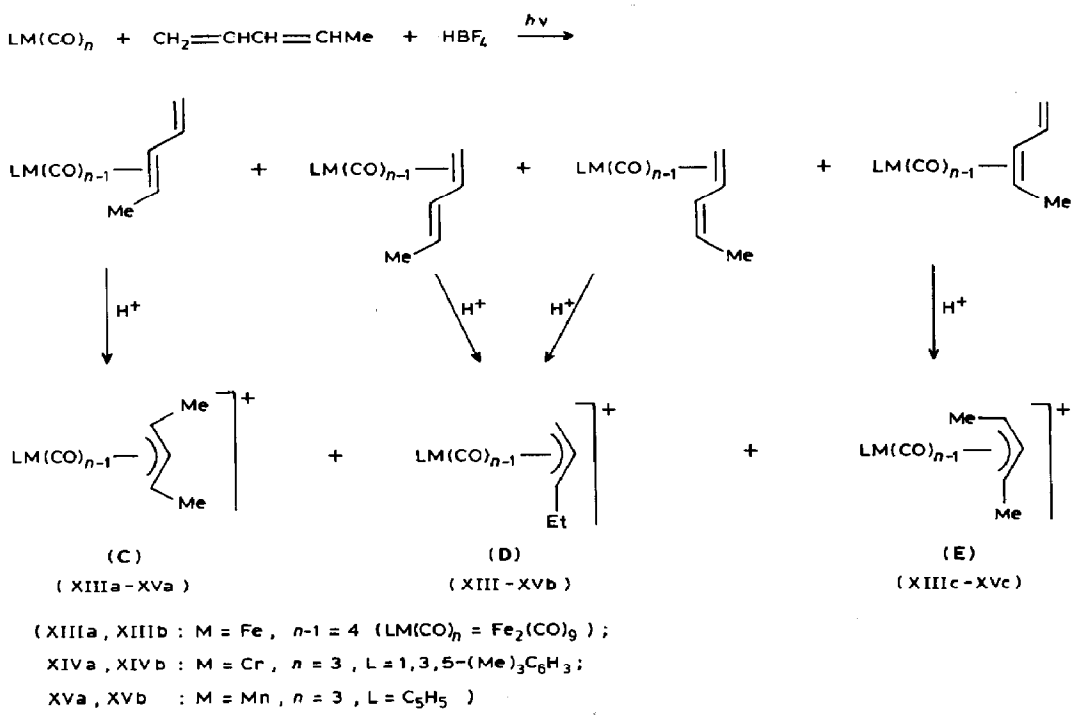


Scheme 1

Similarly, iron, chromium and manganese complexes containing, according to ^1H NMR data, at least two isomers (**C** and **D**, Scheme 2) were obtained from the mixture of *Z*- and *E*-piperylenes (in the ratio 1.0/9.5). Identification of a third minor isomer (*E*) in all cases presents certain difficulties because of its low content;

* Transoid conformation of η^2-butadiene complexes has been confirmed by the results of X-ray structure analysis and NMR data [5a–5d].

** It should be noted that the only isomer with a 1,1-dimethylallyl ligand (IXa) has been obtained from $Fe_2(CO)_9$ and isoprene.



Scheme 2

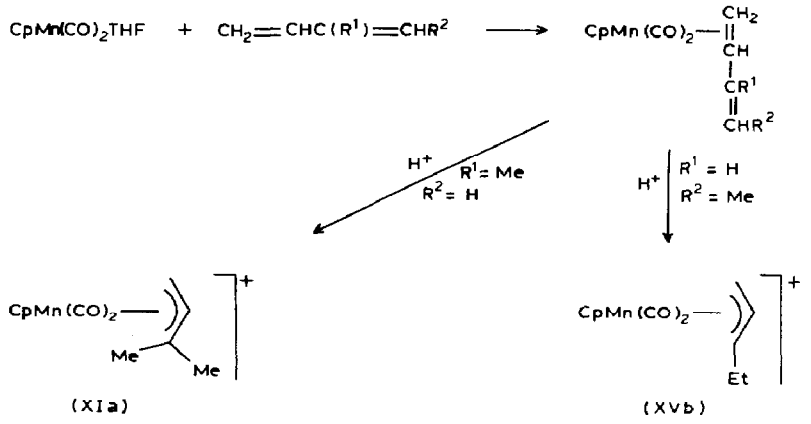
its existence can only be assumed on the basis of the doublet signals of methyl groups in the NMR spectra (Table 1).

