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INSERTION OF ACTIVATED ACETYLENES INTO THE METAL–HYDRIDE BOND OF $[(\eta^5\text{-}C_5H_5)_2M(CO)H]$ (M = Nb, Ta)

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Summary

Reactions of $[Cp_2M(CO)H]$ (M = Nb, Ta; Cp = η^5-C_5H_5) with various acetylenes RC≡CR having electron-withdrawing groups were investigated. They give the σ-alkenyl complexes $[Cp_2M(CO)(CR{=}CHR)]$ via insertion of the alkyne into the M–H bond. On the basis of ^1H and ^{19}F NMR data the reactions were shown to be: (i) regioselective, monosubstituted alkynes giving only the α-R metallated complex; (ii) stereoselective, exclusive formation of the *Z*-isomer being observed with hexafluorobut-2-yne. The *Z* isomer has been shown to exist as two conformers, the steric requirements of the ligands creating a barrier to rotation of the alkenyl group around the M–C σ bond.

Introduction

Insertion of acetylenes into transition metal–hydride bonds is a key step in important catalytic processes such as hydrogenation or polymerization. It also receives considerable attention by virtue of its utility in organic syntheses.

Such insertion reactions may be conveniently classified into two types depending on the nature of the metal hydride/alkyne couple. In the first type, the metal hydride is an electron deficient complex (d^0 derivative for instance) acting as a Lewis acid, and so activation through complexation to the metal complex requires an alkyne having a nucleophilic character; reactions of aliphatic acetylenes with $[Cp_2Zr(Cl)H]$ [1a] (Cp = η^5-C_5H_5) and $[Cp^*_2HfH_2]$ [1b] (Cp^* = η^5-C_5Me_5) constitute

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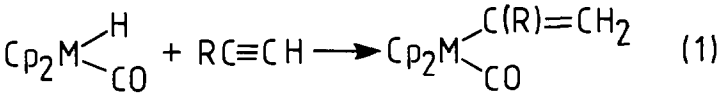
significant examples of this class. In the second type the metal hydride has a high electron density and the alkynes must then have electrophilic character i.e. must bear electron-withdrawing groups; examples of this kind include reactions of alkynes bearing CF_3, CN or CO_2Me groups with ruthenium [2], rhodium [3], molybdenum and tungsten [4,5] hydrides. With Cp_2MoH_2 for instance, only the monoinsertion product [$Cp_2MoH(CR{=}CHR)$ is obtained with hexafluorobutyne, whereas cyano- and dicyano-ethyne may also give the diinsertion derivatives [$Cp_2Mo(CR{=}CHR)_2$] [4,5].

The structure of these σ-alkenyl complexes clearly depends on the regio- and stereo-selectivity of the insertion reaction [6]. At present, there are insufficient data available to allow an accurate assessment of the subtle factors governing this regio- and stereo-selectivity, and further studies are needed. We thus decided to investigate the reaction of a number of activated acetylenes with the niobium and tantalum hydrides [$Cp_2M(CO)H$] (M = Nb, Ta). We have previously shown that, in some cases, the reactions of these compounds are similar to those of the molybdenum and tungsten dihydrides [Cp_2MH_2] (M = Mo, W) [7]; in both cases, the non-bonding filled metal orbital, which is easily accessible, induce relatively strong basic properties.

Results and discussion

The reactions of [$Cp_2M(CO)H$] (**1a**, M = Nb; **1b**, M = Ta) with monosubstituted alkynes RC≡CH (cyanoethyne R = CN; 3,3,3-trifluoropropyne, R = CF_3) occur smoothly at room temperature in toluene to give the insertion products [$Cp_2M(CO)(CR{=}CH_2)$], according to eq. 1:



(1)

(1a: M = Nb; 1b: M = Ta) (2: R = CN; 3: R = CF_3)

The relatively simple NMR spectra observed for complexes **2** and **3** clearly indicate that only one isomer is present in solution. The ^1H NMR spectra contain a sharp singlet attributable to the cyclopentadienyl protons, and two other signals for which chemical shifts and coupling constant ($J \sim 3$–5 Hz) are in agreement with those usually observed for a $C{=}CH_2$ group. For the fluorinated compounds **3**, the downfield proton resonance, which appears as a doublet of quartets ($^2J(HH) \sim 3$ Hz; $^4J(HF) \sim 2$ Hz), has been attributed to the proton in *cis* position relative to the CF_3 group [8], and the second proton appears as a doublet ($^2J(HH) \sim 3$ Hz).

