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Structural comparison of acetylenenickel(0) complexes *

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Abstract

On the basis of X-ray structural parameters and infrared frequencies of nickel(0) complexes of the type $L_xNi(XC_2X)$ we found a good linear correlation between the reduction in frequency of the symmetric stretching mode of the acetylenic triple bond resulting from coordination, $\Delta\nu$(C≡C), and the corresponding C–C bond length of the coordinated triple bond, d(C≡C).

In these complexes donor ligands L and/or acceptor substituents X favor complexation, activation and reactivity of disubstituted acetylenes in acidolysis, insertions and cyclotrimerization as shown by higher shifts of frequency $\Delta\nu$(C≡C) and lengthening of triple bonds.

Introduction

A number of mononuclear complexes have been prepared in which acetylenes are bonded sideways to one metal and have been discussed on the basis of structural parameters and infrared frequencies [1,2]. The extent of lengthening of the C≡C bonds reflects as does the bending of C≡C–C angles upon coordination a major contribution by π–back donation and a minor contribution by σ– and π–donation. The majority of the C≡C bond distances of the coordinated acetylenes lie in a relatively small range (1.28 ± 0.02 Å) as do also the deformation angles (143 ± 5°) [1].

Quantitative interpretation of these structural parameters seemed to be difficult, but the number of structures was limited [1].

Ittel and Ibers found no correlation between C≡C distances and the bending back of substituent groups [2]. Further more it has been shown that no linear

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correlation exists between the stretching frequency and the angle formed by the substituent with the triple bond [3]. An often used experimental criterion of acetylene–metal bond strength is the difference in the C≡C stretching frequency between the uncoordinated and the coordinated acetylene ligand [4].

The significance of these trends has been questioned by Struchkov et al. as this variation seems to depend on the interaction of various factors [5]. Davies and Payne observed a linear correlation between frequency shift, $\Delta\nu$(C≡C), and the bend-back angle for a number of acetylene complexes of different transition metals [6]. There are some arguments in favor of being careful in using C≡C stretching frequencies for the direct calculation of the bond order [7]. However, in all the studies complexes of acetylenes with different metals in different oxidation states were compared.

In studies on platinium–acetylene complexes it was not possible to correlate any trends of structural parameters with electron-withdrawing or -releasing behavior of the acetylene substituents [8].

During our studies [9–12] of acetylenenickel(0) complexes exclusively we noticed that there were only few reliable crystallographic structural data on nickel(0) complexes with symmetrically disubstituted acetylenes and we therefore studied some of these structures [13,14].

We found that "activation" of acetylenes is caused by complexation as shown by the correlation of stretching frequencies with acetylene reactivity in some stoichiometric and catalytic reactions [11,12], such as acidolysis, insertions and cyclotrimerization.

Because there are not many differences in the C≡C triple bond frequencies of these complexes in solution and in the solid state, we had in mind the interesting problem of the correlation of metrical details of the bonding with reactivity parameters.

For this one needs systematic studies of the same acetylene bound to a NiL_x system with different ligands L, and many more studies of complexes in which two or more different acetylenes are bound to the same NiL_x system are necessary [2].

Results and discussion

Although many acetylene complexes of the type L_2Ni(acetylene) are claimed in the literature, there are only few structures with symmetrically disubstituted acetylenes established by X-ray methods. So we investigated the crystal and molecular structure of the two complexes $(Ph_3P)_2Ni(Me_3SiC_2SiMe_3)$ (**2**) [13] and $(Ph_3P)_2Ni(HOCH_2C_2CH_2OH)$ (**9**) [14].

Structural data, submitted by different authors and some infrared data for acetylenenickel(0) complexes in which symmetrically substituted acetylenes are bonded sideways to one metal atom are listed in Table 1. The data are limited, but some comments can be made. There seems to be no correlation between bend-back angles (deviation of the acetylene ligand from linearity) and frequencies of the complexed acetylene ν(C≡C) or reduction of frequency of triple bonds resulting from coordination $\Delta\nu$(C≡C) as found in [6]. Furthermore it does not seem possible to correlate any trends in Ni–C distances or C–Ni–C angles. With one exception, **9**, all the complexes, listed in Table 1 represent the first example of a good correlation between the reduction in frequency of the symmetric stretching mode of the acetylenic triple bond resulting from complexation $\Delta\nu$(C≡C) and the corresponding