Data on the isomeric composition of cationic allyl complexes obtained from non-symmetrically substituted dienes also allow us to assume that intermediate η^2-diene complexes in the transoid conformation * are formed (Schemes 1 and 2). The diene in these complexes is coordinated either by substituted or by non-substituted double bonds.

It should be emphasized that in all neutral η^2-complexes of isoprene and piperylenes hitherto isolated [5b,c; 7a,b], the metal atom was coordinated exclusively by the non-substituted double bond. It has been shown [7a] that the protonation of iron carbonyl complexes yields, in each case, only one isomer of **A** or **D** type, respectively.

Thus, it may be assumed that the two-stage synthesis of cationic allyl complexes, which involves the formation of η^2-diene complexes at the first stage and their subsequent protonation, leads to the only isomer. In order to find out whether this phenomenon is of general significance, we have synthesized η^2-dienemanganese complexes by reaction of $CpM(CO)_2 \cdot THF$ with isoprene or a mixture of piperylenes in neutral medium. In this case, complexes of only one type were isolated and, as with those complexes with a coordinated non-substituted double bond, no traces

* The transoid conformation of η^2-piperylene complexes has also been confirmed by the data of X-ray diffraction and ^1H NMR spectroscopy [5c,d;7b]. In the more complicated case of isoprene complexes coordinated via a non-substituted double bond, protonation does not allow any conclusions to be drawn concerning diene conformation, the literature data also being contradictory [5b,7a].

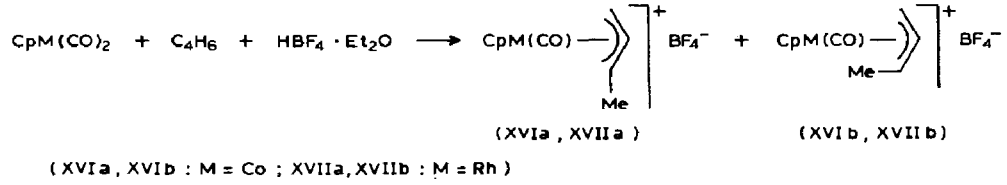


Scheme 3

of any other isomer were found, even in the NMR spectra. Subsequent treatment of $CpMn(CO)_2(\eta^2\text{-diene})$ with HBF_4 leads to the formation of the only isomer (Scheme 3).

At the same time it is important to emphasize that a one-stage synthesis yields mixtures of complexes XIa,XIb and XVa,XVb, which may be formed from intermediate η^2-diene complexes having the η^2-diene ligand coordinated not only by the non-substituted but also by the substituted double bond. Thus, the one-stage syntheses allows isomers to be obtained, which are otherwise inaccessible.

As stated above, the isomeric composition of the cationic complexes formed depends on the nature of the initial compound. Use of the more basic initial complexes, such as $CpM(CO)_2$ (M = Co, Rh), in a one-stage reaction with dienes leads to the principally different results which have been discussed earlier. In the case of butadiene, two isomers, with *syn*- and *anti*-crotyl ligands, are formed, i.e. the reaction is non-stereospecific.

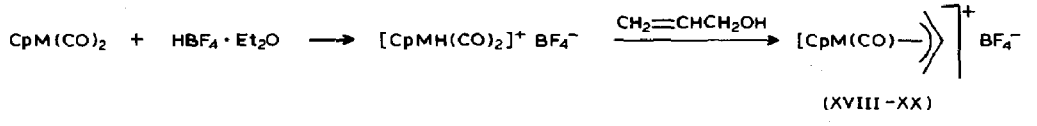


The reasons for the non-stereospecificity of these reactions seem to lie in their different mechanisms. In these cases, the initial complexes are likely to be protonated in the first stage and only the intermediate protonated species add the conjugated diene.

Indeed, analysis of the relevant literature [8] shows that the complexes yield *anti*-allyl derivatives or mixture of *anti*- and *syn*-isomers.