The NMR results thus clearly show the complete regioselectivity of reaction 1, since only the α-metallated complex is formed, but owing to the nature of the reactants information about the stereochemistry cannot be obtained. Such information requires isotopic labeling experiments such as those described by Otsuka and Nakamura [4b] for the reaction between Cp_2MoH_2 and $CF_3C{\equiv}CH$; disappearance of the ^1H NMR signal corresponding to the proton in *trans* position relative to the CF_3 group when Cp_2MoD_2 was used instead of Cp_2MoH_2 clearly showed that there was exclusive *cis* insertion of trifluoropropyne into the Mo–H bond. It should be

TABLE 1

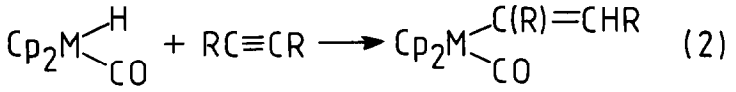
^1H AND ^{19}F NMR DATA AND IR DATA FOR COMPLEXES **2** AND **3** FROM MONOSUBSTITUTED ALKYNES

M	R		^1H NMR [a]			^{19}F NMR [b]	IR (cm^{-1})
	CN	CF_3	Cp	H^a	H^b		
Nb	**2a**		4.59, s, 10	6.64, d, 1 *J* 4.4 Hz	6.06, d, 1 *J* 4.4 Hz		ν(CO) 1915 ν(CN) 2165
Nb		**3a**	4.58, s, 10	6.62, dq, 1 ^2J(HH) 3.1 Hz ^4J(HF) 2.25 Hz	5.55, d, 1 *J* 3.1 Hz	18.3 d ^4J(HF) 2.25 Hz)	ν(CO) 1920
Ta	**2b**		4.48, s, 10	6.79, d, 1 *J* 4.7 Hz	6.17, d, 1 *J* 4.7 Hz		ν(CO) 1900 ν(CN) 2169
Ta		**3b**	4.49, s, 10	6.74, dq, 1 ^2J(HH) 3.5 Hz ^4J(HF) 2.1 Hz	5.75, d, 1 *J* 3.5 Hz	18.7 d ^4J(HF) 2.1 Hz	ν(CO) 1902

[a] C_6D_6; δ ppm; TMS. [b] C_6D_6; δ ppm; CF_3CO_2H. [c] THF.

noted that in an NMR study we obtained no indication of an exchange process for $[Cp_2MH\{(Z)\text{-}C(CF_3)=CH_2\}]$ (**3**) down to −100°C in toluene, whereas conformational isomerism (see below) was observed at room temperature for the equivalent molybdenum complex $[Cp_2MoH\{(Z)\text{-}C(CF_3)=CH_2\}]$ [4b]. This result strongly suggests that with niobium and tantalum reaction 1 gives only one conformer, unless the interconversion of the eventual conformers is too fast to be detected on the NMR time scale. Some NMR data are listed in Table 1.

The reactions of $[Cp_2M(CO)H]$ (**1**) with alkynes bearing two electron-withdrawing groups (hexafluorobut-2-yne $CF_3C{\equiv}CCF_3$ and 1,2-dicyanoethyne $NCC{\equiv}CCN$) proceed analogously to those with monosubstituted acetylenes, yielding only the insertion product (eq. 2). In both cases, the reactions occur rapidly at room temperature and give complexes which are fairly stable in the air.



(2)

(1a: M = Nb ; 1b: M = Ta)

(4: R = CN; 5: R = CF_3)

It is noteworthy that hexafluorobutyne gives a simple insertion reaction with $[Cp_2Nb(CO)H]$ whereas its reaction with $[Cp_2NbH_3]$ is very complex, and involves cleavage of C–F bonds and formation of Nb–F bonds [9].

