Transition Metal–Cyanocarbon Chemistry. Part IV*. Reactions of Bent Biscyclopentadienyl Complexes of Molybdenum and Tungsten of the Type $(\eta^5\text{-}C_5H_5)_2MH(\sigma\text{-}CR{=}CHR')$ (M = Mo, W; R = CN; R' = H; M = Mo; R = CN, CF_3; R' = H; R = R' = CN) and $(\eta^5\text{-}C_5H_5)_2Mo(\sigma\text{-}C(CN){=}CH_2)$ ((Z)-CH=CHCN) with HX (X = Cl, O_2CCF_3, SPh, SMe, SH) Reagents. Protonation of σ-Alkenyl Ligands

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Abstract

Reactions of the title complexes with some protic reagents are described. Protonation of σ-alkenyl ligands giving defined and stable σ-alkyl products of the type $(\eta^5\text{-}C_5H_5)_2MX(\sigma\text{-}CHR{-}CH_3)$ (M = Mo, W; R = CN) occurs upon the action of HX, HO_2CCF_3 and HSPh on $(\eta^5\text{-}C_5H_5)_2MH(\sigma\text{-}C(CN){=}CH_2)$ and (M = Mo, R = CF_3) upon the action of HO_2CCF_3 on $(\eta^5\text{-}C_5H_5)_2MoH(\sigma\text{-}C(CF_3){=}CH_2)$. In this last case a second σ-alkyl product $(\eta^5\text{-}C_5H_5)_2Mo(O_2CCF_3)(\sigma\text{-}CH_2{-}CH_2CF_3)$ is also formed. The mechanism of these reactions is discussed.

Introduction

Homogeneous hydrogenation of unsaturated carbon–carbon bonds is one of the most important topics in organometallic chemistry. It is generally accepted that it involves metal hydrides as intermediates [2]. It is equally well known that strong acids are able to reduce the unsaturated ligands of the alkyne [3] and alkene [4] complexes. Recently we described the properties of compounds resulting from the insertion reactions of mono- and dicyanoacetylenes into one or the two metal–hydride bonds of bent biscyclopentadienyls Cp_2MH_2 (Cp = $\eta^5\text{-}C_5H_5$, M = Mo, W) [5]. The monoinsertion products, $Cp_2MH(\sigma\text{-}C(CN){=}CHR)$ (R = H, CN) are attractive materials for further studies of the reactivity of the residual hydride ligand. Reactions of these complexes with disulfide-type reagents under UV irradiation lead to the substitution of hydride ligand by SR^- group with retention of the σ-alkenyl ligand [1]. Surprisingly, reaction of $Cp_2MoH(\sigma\text{-}C(CN){=}CH_2)$ with HSPh gave a product in which the unsaturated ligand is protonated. This inspired us to study the action of some protic chemicals HX (X = Cl, O_2CCF_3, SPh, SMe and SH) on the following complexes: $Cp_2MH(\sigma\text{-}C(CN){=}CH_2)$ (**1a**: M = Mo, **1b**: M = W), $Cp_2MoH((Z)\text{-}C(CN){=}CH(CN)$ (**2**), $Cp_2Mo(\sigma\text{-}C(CN){=}CH_2)((Z)\text{-}CH{=}CHCN)$ (**3**) and $Cp_2MoH(\sigma\text{-}C(CF_3){=}CH_2)$ (**4**). We report here the results of this study, which shows that the metal–carbon bond is not always broken even with an acid as strong as HCl.

Experimental

Infrared spectra of samples prepared as nujol mulls on CsI plates were recorded on a Pye Unicam SP2000 spectrophotometer. Proton, carbon and fluorine NMR spectra were recorded on a JEOL FX 100 spectrometer operating at 99.60 MHz for ^1H, 25.05 MHz for ^{13}C and 93.70 MHz for ^{19}F relative to an internal reference of TMS for ^1H and ^{13}C and to an external one of $CFCl_3$ for ^{19}F.

