Journal of Organometallic Chemistry, 391 (1990) 119–122
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20737

$^{13}C\{^1H\}$ NMR studies of selected transition metal alkyne complexes

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(Received December 27th, 1989)

Abstract

$^{13}C\{^1H\}$ NMR spectra of selected nickel alkyne complexes $(Ph_3P)_2Ni(RC_2R)$ have been recorded and the results are compared with the relevant data for other alkyne complexes of transition metals. It has been found that the complexes with two-electron alkyne ligands such as $(Ph_3P)_2Ni(RC_2R)$, $(Me_3P)_2Ni(RC_2R)$, $(Ph_3P)_2Pt(RC_2R)$ and the complexes with four-electron alkyne ligands such as $Cp_2Ti(RC_2R)$, $Cp^\star_2Ti(RC_2R)$ ($Cp^\star = \eta^5$-C_5Me_5), $CpV(PMe_3)_2(RC_2R)$, $W(OCMe_3)_4(RC_2R)$ are characterized by the markedly different influence the electronic parameters of the substituents R have on the value of the ^{13}C NMR downfield shift, $\Delta\delta(C{\equiv}C)$, on going from free to complexed C≡C bond. The IR spectra of the two types of complexes show no specific differences in the influence of various alkyne substituents R on the relevant $\Delta\nu(C{\equiv}C)$ values.

Introduction

A very helpful concept to elucidate the influence of various acetylene substituents R in complexes $L_nM(RC_2R)$ on the alkyne complexation (if L = const., M = const.) is the correlation of the electronic parameters σ_I of R with the difference between the C≡C bond stretching frequency of the free and that of coordinated alkyne molecule $\Delta\nu(C{\equiv}C)$ [1,2]. In all cases a high value of $\Delta\nu(C{\equiv}C)$ indicates a high stability of the complex. This approach is also suitable for characterizing the effect of different ligands (if R = const., M = const.) and of different metals (if L = const., R = const.) on alkyne complexation [2].

The ^{13}C NMR chemical shifts of alkyne carbon atoms coordinated to a metal are often a useful diagnostic tool for classifying alkyne complexes. Templeton and

Ward found that an empirical correlation exists between the number of electrons formally donated by an alkyne ligand to a metal and the chemical shift $\delta(C\equiv C)$ of the bound alkyne carbon nuclei [3]. In the case of complexes where the alkyne molecule donates only two electrons, the $\delta(C\equiv C)$ value lies between ~ 100 and 150 ppm [3–6]. If $\delta(C\equiv C)$ is about 190–270 ppm, it can be concluded that the alkyne ligand donates four electrons to the metal [3,4,7–11].

Here we present some data on the influence of the electronic parameters of the alkyne substituents R in two types of complexes on the difference in the chemical shifts of alkyne carbon atoms for coordinated and free alkyne molecule, viz., $\Delta\delta(C\equiv C)$.

Results and discussion

The method based on a comparison of $\Delta\nu(C\equiv C)$ values is insensitive for detecting the specific influence of the electronic parameters of R substituents in various alkyne complexes. This is clearly shown by the data listed in Table 1. For the complexes $(Ph_3P)_2Ni(RC_2R)$, (dmpe)$Ni(RC_2R)$ and $Cp_2Mo(RC_2R)$ in which an alkyne behaves as a two-electron ligand (see Table 2 and refs. 6 and 12) and for complexes $Cp_2Ti(RC_2R)$, $Cp^{*}_2Ti(RC_2R)$ and $[WCl_4(RC_2R)]_2$ where the alkyne is a four-electron ligand [7–10,13], practically the same trend in changing of $\Delta\nu(C\equiv C)$ is observed if for instance an alkyne with electron-withdrawing substituents is replaced by an alkyne with electron-releasing substituents and vice versa.

The use of the $\Delta\delta(C\equiv C)$ values to classify alkyne complexes and to find out the influence of electronic character of the alkyne substituents in the various complexes, $L_nM(RC_2R)$, is novel. In some of the investigated examples of $(Ph_3P)_2Pt(RC_2R)$ [5] and $(Me_3P)_2Ni(RC_2R)$ [6] (R = Rh, Me) there was little or no effect of the electronic parameters of R on the $\Delta\delta(C\equiv C)$ values, and so this effect was not further studied.

We have recorded the $^{13}C\{^1H\}$ NMR spectra of the series of complexes $(Ph_3P)_2Ni(RC_2R)$ in order to calculate their $\Delta\delta(C\equiv C)$ values and to compare them

Table 1

Inductive parameters (σ_I) of the alkyne R substituents and IR data for selected transition metal alkyne complexes $L_nM(RC_2R)$

R	Me_3Si	Me	Ph	COOMe	
σ_I	−0.11	−0.01	0.12	0.32	
$\nu(C\equiv C)$ for free alkyne (cm^{-1}) [a]	2107	2233	2223	2256	
Complex [b]	$\Delta\nu(C\equiv C)$ (cm^{-1})				Refs.
$Cp^{*}_2Ti(RC_2R)$	509, 544	550	576	–	8, 10
$[WCl_4(RC_2R)]_2$	484	490	535	–	13
$Cp_2Ti(RC_2R)$	420	–	510	–	7, 9
$Cp_2Mo(RC_2R)$	375	403	450	473	1
(dmpe)$Ni(RC_2R)$	–	450	477	–	6
$(Ph_3P)_2Ni(RC_2R)$	370	393	419	449	2, 14, 15

[a] The $\nu(C\equiv C)$ values for free alkynes are taken from ref. [1]. [b] Cp = η^5-C_5H_5, Cp* = η^5-C_5Me_5, dmpe = $Me_2PCH_2CH_2PMe_2$.