The ^1H NMR data for compounds **4a** and **4b** (Table 2) indicate that both are present in two isomeric forms, since every type of proton (cyclopentadienyl protons and vinylic proton) gives rise to a pair of resonances. At room temperature, the ratio of the two isomers, estimated from the ratio of the Cp signals, is about 86/14 for the niobium complex **4a** and 83/17 for the tantalum derivative **4b**. In contrast the ^1H NMR data for complexes **5a** and **5b** with hexafluorobut-2-yne do not provide convincing arguments for the presence of two isomers, since each of the spectra consists of a singlet (cyclopentadienyl protons) and an ill-defined quartet of quartets

TABLE 2

^1H AND ^{19}F NMR DATA AND IR DATA FOR COMPLEXES **4** AND **5** FROM DISUBSTITUTED ALKYNES

M	R		Conf.	^1H NMR [a]		^{19}F NMR [b]		IR (cm^{-1}) [c]
	CN	CF_3		Cp	H	α-CF_3	β-CF_3	
Nb	**4a**		I (86%)	4.54, s, 10	6.04, s, 1			ν(CO) 1937
			II (14%)	4.39, s, 10	5.75, s, 1			ν(CN) 2209 and 2175
Nb		**5a**	I (88%)			15.0, quint., 3	18.2, dq, 3	
				4.56, s, 10	6.86, qq, 1	^5J(FF) = ^4J(HF) = 2.5 Hz	^5J(FF) 2.5 Hz ^3J(HF) 9.16 Hz	ν(CO) 1929
			II (12%)		^3J(HF) 9.16 Hz ^4J(HF) 2.5 Hz	23.8, quint., 3 ^5J(FF) = ^4J(HF) = 2.5 Hz	20.2, dq, 3 ^5J(FF) 2.5 Hz ^3J(HF) 8.7 Hz	
Ta	**4b**		I (83%)	4.42, s, 10	6.07, s, 1			ν(CO) 1922
			II (17%)	4.26, s, 10	5.79, s, 1			ν(CN) 2207 and 2177
Ta		**5b**	I (83%)			19.7, quint., 3	23.6, dq, 3	
				4.43, s, 10	6.81, qq, 1 [d]	^5J(FF) = ^4J(HF) = 2.45 Hz	^5J(FF) 2.45 Hz	
					^3J(HF) 9.3 Hz		^3J(FH) 9.3 Hz	ν(CO) 1914
			II (17%)		^4J(HF) 2.45 Hz	28.8, quint., 3 ^5J(FF) = ^4J(HF) = 2.45 Hz	25.5, dq, 3 ^5J(FF) 2.45 Hz ^3J(HF) 9.3 Hz	

[a] C_6D_6; δ ppm; TMS. [b] C_6D_6; δ ppm; CF_3COOH. [c] THF. [d] 7.02 (II).

(vinyl proton), but upon ^{19}F decoupling two signals are observed for the vinyl proton of the tantalum derivative **5b**. However the ^{19}F NMR spectra of these complexes clearly exhibit four multiplets which are assignable to two isomeric forms with an isomer ratio of 88/12 for **5a** and 83/17 for **5b** (see Fig. 1). In both cases, for the more abundant isomer the lower field signal is a pair of quartets arising from spin coupling with the proton (^3J(HF) ~ 9 Hz) and with the other CF_3 group (^5J(FF) ~ 2.5 Hz), while the upper field signal appears as a quintuplet because the coupling constants have similar values (^5J(FF) ~ ^4J(HF) ~ 2.5 Hz). That the two isomeric forms are not the *E* and *Z* isomers is clearly demonstrated by the coupling constants values; in both cases the low ^5J(FF) coupling constant unambiguously reveals the presence of two CF_3 groups in mutually *trans* positions around the double bond [8,10]. It is noteworthy that the quintuplet is the higher field signal for the first isomer but the lower field signal for the second.

These ^{19}F NMR data, together with some previously reported results, strongly suggest that hexafluorobutyne gives exclusively a *Z* adduct which is present as two conformers because the steric requirements of the ligands create a barrier to rotation around the M–C σ bond (see Fig. 1).