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk tube techniques and freshly distilled and degassed solvents. Starting complexes (**1**) to (**4**) were prepared as described elsewhere [4, 5].

Reactions with HCl

Reactions of HCl with the complexes (**1**)–(**4**) were carried out by bubbling dry HCl through their solutions in ether at room temperature.

An immediate and quantitative precipitation of yellow σ-alkyl complexes (**5a**) and (**5b**) was observed with (**1a**) and (**1b**), respectively. (**2**) gave an initial precipitation of an unidentified yellow product,

*For Part III, see ref. 1.

0020-1693/85/$3.30

which immediately underwent a transformation to the known Cp_2MoCl_2. Di-insertion complex (**3**) as well as the complex (**4**) gave almost quantitatively the precipitation of Cp_2MoCl_2 without apparent observation of the intermediates.

Reactions with HO_2CCF_3

Equimolar mixtures of HO_2CCF_3 with molybdenum complexes (**1**)–(**4**) in THF were stirred overnight at room temperature.

σ-Alkyl complexes were separated after chromatography on florisil (CH_2Cl_2/THF 2% as eluent) in the case of (**1a**) (**6**, 64% yield), (**2**) (**7**, 10% yield) and (**4**) (**8**, 40% yield). No defined product was isolated with di-insertion complex (**3**).

Traces of a second new complex were detected on the ^{19}F NMR spectrum of (**8**), so the reaction of (**4**) with HO_2CCF_3 was carried out in C_6D_6 in a sealed NMR tube. The ^{19}F spectrum recorded 15 min. after mixing the reagents exhibited a triplet at $\delta = -68.4$ ppm and a singlet at $\delta = -76.1$ ppm corresponding to the complex (**8**) separated previously by chromatography, together with a set of the two new resonances (a doublet at $\delta = -56.0$ ppm and a singlet at $\delta = -75.6$ ppm). The ratio of these two isomers of **8** (**8a**/**8b**, see below) is equal to 2/1 and does not vary after 6 h.

Reactions of HSPh

Solutions of (**1**)–(**4**) in refluxing ether were stirred with 5 fold excess of HSPh for 16 h.

(**1a**) and (**1b**) gave after chromatography on florisil the red crystalline σ-alkyl products (**9a**) and (**9b**) in 80 and 45% yields, respectively. Small amounts of σ-alkenyl, SPh substituted complexes $Cp_2M(SPh)(\sigma\text{-}C(CN)=CH_2)$ [1] and of the $Cp_2M(SPh)_2$ ones were detected by means of ^1H NMR spectroscopy. When reaction of (**1a**) was carried out in refluxing THF the first band eluted with CH_2Cl_2 contained σ-alkenyl complex $Cp_2Mo(SPh)(\sigma\text{-}C(CN)=CH_2)$ (34% yield). The yield of σ-alkyl complex (**9a**) eluted as a second band with CH_2Cl_2/2% THF was of only 30%.

Unreacted starting materials together with $Cp_2Mo(SPh)_2$ (30% yield) were recovered in the case of complex (**2**). σ-Alkenyl complex $Cp_2Mo(SPh)(\sigma\text{-}C(CF_3)=CH_2)$ (25% yield) and $Cp_2Mo(SPh)_2$ (10% yield) have been formed with (**4**).

Reactions with HSMe and H_2S

Gaseous HSMe or H_2S was trapped via a vacuum line on the solutions of (**1**)–(**4**) in ether frozen in liquid air. The mixtures were allowed to warm to room temperature, stirred for 16 h and chromatographed on florisil.

(**1a**) gave the σ-alkenyl complexes $Cp_2MoX(\sigma\text{-}C(CN)=CH_2)$ X = SMe in 60% yield, X = SH in 50% yield. A metallacyclopropane complex, $Cp_2\overline{W-CH(CN)CH_2}$ formed from (**1b**) and HSMe (60% yield), and H_2S (80% yield). Identification of this compound was made by comparison of its ^1H NMR spectrum with that of the known molybdenum analogue prepared by Nakamura and Otsuka from the reaction of Cp_2MoH_2 with acrylonitrile [4]. Complex (**2**) gave rise to the formation of $Cp_2Mo(SMe)(\sigma\text{-}C(CN)=CH(CN)$ (30% yield) and $Cp_2Mo(SMe)_2$ (10% yield) with HSMe, but no defined product was isolated from the reactions of (**3**) and (**4**) with HSMe and of (**2**), (**3**) and (**4**) with H_2S.