We have confirmed the participation of protonation products in the synthesis of Co and Ir non-substituted cationic allyl complexes by means of IR spectroscopy. New bands appear in the IR spectrum on the addition of $HBF_4 \cdot Et_2O$ to the

solution of $CpM(CO)_2$ in nitromethane, 2115, 2076 cm^{-1} (M = Co) and 2136, 2096 cm^{-1} (M = Ir). When allyl alcohol is added to the reaction mixture, the corresponding allyl complexes are formed at room temperature in the case of cobalt and on heating in the case of iridium.



(XVIII–XX)

(XVIII : M = Co , XIX : M = Rh , XX : M = Ir)

It is noteworthy that the *anti*-crotyl comlexes of cobalt and rhodium spontaneously isomerize into *syn*-crotyl derivatives. Thus, the ratio of *anti*- and *syn*-crotyl isomers of cobalt decreases from 1.7/1.0 to 0.6/1.0 in solution in deutero-acetone on standing for 23 h at 20 °C, and on subsequent heating at 50 °C for 0.5 h the ratio decreases further to 0.3/1.0. On heating a mixture of *anti*- and *syn*-crotyl complexes of rhodium (50 °C, 4 h, deutero-acetone) the *syn*-isomer content increases from 1.0/17.2 to 1.0/43.3.

In contrast to the cases of isomerism discussed above (Ia, Ib and IIa, IIb, where the formation of certain isomers depends on the nature of the initial compound and the synthetic route, conformational isomerism is more dependent on the nature of the cationic allyl complex itself. This type of isomerism of neutral allyl complexes has been studied previously [9a,b]. It has been shown that *exo*- and *endo*-isomers of the $CpM(CO)_2$(allyl)-type compounds (where M = Mo, W) exist in the form of equilibrium mixtures [9b]. It is noteworthy that the *exo*-isomers of this compounds are, in general, thermodynamically more stable, a few exceptions being observed only in some specific cases (e.g. substitution at the central carbon atom of the allyl ligand) [9b].

In comparison with the information available on conformational isomerism of neutral allyl complexes, data on the cationic compounds are scant and contradictory [3,10]. Rosan [3] has observed only one set of signals in the NMR spectra of the complex $[CpMn(CO)_2(\eta\text{-}C_3H_5)]^+ BF_4^-$ (XXI), and has interpreted the fact as fast interchange of *endo*- and *exo*-isomers, with a predominance of the latter. It has been shown in the course of our investigation that both isomers can be observed in the NMR spectrum, even at room temperatures, *endo*-isomers being present only to an extremely low extent (the *exo*/*endo* ratio is 21.4/1.0 in $(CD_3)_2CO$). The use of trifluoroacetic acid as a solvent increases the content of *endo*-isomer (*exo*/*endo* 7.2/1.0). The influence of solvent on the equilibrium has been observed previously for neutral allyl complexes [10]. Low *endo*-isomer content, as well as its solubility in polar solvents only, prevents its detection by means of IR spectroscopy. For the *exo*-isomer, ν(CO) (acetone) 2041 and 2002 cm^{-1}.

We have also shown that both conformers are observed in the ^1H NMR spectra of Re complex $[CpRe(CO)_2(\eta\text{-}C_3H_5)]^+ BF_4^-$ (XXII); the predominance of the *endo*-isomer, even in acetone, was absolutely unexpected (*exo*/*endo*—1.0/2.7; 1.0/3.3 and 1.0/8.0 in CD_3NO_2, $(CD_3)_2CO$ and CF_3COOH, respectively). In this case, assignment was made as in ref. 10, on the basis of mutual positions of allyl proton signals in NMR spectra, high field shifts of *anti*-proton signals for the *endo*-conformer ($\Delta\delta(CD_3NO_2)$ 2.9 ppm) and the high field shift of the central proton signal for the *exo*-conformer ($\Delta\delta$ 3.4 ppm) in the indenyl analogue [(Ind-

$Re(CO)_2(\eta\text{-}C_3H_5)]^+ BF_4^-$ prepared by us. The predominance of the *endo*-conformers is observed also in the IR spectra of both of the rhenium complexes.