Examination of the molecular models does not suggest very important differences in stability between conformers I and II. In structure I the β-CF_3 group lies on the side of the molecule but at the same time the α-CF_3 group is close to the carbonyl ligand and comes under its anisotropic effects. On the other hand, in II the β-CF_3 group is under the influence of the nearly CO ligand and therefore the corresponding ^{19}F NMR signal is shielded and appears at higher field than those from the

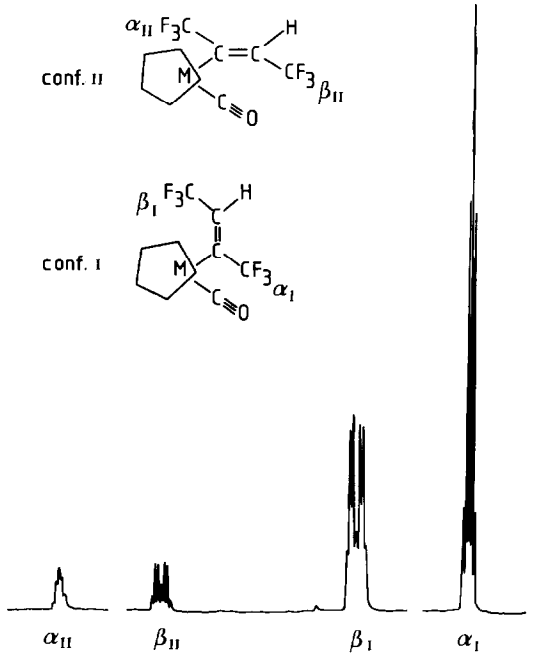


Fig. 1. ^{19}F NMR spectrum of $[Cp_2Ta(CO)\{(Z)\text{-}C(CF_3)=CHCF_3\}]$ (**5b**) in C_6D_6 at room temperature. Projections of the two conformers on the mirror plane showing the labelling of the CF_3 groups.

α-CF_3 groups; the α-CF_3 group lies close to the metal center, giving rise to unfavourable steric effects. The structure of the conformer predominantly formed in the reaction of $[Cp_2M(CO)H]$ with hexafluorobutyne may thus be assigned to I. Similar results have been previously reported for $[Cp^{\star}_2MoH\{(Z)\text{-}C(CF_3)=CHCF_3\}]$ ($Cp^{\star} = MeC_5H_4$) in solution in toluene [4a] and for $[Cp_2MoH\{(Z)\text{-}C(CO_2Me)=CHCO_2Me\}]$ in the solid state [11].

The free energy of activation for the interconversion I $\rightleftarrows$ II appears to be high, since up to 90°C, the limit of our study, the ^{19}F NMR spectrum of **5b** shows no significant changes. This is in sharp contrast with the behaviour of the molybdenum complex $[Cp_2MoH\{(Z)\text{-}C(CF_3)=CHCF_3\}]$, for which equilibration to 1/1 mixture was complete in a few hours at room temperature starting from a 4/1 mixture prepared at −77°C [4]. Two types of effects may be responsible for this high activation barrier: (i) Steric factors. It is clear that during the conversion I $\rightleftarrows$ II by rotation of the alkenyl group about the M–C bond the CF_3 groups come close to the cyclopentadienyl ligands. This steric crowding, which inhibits the rotation, is similar to that leading to atropisomerism, and from this point of view I and II may be regarded as atropisomers.

(ii) Electronic factors. The presence of two strongly electron-withdrawing groups on the alkenyl ligand induces an electronic delocalization which includes the lone pair of the metal atoms. This delocalization gives a metal–carbon bond having a partial double bond character and therefore restricts the rotation of the alkenyl group.

Similar conclusions are likely for dicyano complexes **4a** and **4b** for which, as seen above, the ^1H NMR data clearly show the presence of two isomers.

Reaction mechanism

It is noteworthy that reactions 1 and 2 can be regarded as simple nucleophilic additions of [M]–H to electron-poor alkynes, with the lone pair of the metal ion acting as the nucleophilic centre; examples of similar addition reactions may be found in organic chemistry for nitrogen-, phosphorus- and sulfur-containing compounds [12]. A stepwise ionic mechanism (eq. 3) can thus be suggested.

$$L_n(H)M: + RC{\equiv}CR \rightarrow L_n(H)\overset{+}{M}{-}C(R){=}\overline{C}R \rightarrow L_nM{-}C(R){=}CHR \qquad (3)$$

The second step (proton transfer) is likely because after donation of its lone pair the metal bears a positive charge. We have previously suggested similar proton transfers initiated by production of an electrophilic centre on niobium or tantalum [13,14].