In refluxing ether (**1a**) gave $Cp_2Mo(SMe)_2$ (10% yield) with HSMe and $Cp_2Mo(SH)(\sigma\text{-}C(CN)=CH_2)$ (15% yield) with H_2S, but no defined new product has been isolated from the reactions of (**1b**), (**2**), (**3**) and (**4**) with HSMe and H_2S under the same conditions.

Discussion

The results of this study concerning the protonation of σ-alkenyl complexes are summarized in Table I, and the spectroscopic data for new compounds are given in Table II. These results are as follows:

(i) strong acids (HCl and HO_2CCF_3) are able to reduce the σ-alkenyl ligands at room temperature;

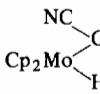
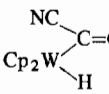
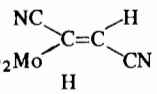
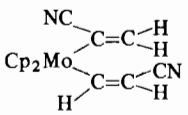
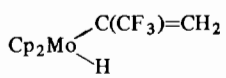
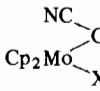
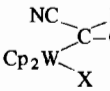
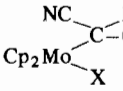
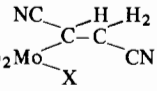
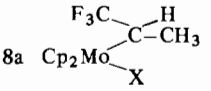
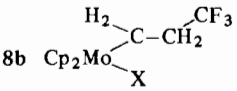
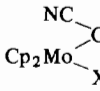
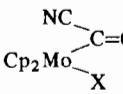
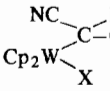
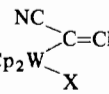
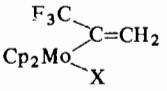
(ii) among thiols, HSPh can reduce the unsaturated C=C bond activated by nitrile group at elevated temperature, but not that activated by trifluoromethyl group; HSMe and H_2S seem to be not acidic enough to give the σ-alkyl products;

(iii) presence of hydride ligand in the starting complexes is necessary for saturation of the σ-alkenyl ligands, so a mechanism of reduction would involve its intramolecular interaction with the ligand in the complex activated by the action of proton.

(iv) HO_2CCF_3 action leads to the formation of a single isomer with cyano-σ-alkenyl complex (**1a**) but two isomers are formed with the trifluoromethyl-σ-alkenyl complex (**4**).

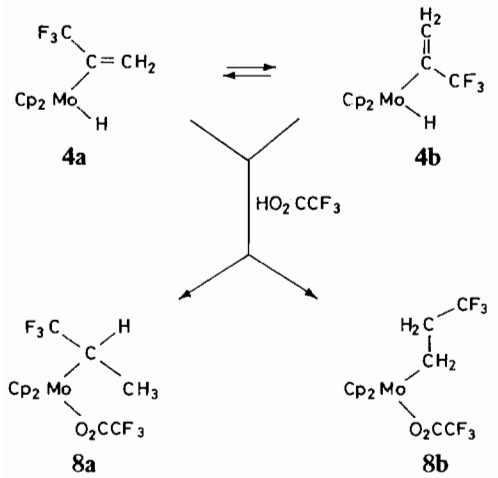
The structure of the isomer of (**8**) separated by chromatography (**8b**) was elucidated from its ^1H and ^{19}F NMR spectra. A triplet centered at −68.4 ppm (^{19}F) indicates that there are two protons on a carbon atom bearing the corresponding CF_3 group, and that this carbon atom must be in β position with respect to the molybdenum atom. ^1H spectrum shows equivalence of the Cp rings (appearing as one resonance, Table II) and as consequence a lack of chirality of the C_α carbon atom. Identification of the second isomer (**8a**) was based on the ^{19}F and ^1H spectra recorded on the mixture of both isomers (see experimental). A doublet centered at −56.0 ppm (^{19}F) corresponds to the structure in which the CF_3 of the σ-alkyl ligand is coupled with one proton and thus bound to the C_α carbon atom. Consequently,

TABLE I. Protonation of σ-alkenyl Complexes with HX Reagents.