Table 1

Structural data of acetylenenickel(0) complexes

No.	Compounds [a]	$\Delta\nu$(C≡C) (cm^{-1})	d(C≡C) (Å)	ν(C≡C) (cm^{-1})	bend-back angle (°)	Ref.
1	$(Ph_3)P_2Ni(CH)_2$	344	1.239(4)	1630	148 ± 2	15
2	$(Ph_3P)_2Ni(CSiMe_3)_2$	370	1.256(2)	1737	143.3(1)	13
3	$(dad)Ni(CCH_2OH)_2$	399	1.273(7)	1811	152.4(3)	16
4	$(^tBuNC)_2Ni(CPh)_2$	413	1.285(20)	1810	148.6(1,4)	17
5	$(cod)Ni(CPh)_2$	423	1.280(4)	1800	–	18
6	$(bdmpe)Ni(CPh)_2$	451	1.290(3)	1772	146.4(2) 145.6(2)	19
7	(bdcype)Ni(cyclohexyne)	502	1.332(6)	1583	122.9(4)	20
Exception						
9	$(Ph_3P)_2Ni(CCH_2OH)_2$	405	1.228(6)	1805	140.5(4) 142.1(5)	14

[a] Abrevations: dad = N,N'-ethanediylidenebis(2,6-diisopropylaniline), bdmpe = 1,2-bis(dimethylphosphino)ethane, bdcype = 1,2-bis(dicyclohexylphosphino)ethane.

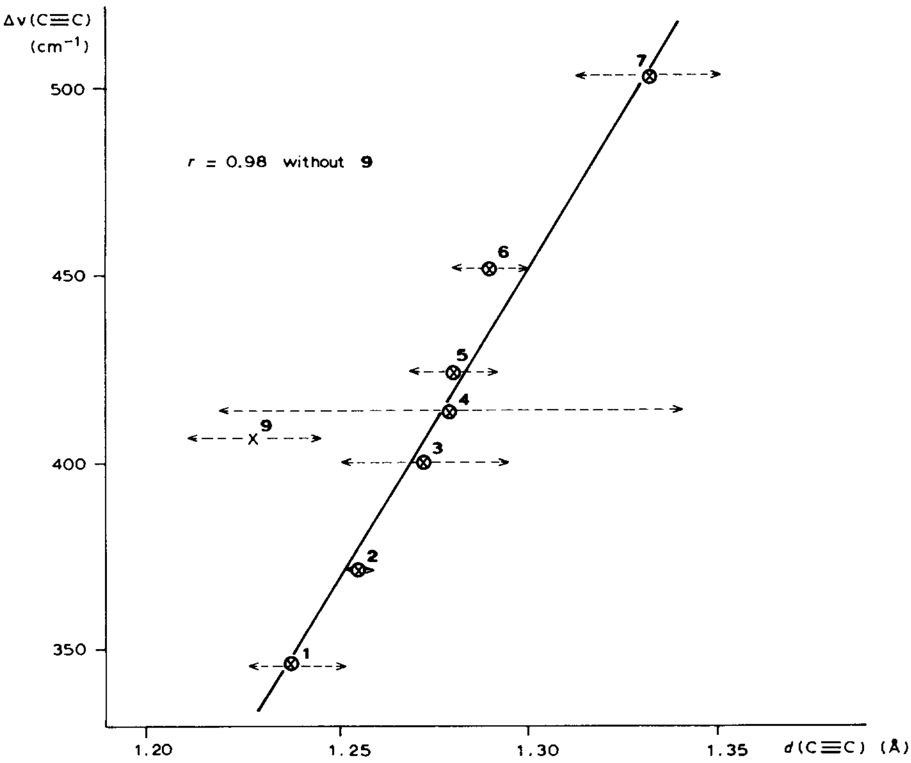

Fig. 1. A plot of $\Delta\nu$(C≡C) vs. acetylenic triple bond lengths d(C≡C). Error bars are ± σ on d(C≡C). All points on the graph are labeled to correspond to the compound numbers in Table 1.