This mechanism is not at variance with the *trans* stereospecificity observed in the reactions of $[Cp_2M(CO)H]$ with dicyanoethyne (complexes **4**) and hexafluorobutyne (complexes **5**). It does not, however, provide an explanation of the exclusive formation of the α-metallated isomer in the case of reactions with monosubstituted alkynes, since careful examination of the relative stabilities of the two carbanions which may arise from these acetylenes lead one to expect the opposite.

Another plausible mechanism involves an eighteen electron intermediate arising from a σ-donor–π-acceptor interaction between the lone pair of the metal complex and the LUMO of the organic acceptor; the latter is readily accessible because of the pronounced lowering which can be expected if the substituents on the alkyne exert purely inductive effects [15]. The MO studies for bent di-η-cyclopentadienylmetal derivatives by Green [16] and Hoffmann [17] show that in a d^2 complex such as $[Cp_2M(CO)H]$ the lone pair is located in an $1a_1$ orbital; this orbital lies in the mirror plane outside the [MH(CO)] system, and only permits lateral access of the alkyne (Fig. 2a). Since the interconversion I $\rightleftarrows$ II is impossible this mechanism cannot account for the simultaneous formations of both isomers, and the possibility of frontal access of the alkyne inside the HM(CO) angle must also be considered, a partial delocalization of the electron pair in this part of space being assumed (Fig. 2b). This dual possibility of attack (frontal and lateral) has been previously described for $[Cp_2MoH_2]$ [4,5,18]; it is consistent with the observed *trans* insertion of the alkyne.

Conclusion

The reactions of hydride carbonyl complexes $[Cp_2M(CO)H]$ (**1**) (M = Nb, Ta) with activated alkynes strongly resemble those of the dihydrides $[Cp_2MH_2]$ (M = Mo,

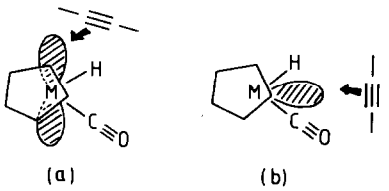


Fig. 2. Projection of $[Cp_2Nb(CO)H]$ on the mirror plane showing the delocalization of the lone pair and the lateral (a) or frontal (b) approach of the alkyne.

W). However, complex **1** is not markedly less reactive towards various activated alkenes than $[Cp_2MH_2]$. Thus diethylmalonate and diethylfumarate react with $[Cp_2MoH_2]$ to give the substitution product $[Cp_2MoL]$ but do not react with **1** under the same conditions. This difference may arise from differences in the base strengths of these metal complexes.

Experimental

Elemental analyses were carried out by the CNRS Microanalytical Service. Infrared spectra were recorded on Perkin–Elmer 589B spectrophotometer, ^1H and ^{19}F NMR spectra on a JEOL FX100 instrument, and mass spectra on a Finnigan 3002 spectrometer (70 eV).

All reactions were carried out under dry argon, and the solvents were dried by standard methods and distilled before use. Compounds **1a** and **1b** were made by published methods [19,20].

Reaction of $[Cp_2M(CO)H]$ (M = Nb or Ta) with $HC{\equiv}CCN$ and $NCC{\equiv}CCN$

Mono- [21] or di-cyano-ethyne [22] (1.1 mmol) was added at 0°C to a stirred solution of $[Cp_2M(CO)H]$ (1 mmol) in 50 ml of toluene. After 1 h the mixture was allowed to warm to room temperature and then stirred for an additional 24 h. The toluene was then evaporated to leave a brown solid in quantitative yield. Recrystallization from toluene and pentane gave a pure sample.

*$[Cp_2Nb(CO)(CH(CN){=}CH_2)]$ (**2a**).* Anal. Found: C, 56.51; H, 4.10; Nb, 30.73. $C_{14}H_{13}NONb$ calcd.: C, 55.46; H, 3.99; Nb, 30.64%. Mass fragments *m/e*: 303 (9) *M*, 275 (30) *M* − CO; 249 (100) Cp_2NbCN; 223 (28) Cp_2Nb.