Table 2

$^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR data for selected nickel alkyne complexes $(Ph_3P)_2Ni(RC_2R)$ and the inductive parameters (σ_I) of the alkyne substituents R [a]

R	σ_I	^{13}C NMR			^{31}P NMR δ (ppm)
		$\delta(C{\equiv}C)$ (ppm)		$\Delta\delta(C{\equiv}C)$ (ppm)	
		free alkyne	alkyne in complex		
Me_3Si	−0.11	114.0	152.8	38.8	38.0
Et	−0.01	81.0	126.0	45.0	40.6
Me	−0.01	74.4	119.7	45.3	38.8
Me_3SiOCH_2	–	83.8	126.2	42.4	39.9
$MeOCH_2$	0.11	82.8	123.9	41.1	39.5
Ph	0.12	90.1	135.4	45.3	39.8
$MeCOOCH_2$	0.15	81.2	124.4	43.2	39.7
MeOOC	0.32	74.9	130.0	55.1	39.5

[a] $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker WP-200-SY spectrometer (200.13 MHz) in benzene-d_6 at 50.31 and 81.01 MHz respectively with benzene-d_6 as internal standard (δ 127.96 ppm) or 1% H_3PO_4 as external standard. The initial complexes were prepared by published methods (see refs. 2, 15 and refs. therein).

with the relevant data on other alkyne complexes for which the $\delta(C{\equiv}C)$ values have appeared.

Table 2 shows the chemical shifts $\delta(C{\equiv}C)$ and the $\Delta\delta(C{\equiv}C)$ values for $(Ph_3P)_2Ni(RC_2R)$ complexes while in Table 3 are listed selected values of $\Delta\delta(C{\equiv}C)$ for $(Ph_3P)_2Ni(RC_2R)$ together with those for some other alkyne complexes of nickel, platinum, titanium, vanadium and tungsten. The complexes $W(OCMe_3)_4(RC_2R)$ and $CpV(PMe_3)_2(RC_2R)$, like $Cp_2Ti(RC_2R)$ and $Cp_2^{\star}Ti(RC_2R)$, are characterized by $\delta(C{\equiv}C)$ values at 190–250 ppm so that the

Table 3

Inductive parameters (σ_I) of the alkyne R substituents and $^{13}C\{^1H\}$ NMR data for selected transition metal alkyne complexes $L_nM(RC_2R)$

R	Me_3Si	Et	Me	Ph	COOMe		
σ_I	−0.11	−0.01	−0.01	0.12	0.32		
δ (C≡C) for free alkyne (ppm) [a]	114.0	81.0	74.4	90.1	74.9		
Complex	$\Delta\delta(C{\equiv}C)$ (ppm)					Solvent	Refs.
$CpV(PMe_3)_2(RC_2R)$	–	144.6	–	136.7	–	not given [b]	16
$W(OCMe_3)_4(RC_2R)$	–	132.2	–	112.2	–	C_6D_6	11
$Cp_2^{\star}Ti(RC_2R)$	134.4	–	125.7	110.8	–	$C_6D_5CD_3$,C_6D_6	8,10
$Cp_2Ti(RC_2R)$	130.9	–	–	106.4	–	C_6D_6	7,9
$(Me_3P)_2Ni(RC_2R)$	–	–	45.8	46.6	–	THF-d_8	6
$(Ph_3P)_2Ni(RC_2R)$	38.8	45.0	45.3	45.3	55.1	C_6D_6	this work
$(Ph_3P)_2Pt(RC_2R)$	–	–	38.8	38.3	–	$CDCl_3$	5

[a] In C_6D_6 as solvent; the values of $\delta(C{\equiv}C)$ for R = Ph and for R = Me are 90.0 and 74.4 ppm, respectively, in THF-d_8; the value of $\delta(C{\equiv}C)$ for R = Me is 74.5 ppm in $C_6D_5CD_3$ (data: this work).
[b] The $\Delta\delta(C{\equiv}C)$ values for $CpV(PMe_3)_2(RC_2R)$ complexes are calculated on the assumption that C_6D_6 is the solvent. A change of a solvent should not significantly affect the $\Delta\delta(C{\equiv}C)$ values.

alkyne ligand in all these complexes can be regarded as a donor of four electrons. In the complexes $(Ph_3P)_2Ni(RC_2R)$, $(Me_3P)_2Ni(RC_2R)$ and $(Ph_3P)_2Pt(RC_2R)$ the $\delta(C{\equiv}C)$ values are in the region 100–150 ppm and hence the coordinated alkyne molecule is a two-electron ligand.

It is seen from Table 3 that the two types of complexes differ markedly in the magnitude of the $\Delta\delta(C{\equiv}C)$ values and in the influence of the electronic parameters of the alkyne substituents R on these values. In the titanium, vanadium and tungsten complexes the $\Delta\delta(C{\equiv}C)$ values attain 106–145 ppm, which tend to decrease on going from complexes with electron-releasing R substituents to complexes with electron-withdrawing R substituents. In the nickel and platinum complexes the $\Delta\delta(C{\equiv}C)$ values are much lower (38–55 ppm) and these values either remain constant or increase slightly on going to complexes with electron-withdrawing R substituents in the alkyne molecule. The fact that the titanium, vanadium and tungsten complexes are characterized by considerably higher $\Delta\delta(C{\equiv}C)$ values compared with the nickel and platinum complexes means that involvement of two π-electron pairs of alkyne in the bonding with a metal causes a stronger change of the chemical shift of alkyne carbon atoms than the bonding of alkyne by only one π-electron pair. Further studies should show to what extent the above differences between the titanium, vanadium and tungsten complexes on the one hand and the nickel and platinum complexes on the other hand are shared by other complexes with two- and four-electron alkyne ligands.

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