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Metal-side chain interaction in tricarbonylchromium complexes of phenylacetylenes studied by ^{13}C NMR and IR spectroscopy

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Abstract

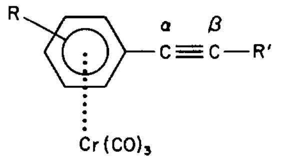
^{13}C NMR spectra of several η^6-arenetricarbonylchromium complexes of phenylacetylene and phenyltrimethylsilylacetylene have been interpreted. The complexing chemical shifts (CCS) observed for α and β acetylenic carbons suggest the existence of a direct interaction between the metal atom and π-electron system of the ethynyl substituent. The overall complexing effect is of the electron-withdrawing type which was confirmed by $\delta(^{29}Si)$, $^2J(CH)$ and IR data. Some observations concerning synthesis of the investigated complexes have been also reported.

Introduction

Formation of η^6-tricarbonylchromium complexes remarkably changes the properties of the organic ligand [1]. This fact is exploited in organic synthesis [2,3]. There is numerous chemical and spectroscopical evidence that those changes also concern the side chain groups. The influence of the metal on the side chain is transmitted not only through bonds but also by the direct interaction of the metal with the atom at the benzylic position [1,4]. Those two effects are opposite so that the net effect is difficult to predict. In this work we discuss this problem as it concerns the phenylacetylene complexes **1–8** (Fig. 1), based upon ^{13}C NMR and IR data.

Discussion

The complexing of the aromatic ring leading to the formation of η^6-arenetricarbonylchromium complexes is known to diminish the electron density in the ligand and the influence of the tricarbonylchromium group used to be compared with the effect of the ring substitution by the nitro group [1–3]. On this basis, and taking into account the substituent chemical shift (SCS) for uncomplexed *para*-substituted phenyltrimethylsilylacetylenes [5] and phenylacetylenes [6], one may expect that complexing of compounds **1a–8a** results in shielding of the α and



R	R′	
	SiMe$_3$	H
H	**1**	**6**
p-NMe$_2$	**2**	**7**
m-NMe$_2$	**3**	**8**
p-^{t}Bu	**4**	
m-^{t}Bu	**5**	

Fig. 1. Complexes **1–8**.

deshielding of the β acetylenic carbons. The complexing chemical shifts (CCS) are collected in Table 1. Inspection of these data shows that the direction of the observed changes is in accord with the above prediction.

The effects observed for sililated compounds are somewhat larger than those for nonsilylated ones. This observation parallels the increased sensitivity for *para*-substitution of phenyltrimethylsilylacetylenes as compared to phenylacetylene, which was attributed to the higher polarisability of the trimethylsilylethynyl group [5].

The magnitude of the deshielding effect observed for the β carbons (~ 2 ppm for complexes **1–5** and ~ 0.5 ppm for compounds **6–8**) indicates that the complexing resembles the *para*-substitution of the ring by a weakly electron-withdrawing substituent [5,6]. On the other hand, the CCS for the α carbons are twice as large as for *para*-substitution by the nitro group [5,6]. This discrepancy can be well

Table 1

Complexing chemical shifts (CCS) [a] and substituent chemical shifts (SCS) [b] for investigated compounds

Ligand	CCS		SCS for complex		SCS for ligand	
	C-α	C-β	C-α	C-β	C-α	C-β
1a	−4.50	1.71				
2a	−5.76	1.55	0.21	−3.11	1.47	−2.95
3a	−4.50	2.77	1.12	−0.43	1.12	−1.49
4a	−4.89	2.32	−0.07	−0.18	0.32	−0.79
5a	−4.82	1.60	0.41	−0.97	0.73	−0.86
6a	−3.86	0.48				
7a	−5.09	0.48	0.15	−2.38	1.35	−2.83
8a	−3.89	0.69	1.18	−1.04	1.18	−1.25
p-$\mathrm{NO_2C_6H_4C{\equiv}CH}$					−1.89	5.15
p-$\mathrm{NO_2C_6H_4C{\equiv}CSiMe_3}$					−2.48	6.46
Toluene	−0.57					
Indene [c,d]	−0.83					
Fluorene [c,e]	−0.24					

[a] CCS = δ(complex) − δ(ligand). [b] SCS = δ(ring substituted compound) − δ(parent compound). [c] The value concerns CH$_2$-carbon. [d] δ(CH$_2$) for ligand was taken from [7]. [e] δ(CH$_2$) for ligand was taken from [8] and for complex from [9].