*$[Cp_2Ta(CO)(CH(CN){=}CH_2)]$ (**2b**).* Mass fragments *m/e*: 391 (47) *M*; 363 (88) *M* − CO; 337 (100) Cp_2TaCN; 311 (50) Cp_2Ta.

*$[Cp_2Nb(CO)((Z)\text{-}C(CN){=}CHCN)]$ (**3a**).* Anal. Found: C, 54.45; H, 3.50; Nb, 27.58. $C_{15}H_{11}N_2ONb$ calcd.: C, 54.87; H, 3.35; Nb, 28.35%. Mass fragments *m/e*: 328 (8) *M*; 300 (21) *M* − CO; 249 (100) Cp_2NbCN; 223 (24) Cp_2Nb.

*$[Cp_2Ta(CO)((Z)\text{-}C(CN){=}CHCN)]$ (**3b**).* Anal. Found: C, 44.58; H, 2.76. $C_{15}H_{11}N_2OTa$ calcd.: C, 43.27; H, 2.64%. Mass fragments *m/e*: 416 (6) *M*; 388 (9) *M* − CO; 337 (100) Cp_2TaCN; 311 (7) Cp_2Ta.

Reactions of $[Cp_2M(CO)H]$ (M = Nb or Ta) with $HC{\equiv}CCF_3$ and $CF_3C{\equiv}CCF_3$

3,3,3-Trifluoropropyne or hexafluorobutyne (1 mmol) was added to a toluene solution of $[Cp_2(M(CO)H]$ (1 mmol). The mixture was stirred for 24 h and the solvent then evaporated. Recrystallization of the red-brown residue in pentane (**4a** and **4b**) or toluene (**5a** and **5b**) gave pure samples.

*$[Cp_2Nb(CO)(CF_3C{=}CH_2)]$ (**4a**).* Anal. Found: C, 48.52; H, 3.49. $C_{14}H_{12}F_3ONb$ calcd.: C, 48.55; H, 3.47%. Mass fragments *m/e*: 346 (17) *M*; 318 (3) *M* − CO; 242 (100) Cp_2NbF; 223 (36) Cp_2Nb; 215 (24) $CpNbF_3$; 196 (30) $CpNbF_2$; 177 (55) CpNbF. IR; ν(C–F): 1225, 1130, 1095, 1070 cm^{-1}.

*$[Cp_2Ta(CO)(CF_3C{=}CH_2)]$ (**4b**).* Anal. Found: C, 38.97; H, 2.82. $C_{24}H_{12}F_3OTa$ calcd.: C, 38.71; H, 2.76%. Mass fragments *m/e*: 434 (19) *M*; 330 (100) Cp_2TaF; 311 (10) Cp_2Ta; 303 (40) $CpTaF_3$. IR; ν(C–F): 1225, 1130, 1095, 1070 cm^{-1}.

*$[Cp_2Nb(CO)((Z)\text{-}CF_3C{=}CHCF_3)]$ (**5a**).* Anal. Found: C, 43.72; H, 2.58; Nb, 22.17. $C_{15}H_{11}F_6ONb$ calcd.: C, 43.49; H, 2.66; Nb, 22.44%. Mass fragments *m/e*:

414 (26) M; 386 (16) $M - CO$; 367 (6) $M - CO - F$; 261 (34) Cp_2NbF_2; 242 (100) Cp_2NbF; 223 (44) Cp_2Nb; 215 (65) $CpNbF_3$; 196 (98) $CpNbF_2$; 177 (82) CpNbF. IR; ν(C–F): 1290, 1220, 1140, 1120 cm^{-1}.

*[$Cp_2Ta(CO)((Z)$-$CF_3C{=}CHCF_3)$] (**5b**).* Anal. Found: C, 36.77; H, 2.43. $C_{15}H_{11}F_6OTa$ calcd.: C, 35.87; H, 2.27%. Mass fragments m/e: 502 (12) M; 474 (0.5) $M - CO$; 349 (32) Cp_2TaF_2; 330 (100) Cp_2TaF; 311 (6) Cp_2Ta; 303 (47) $CpTaF_3$; 284 (47) $CpTaF_2$. IR; ν(C–F): 1290, 1220, 1140, 1125 cm^{-1}.

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