X	Complex				
	1a 	1b 	2 	3 	4 
Cl	5a 	5b 	Cp_2MoX_2	Cp_2MoX_2	Cp_2MoX_2
O_2CCF_3	6 	[a]	7 	undefined products	8a  8b 
SPh	9a  +  + Cp_2MoX_2	9b  +  + Cp_2WX_2	Cp_2MoX_2	no reaction	 Cp_2MoX_2

[a]Not studied.

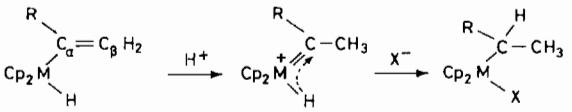
this carbon atom should be asymmetric which is confirmed by the presence of two signals of unequivalent Cp rings. The different structures of (**8a**) and (**8b**), [(**8a**) being analogous to that of (**6**)] may be explained by the fact that there exist two conformational isomers of the starting complex (**4**) [5, 6] (Scheme 1).



Scheme 1.

Important conclusions on the mechanism of hydrogenation reactions described here can be drawn from the fact that two isomers of (**8**) are formed. This mechanism, as mentioned above, should involve an initial activation of the σ-alkenyl ligand by H^+ followed by intramolecular migration of the hydride to the activated ligand. A question arises as to which is the site of this initial attack of proton: is it a non-bonding occupied orbital on the metal, or directly the unsaturated ligand via addition to C_α or C_β carbon atom ?

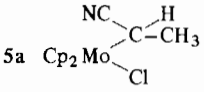
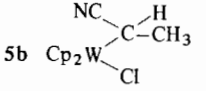
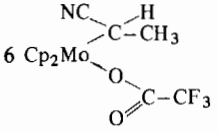
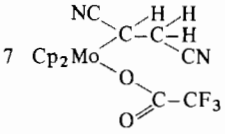
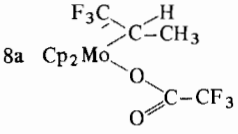
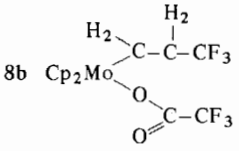
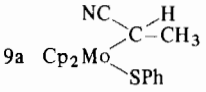
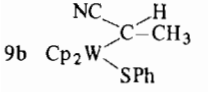
In the last mentioned case of the attack on C_β carbon atom (Markovnikov type), the formation of intermediate carbene complex (Scheme 2) should facilitate a hydride transfer to the C_α carbon atom.



Scheme 2.

Recently Malisch reported an example of such a H^+ attack on C_β carbon atom in $Cp(PMe_3)_2Fe{-}C_\alpha(OMe){=}C_\beta H_2$ [7]. The C_β atom in this complex is shielded and nucleophilic (^{13}C NMR: $\delta(C_\beta) = 91.97$,

TABLE II. Spectroscopic (NMR and IR) Data for σ-alkyl Complexes.