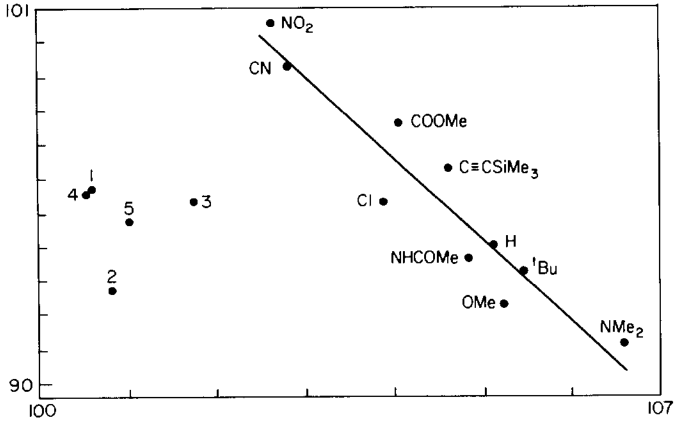
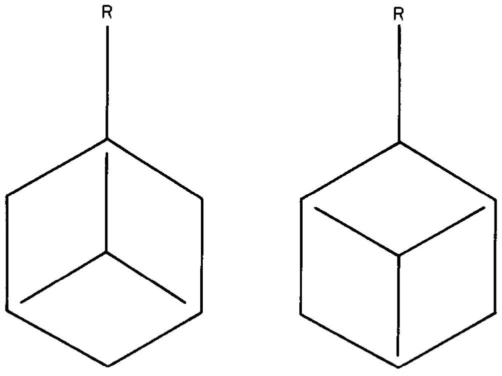


Fig. 2. ^{13}C chemical shift of C-β versus chemical shift of C-α in phenyltrimethylsilylacetylene series.

visualised by the δ(C-α) versus δ(C-β) plot (Fig. 2) for the phenyltrimethylsilylacetylene series. The data for complexes of toluene, indene and fluorene (Table 1) show that this effect can be attributed neither to long-range shielding by the diamagnetic anisotropy of the tricarbonylchromium moiety, nor to ring current quenching, nor to any effect transmitted through the sigma bond. Those factors should equally well affect the chemical shifts of the saturated carbons bonded directly to the complexed ring, which is actually not observed (Table 1). Thus, it seems that the large shielding effects of unsaturated α carbons, and smaller than expected deshielding effect for β carbons, are a result of the direct interaction of the chromium *d*-orbitals with the π electron system with the side chain. Such an interaction was postulated in the past in order to explain various physico-chemical observations [1,4]. One may expect such back-donation to be dependent on the conformation of the tricarbonylchromium tripod against the side chain.

In order to check this expectation we compared ^{13}C NMR spectra of compounds **1** and **6** to spectra of their ring substituted derivatives. The dimethylamino group is known to strongly prefer the *syn*-eclipsed conformation (Fig. 3) due to electronic reasons, whereas the *tert*-butyl group sterically favours the *anti*-eclipsed conformation [1,10]. The trimethylsilylethynyl and the ethynyl groups are weakly directing substituents. Unfortunately, the changes of the CCS values observed for C-α are difficult to interpret. Some conformational effect can however be observed for β-carbons. Comparing the SCS values of C-β in ligands and complexes (Table 1), one may notice the similarity of changes in groups of these compounds of the same prefered conformations, i.e. for compounds **2**, **5** and **7**; and on the other hand for compounds **3**, **4** and **8**. The same property is reflected in the CCS data. The overall conformational effect is however not very large.

In light of the proposed interpretation of the CCS of the acetylenic carbons, it is clear that those changes, especially in the case of C-α, cannot be used as a direct measure of the electron density changes in the side chain caused by complexing. Nevertheless, the downfield shift observed for the β-carbons indicates that the net effect is of the electron-withdrawing type [5,6]. This conclusion is confirmed by several other observations. The silicon chemical shift of complex **1** ($\delta = -16.53$) is close to that observed for *para*-nitrophenyltrimethylsilylacetylene ($\delta = -16.62$) [5].



a b

Fig. 3. *syn*-Eclipsed (a) and *anti*-eclipsed (b) conformations of substituted η^6-benzenetricarbonylchromium.