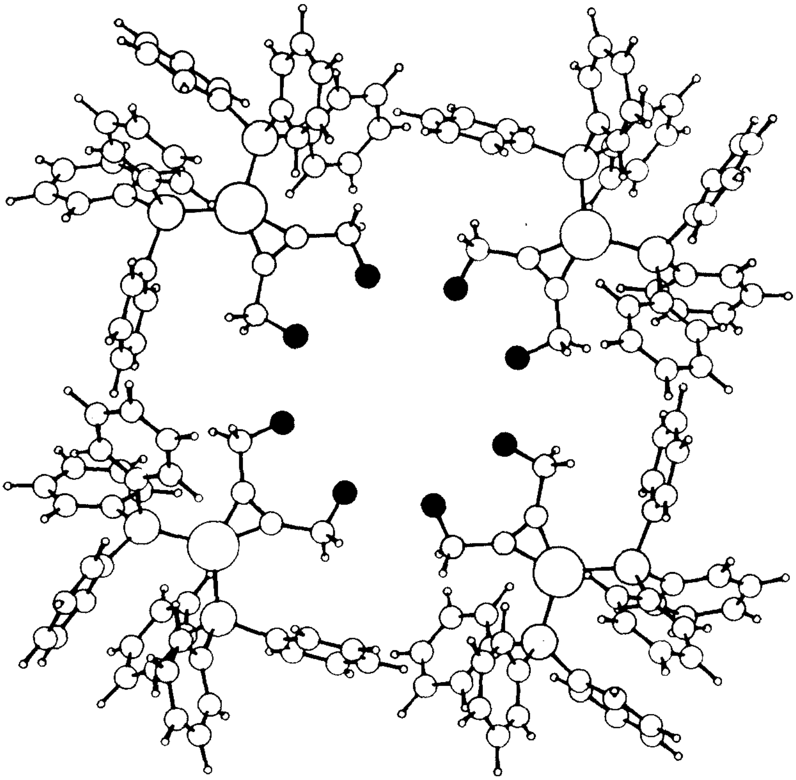

Fig. 2. Eight-membered oxygen ring in the molecular structure of **9** (black points represent oxygen atoms) [14].

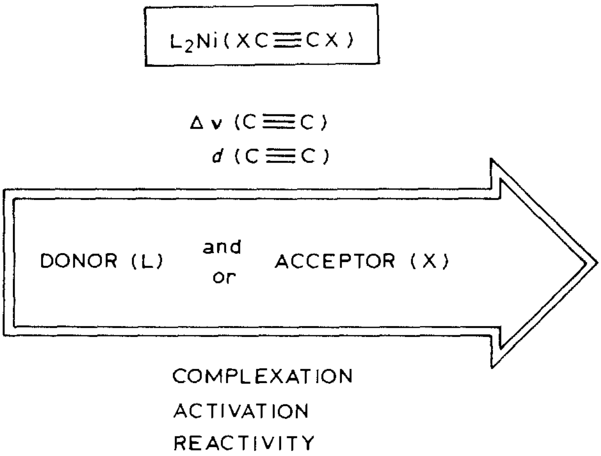

Fig 3. Schematic representation of the influence of donor and acceptor properties of ligands L and substituents X on complexation, activation and reactivity of acetylenes and on $\Delta\nu(C\equiv C)$ and $d(C\equiv C)$ in complexes of the type $L_2Ni(XC_2X)$.

C–C bond length of the coordinated triple bond $d(C{\equiv}C)$ ($r = 0.98$) (Fig. 1). Only the exception **9** is a special case [14] in which the complexed disubstituted acetylene $HOCH_2{-}C_2{-}CH_2OH$ is probably distorted by the existence of intra- and intermolecular OH...O hydrogen bonds (Fig. 2).

A general qualitative picture for complexation and activation of disubstituted acetylenes in nickel(0) complexes is shown in Fig. 3.

As we were able to show for complexes of the type $L_2Ni(XC_2X)$, donor ligands L and/or acceptor substituents X favor the complexation and activation of disubstituted acetylenes for some reactions such as acidolysis, insertions and cyclotrimerization. This correlates with higher shifts of frequency $\Delta\nu(C{\equiv}C)$ [12] and is connected with a lengthening of triple bonds. In complexes of acetylene itself and terminal acetylenes the extensive mechanical coupling between the stretching of the triple bond and the adjoining CH bond makes a comparison with complexes of disubstituted acetylenes impossible.

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