Complex	Solvent for NMR study	^1H[a]			^{13}C[a]			^{19}F[b] (CF_3)		ν(CN)[c] (cm^{-1})
		Cp	on C_α	on C_β	Cp	C_α	C_β	on alkyl	on O_2CCF_3	
5a 	$CDCl_3$	5.25 (s, 5) 5.21 (s, 5)	2.12 (q, 1, ^3J = 7.0 Hz)	1.40 (d, 3, ^3J = 7.0 Hz)	97.9 97.0	−11.1	19.9	–	–	2200
5b 	$CDCl_3$	5.20 (s, 5) 5.18 (s, 5)	2.22 (q, 1, ^3J = 7.0 Hz)	1.47 (d, 3, ^3J = 7.0 Hz)	d	d	d	–	–	2205
6 	$CDCl_3$	5.38 (s, 5) 5.33 (s, 5)	2.13 (q, 1, ^3J = 7.0 Hz)	1.22 (d, 3, ^3H = 7.0 Hz)	98.4 97.6	−10.2 (d, J_{CH} = 140 Hz)	18.4 (q, J_{CH} = 137 Hz)	–	76.0 (s)	2195
7 	acetone D_6	5.47 (s, 5) 5.43 (s, 5)	2.53–2.21 complex multiplet		d	d	d	–	d	d
8a 	C_6D_6	4.58 (s, 5) 4.54 (s, 5)	1.80–1.1 complex multiplet		d	d	d	−56.0 (d, $^3J_{FH}$ = 13.4 Hz)	−75.6 (s)	–
8b 	C_6D_6	4.22 (s, 10)	0.95–0.85 (m, 2)	1.57 (q, 2, $^3J_{FH}$ = 11 Hz)	96.2	−2.2 (broad singlet)	40.4 (q, $^2J_{CF}$ = 27 Hz)	−68.4 (t, $^3J_{FH}$ = 11 Hz)	−76.1 (s)	–
9a 	$CDCl_3$	5.08 (s, 5) 5.06 (s, 5)	2.10 (q, 1, ^3J = 7.0 Hz)	1.40 (d, 3, ^3J = 7.0 Hz)	96.4 95.4	−11.7	19.3 total decoupling	–	–	2195
9b 	$CDCl_3$	5.08 (s, 5) 5.06 (s, 5)	2.25 (q, 1, ^3J = 7.0 Hz)	1.49 (d, 3, ^3J = 7.0 Hz)	92.8 91.7	−26.8 ($^1J_{WC}$ = 69 Hz)	20.4	–	–	2200

[a] Downfield from TMS; [b] downfield from $CFCl_3$; [c] nujol mulls; [d] not recorded.

TABLE III. ^{13}C NMR Data for Some σ-alkenyl Complexes.

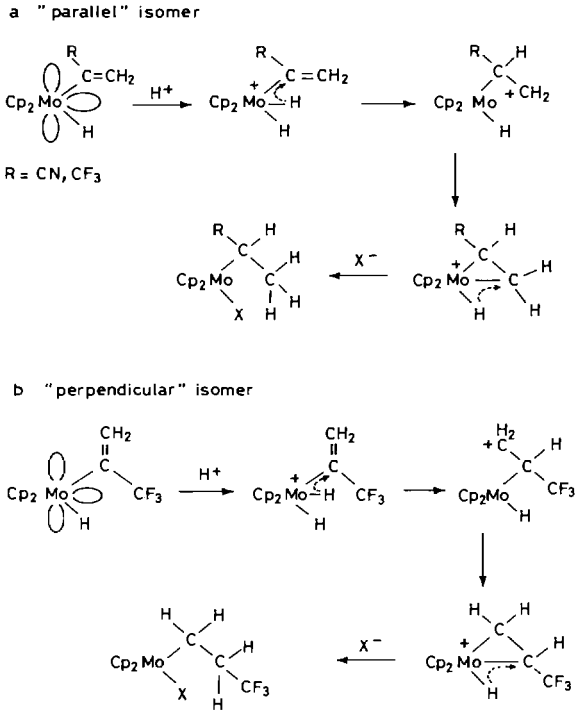
	C_α	C_β	Solvent
$Cp_2MoH(\sigma\text{-}C_\alpha(CN){=}C_\beta H_2)$ (1a)	130.6	148.9	$(CD_3)_2CO$
$Cp_2Mo(SH)(\sigma\text{-}C_\alpha(CN){=}C_\beta H_2)$[a]	124.8	148.0	$CDCl_3$
$Cp_2Mo(Cl)(\sigma\text{-}C_\alpha(CN){=}C_\beta H_2)$[a]	120.0	148.7	$CDCl_3$
$Cp_2MoH((Z)\text{-}C(CN){=}CHCN)$ (2)[b]	158.4	128.5	$CDCl_3$
$Cp_2MoH(\sigma\text{-}C_\alpha(CF_3){=}C_\beta H_2)$ (4)	147.6	136.3	C_6D_6
$Cp_2Mo(Cl)(\sigma\text{-}C_\alpha(CF_3){=}C_\beta H_2)$[a]	139.1	137.4	$CDCl_3$
$(NC)C_\alpha H{=}C_\beta H_2$[c]	108.1	137.5	

[a] Ref. 1; [b] ref. 5; [c] ref. 10.