The *endo*-isomers also prevails in the case of the $[1,3,5\text{-}Me_3C_6H_3Mo(CO)_2(\eta\text{-}C_3H_5)]^+ BF_4^-$ (XXIII) complex (*exo*/*endo* 1.0/4.0 in CD_3NO_2 at −25 °C). There are two sets of CO-group vibration bands in the IR spectra of the complex: ν(CO) ($MeNO_2$) 2010, 1967 (*endo*) and 1992, 1924 (*exo*) cm^{-1}. The IR spectrum of complex $[(1,3,5\text{-}Me_3C_6H_3)W(CO)_2(\eta\text{-}C_3H_5)]^+ BF_4^-$ (XXIV), which was obtained using UV immersion lamp, also demonstrates a predominance of the *endo*-conformer (ν(CO) ($MeNO_2$): 2012, 1960 (*endo*); 1995, 1935 (*exo*) cm^{-1}). Unlike molybdenum and tungsten complexes, the mesityleneallyldicarbonylchromium cation (XXIV) gives a single set of signals in the ^1H NMR spectrum and two bands (ν(CO) (acetone) 1980, 1927 cm^{-1}) in the IR spectrum. On the basis of these data, the chromium complex may be assumed to be an *exo*-isomer. However, fast exchange between *endo*- and *exo*-isomers, with a predominance of the latter, cannot be excluded either.

An analogous pattern is observed in the NMR and IR spectra of rhenium(III), manganese(VII) and chromium(VI) complexes with a *syn*-crotyl ligand. Thus, the *exo*/*endo* ratio for the rhenium(III) complex is 1.0/2.2 (CD_3NO_3) and 1.0/2.7 ($(CD_3)_2CO$). Only the *endo*-isomer was observed in CF_3COOH. Two pairs of bands were observed in the IR spectrum of VIII: 2054, 2001 (*endo*) and 2043, 1981 (*exo*) cm^{-1} ($(Me)_2CO$). For Mn (VII) and Cr (VI) complexes, only the *exo*-isomer was detected (Table 1).

The introduction of an Me-substituent into the *syn*-position of the allyl ligand does not lead to significant differences in conformer ratio in comparison with complexes with non-substituted allyl ligands. Yet, the presence of the same substituents in the *anti*- or central positions of the allyl ligand leads to drastic changes in the stereochemistry. In the case of chromium (Xa,Xb), manganese (XIa,XIb) and rhenium (XIIa,XIIb) complexes obtained from isoprene, the presence of an Me-substituent in the *anti*-position (isomer A, Scheme 1) leads only to an *exo*-conformer, even in the case of rhenium complexes. The substituent at the central carbon atom, on the other hand, gives exclusively *endo*-conformers for complexes of all the above-mentioned metals, the fact being made perfectly clear from the complementary IR and NMR spectral data (Table 1).

The analogous influence of substituents in the *anti*-position and at the central carbon atom on the conformation of neutral cyclopentadienylallyldicarbonyl complexes of molybdenum and tungsten has been observed previously [10].

The rate constants, as well as the free energies of the interconversions of the conformers of non-substituted molybdenum, manganese and rhenium complexes and of the *syn*-crotyl rhenium complex, were estimated according to the approximate equation at the collapse point. The data obtained, which are listed in Table 2, are in good agreement with those obtained for the rhenium compounds by analysis of the temperature dependence of the full spectral line configuration (Table 3). The free energy values given in the table are compared with those published earlier [10] for neutral molybdenum and tungsten complexes.

Thus, for cationic half-sandwich pseudo-seven-coordinated chromium, molybdenum, manganese and rhenium complexes there exists an equilibrium between the *exo*- and *endo*-isomers. Factors determining this equilibrium (the presence and position of the substituents in the allyl ligand, the nature of the metal, the polarity

Table 2

Kinetic and activation parameters at the collapse point of the isomerization process of $[LM(CO)_2(allyl)]^+$ complexes, calculated in accordance with the approximate equation

Compound	k (s^{-1})	K_p	$\Delta G^{\neq}$ (kJ mol^{-1})	T_{col}	$\Delta\nu$ (Hz)
$[CpMn(CO)_2(C_3H_5)]^+$	67.9	0.1	56.0±0.7	306	30.5
$[(C_6H_3Me_3)Mo(CO)_2(C_3H_5)]^+$	106.6	4.0	45.9±0.5	275	48.0
$[CpRe(CO)_2(C_3H_5)]^+$	17.3	3.6	54.0±0.5	303	7.5
$[CpRe(CO)_2(C_4H_7)]^+$	30.0	2.2	57.0±0.9	311	13.5

of the solvent) and kinetic characteristics of the interconversions of the conformers are actually the same, as in the case of neutral molybdenum and tungsten complexes [10]. The predominance of *endo*-isomer indicates a significant difference in the cationic allyl derivatives of molybdenum, tungsten and rhenium compared with neutral metal complexes.