$\delta(C_\alpha)$ = 201.77 ppm). We show below that an opposite statement can be drawn in the presence of nitrile group on the C_α atom of the σ-alkenyl ligand. Moreover, the formation of two isomers of (8) excludes such a pathway. If the C_β carbon atom would undergo a H^+ attack, a single isomer (8a) could be formed.

An unprecedented attack of H^+ on C_α carbon atom cannot be dismissed in the case of cyano activated complexes (1). Nitrile groups exhibit an important shielding effect on the carbon atom bearing this group, mainly by magnetic anisotropy of the triple C≡N bond. However many factors influence the ^{13}C chemical shift values and the conclusions on the electron distribution in the molecules from these values must be considered with care. In the cyano substituted α, β unsaturated molecules, the mesomeric and inductive effects can give rise to a polarization over carbon–carbon bond of the type $C_\alpha^{\delta-} = C_\beta^{\delta+}$. This is likely to be manifested by reactivity of acrylonitrile, $NCHC{=}CH_2$, which undergoes a Michael addition, *e.g.* of ethylene glycol [8], at C_β carbon atom, the C_α one can be a site of an electrophilic attack of H^+. The ^{13}C NMR chemical shift values of C_α and C_β carbons observed in some biscyclopentadienyl complexes containing $\sigma\text{-}C(CN){=}CH_2$ ligand parallel those reported for acrylonitrile (Table III). Thus, the C_α atom in complexes (1) may have a nucleophilic nature. However, a similar conclusion cannot be drawn from ^{13}C NMR data neither for CF_3 activated alkenyl ligand, nor for the dicyanovinylic one (Table III).

As a consequence a uniform mechanism of hydrogenation reactions reported here should involve an initial addition of H^+ to the nonbonding $1a_1$ orbital [9] localized on the metal center (Scheme 3). This addition is followed by proton migration to the C_α carbon atom with the formation of metallacyclopropane structure, hydride displacement by X^- with its concomitant transfer to the adjacent carbon atom of the cycle accompanied by ring opening. The conformational orientation of the σ-alkenyl ligand in the starting complex determines the structure of the σ-



Scheme 3.

alkyl product. The distinction is shown in scheme 3 (a, parallel isomer; b, perpendicular isomer). The formation of only one isomer for each of the complexes (5), (6) and (9) indicates that (1a) has a sole conformational configuration, which is a parallel one. Formation of metallocyclopropane complex $Cp_2\overline{WCH(CN)CH_2}$ accounts for any intermediary of the ring structure.

The attempts to confirm the mechanism proposed in Scheme 3 by means of the labelling studies with deuteriated derivatives of (1a), (1b) and (4) failed because of the poor quality of the ^1H NMR spectra of the corresponding deuteriated σ-alkyl products, and of the incomplete deuteriation of the starting dihydrides Cp_2MH_2. However, the reaction of non-

deuteriated (**1a**) with DO_2CCF_3 seems to support this mechanism. A new peak appears as a singlet on the ^1H NMR spectrum of the product [deuteriated (**6a**)] exactly at the center of the doublet corresponding to the CH_3 group of the σ-alkyl ligand. This singlet may indicate the presence of the σ-C(CN)D–CH_3 ligand. The fact that the doublet is still present can be due to an exchange between the hydride ligand in the starting complex (**1a**) and deuterium D^+ of DO_2CCF_3 occurring either before or during the attack of the last one on (**1a**).

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