As mentioned above, the conformational isomerism of allyl complexes depends greatly on their structure. For neutral pseudo-six-coordinated complexes of type CpM(CO)(allyl) (where M = Fe, Ru), the conversion of *endo*-isomer into the *exo*-form was shown to be irreversible and to involve the η^3-η^1-η^3 transitions of the allyl ligand [11a,b]. We have studied the conformational isomerism of cationic allyl complexes $[CpM(CO)(allyl)]^+$ (where M = Co, Rh, Ir). An NMR study of the isomerism of the complexes $[CpM(CO)(allyl)]^+$ BF_4^- of the cobalt sub-group has shown that in the course of time the *exo*-isomer content quickly increases. Thus, the iridium complex XX with the non-substituted allyl ligand exists in solution in the form of a mixture of *exo*- and *endo*-conformers (*exo*/*endo* ratio 5.5/1.0), the ratio being independent on the solvent used. On heating this complex, the *endo*-conformer disappears.

The *exo*/*endo* ratio for the analogous rhodium comples $[CpRh(CO)(\eta\text{-}C_3H_5)]^+$ BF_4^- (XIX) at 25 °C is 78/1; the *exo*-conformer was the only form registered for the corresponding cobalt complex $[CpCo(CO)(\eta\text{-}C_3H_5)]^+$ BF_4^- (XVIII). The rhodium complex with the crotyl ligand (XVIIa,XVIIb) exhibits the same trend (predominance of the *exo*-isomer), although complicated by *syn–anti*-isomerism. Thus, the ratio of *syn(exo)*/*syn(endo)*/*anti(exo)*/*anti(endo)* is 77.5/35.5/4.5/1.0. On heating this mixture in $(CD_3)_2CO$ (50 °C, 4 h), the *endo*-conformers disappear and the *anti(exo)*-isomer content decreases, the *syn(exo)*/*anti(exo)* ratio becoming 43/1.

The results obtained for complexes $[CpM(CO)(allyl)]^+$ BF_4^- of the cobalt sub-group suggest that the *exo*-conformer is thermodynamically more stable. This fact is in good agreement with data obtained previously for isostructural neutral iron and ruthenium complexes CpM(CO)(allyl) (M = Fe, Ru) but contradicts the theoretical suggestion put forward in ref. 1e, where the *endo*-conformer was stated as being the most stable for complexes $[CpM(CO)(allyl)]^+$ (M = Co, Rh, Ir).

Experimental

^1H NMR spectra were recorded with a Bruker WP-200SY spectrometer at 200.13 MHz and a Tesla BS-467 spectrometer at 60 MHz; IR spectra were recorded with a Specord-75IR spectrophotometer.

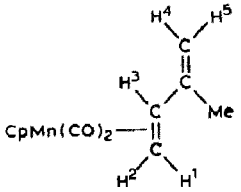
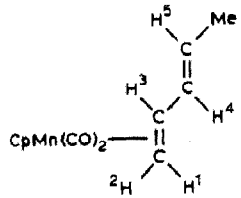
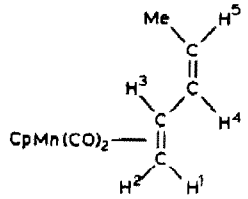
Table 3

Kinetic and activation parameters of isomerization processes of complexes $[CpRe(CO)_2(\eta^3\text{-}C_3H_4R)]^+ BF_4^-$ (XX, R = H; VIII, R = Me)

Complex	$k_{298\,K}$ (s^{-1})	k_1(298 K)	k_{-1}(298 K)	k_p(298 K)	$H^{\neq}$(298 K) (kJ mol^{-1})	$S^{\neq}$(298 K) (J mol^{-1} $degree^{-1}$)	$G^{\neq}$(298 K) (kJ mol^{-1})	E (kJ mol^{-1})	T_{col}	$\Delta\nu$ (Hz)
XX	14.3	18.3	65.0	3.6	48.6 ± 1.3	-59.5 ± 2.5	66.2	51.1 ± 4.2	305	7.5
VIII	16.7	24.2	53.2	2.2	49.9 ± 3.8	-54.5 ± 2.5	66.2	50.3 ± 5.0	310	13.5

Table 4

IR and ^{1}H NMR data for complexes of type $CpMn(CO)_2$ (η^2-diene)

Complex	ν(CO)(cm^{-1}) (heptane)	Chemical shifts (ppm) and coupling constants (Hz) in C_6D_6						
		H^1	H^2	H^3	H^4	H^5	CH_3	Cp
	1984,1912	2.130dd, J_{13} 12.8, J_{12} 1.7	2.370ddd, J_{23} 8.4, J_{12} 1.7, J_{25} 0.4	3.917ddd, J_{13} 12.8, J_{23} 8.4, J_{35} 0.7	4.945m	5.165m	1.412dd, $J(CH_3\text{-}4)$ 1.4 $J(CH_3\text{-}5)$ 0.7	3.948s
	1981.1912	2.074dd, J_{13} 12.4, J_{12} 1.1	2.340dd, J_{23} 8.2, J_{12} 1.1	3.654ddd, J_{13} 12.4, J_{34} 10.0, J_{23} 8.2	4.933ddq, J_{45} 15.0, J_{34} 10.0, $J(CH_3\text{-}4)$ 1.5	5.789dq, J_{45} 15.0, $J(CH_3\text{-}5)$ 6.6	1.722dd, $J(CH_3\text{-}5)$ 6.6, $J(CH_3\text{-}4)$ 1.5	4.018s
		2.090d J_{13} = 12.4	2.378d J_{23} = 6.0	–	–	–	1.951dd, $J(CH_3\text{-}4)$ 7.0, $J(CH_3\text{-}5)$ 1.7,	4.033s

The synthesis of cationic allyl complexes has been described previously [2a–f]. Neutral η^2-diene complexes of manganese with isoprene and piperylene have been obtained according to the technique given in ref. 12 for cyclopentadiene, with yields 19 and 28%, respectively; IR and ^{1}H NMR data are listed in Table 4.

Rate constants for the isomerization processes have been evaluated from the equation $k = 1/\tau$, where τ is the effective lifetime. Estimation of the values has been carried out on the basis of a correlation between experimental and theoretical spectral in the vicinity of the collapse point. Calculations were carried out with an Iskra computer using the EX 2 program for a two-position non-degenerated exchange. The differences between signal frequencies and line widths do not vary with temperature and were used for the evaluation of τ in the vicinity of the collapse point. The relative occupation of the P_A and P_B states in the case of the methylallyl complex hardly vary in the temperature range 20–35 °C ($P_A = 0.31$, $P_B = 0.69$). The P_A value for the non-substituted compound is 0.17 at −10 °C. An increase in temperature leads to a decrease in the differences in occupation of the P_A and P_B states; the P_A value is 0.21 at 20 °C. For temperatures higher than the collapse point, the P_A value was found by linear extrapolation from the lower temperatures.

Values of the free activation energy $\Delta\sigma^{\neq}$ and the activation energy E_a of the process were calculated according to the Eiring and Arrhenius equations, from the dependencies of ln k/T or K from $1/T$, respectively.

Kinetic and thermodynamic data for the process are summarized in Table 3.

Estimation of the rate constants of the exchange processes and of the free energy values at the collapse point for compounds $[CpM(CO)_2(\eta\text{-}C_3H_5)]^+ BF_4^-$ (where M = Mn, Re), $[1,3,5\text{-}(Me)_3C_6H_3Mo(CO)_2(\eta\text{-}C_3H_5)]^+ BF_4^-$ and $[CpRe(CO)_2(\eta\text{-}C_4H_7)]^+ BF_4^-$ listed in Table 2 were carried out in accordance with the approximate equation [8]:

$$k = 2.22\Delta\nu$$

$$k_T = \frac{KT}{h} + e^{-\Delta G^{\neq}/RT}$$

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