In view of the data for *p*-substituted phenyltrimethylsilylacetylenes, that fact shows the similarity of the electronic effect of complexing and the *para*-nitro substitution [5]. Moreover, the values of ^1J(CH) and ^2J(CH) involving the acetylenic protons in compounds **6** and **7** (Table 2) suggest the increased polarization of the C–H bond compared to the free ligand [6,11].

Finally the IR data for the free and the hydrogen bonded stretching C–H modes show that the acidity of the acetylenic C–H is higher than in phenylacety-

Table 2

One-bond and two-bond $^{13}C-^{1}H$ spin–spin coupling constants involving acetylenic protons in phenylacetylene derivatives [a]

Compound	^1J(CH) (Hz)	^2J(CH) (Hz)
6	50.1	255.1
6a	49.6	251.3
7	50.3	253.9
7a	49.3	249.4
8	50.5	254.7
8a	49.7	250.6
p-$NO_2PhC{\equiv}CH$	50.0	254.1

[a] Accuracy ±0.3 Hz.

Table 3

Acetylenic C–H stretching frequencies (cm^{-1}) in IR spectra for phenylacetylene derivatives in CCl_4/HMPT (9:1) solution

Compound	$\nu(\equiv C-H)$	$\nu(\equiv C-H\cdots O)$	$\Delta\nu$
p-$NO_2PhC{\equiv}CH$	3309.6 [a]	3146.8	162.8
6	3304.0	3150.8	153.2
6a	3314.0	3176.8	137.2
7a	3312.0	3184.0	128.0

[a] Mean value calculated according to [13a] from values 3316.0 and 3304.0 cm^{-1}.

Table 4

^{13}C NMR spectra of complexes **1–8** and their ligands **1a–8a** in $CDCl_3$

No.	C-1	C-2 C-6	C-3 C-5	C-4	C-α	C-β	Me	CO	Other signals		m_p/b_p
1	90.21	94.74	91.54	90.27	100.62	95.77	−0.29	231.98			75–76
1a	123.13	131.94	128.16	128.44	105.12	94.06	−0.03				45–46/0.1 mmHg
2	80.45	99.08	73.29	133.70	100.83	92.66	−0.18	233.51	NMe_2	39.71	
2a	109.97	133.09	111.59	150.21	106.59	91.11	0.21		NMe_2	40.10	77–78
3	93.66	76.39 85.78	134.03 95.42	72.44	101.74	95.34	−0.27	234.29	NMe_2	39.69	
3a	123.46	115.63 120.30	150.20 128.84	113.04	106.24	92.57	−0.31		NMe_2	40.34	25–26
4	90.89	91.22 [a]	92.89 [a]	120.59	100.55	95.59	−0.33	232.70	C Me	33.81 30.89	
4a	120.25	131.72	125.16	151.74	105.44	93.27	−0.06		C Me	34.75 31.16	29–30
5	88.19	94.48 [a] 93.50 [a]	121.76 88.70	90.18 [a]	101.03	94.80	−0.22	232.55	C Me	34.10 30.89	
5a	122.73	128.92 [a] 129.15 [a]	151.07 127.96	125.69 [a]	105.85	93.20	0.05		C Me	34.57 31.26	oil
6	88.40	95.17	91.09	90.99	79.60	77.59		231.72			70–71
6a	121.99	131.96	128.14	128.60	83.49	77.11					143–144
7	78.68	99.34	73.07	134.08	79.75	75.21		233.32	NMe_2	39.66	
7a	108.79	133.18	111.68	150.64	84.84	74.73			NMe_2	40.11	52–53
8	92.29	77.42 85.94	133.85 95.12	72.82	80.78	75.86		234.05	NMe_2	39.64	
8a	122.51	115.86 120.33	150.33 128.97	113.27	84.67	76.56			NMe_2	40.34	47–48

[a] Tentative assignment.

lene and comparable to that of the *p*-nitro substituted derivative (Table 3) (see e.g. [12]).

The magnitude of those three last effects (i.e. changes of $\delta(^{2}\mathrm{Si})$, $^{1}J(\mathrm{CH})$ and δ_{ν}) suggests that the tricarbonylchromium group behaves like an electron-withdrawing substituent. All the observations discussed in this paper confirm the complexity of the interaction mechanism between the metal and the side chain in η^6-arenetricarbonylchromium complexes.

Experimental

Ligands **1a**–**8a** were synthesized from the appropriate aryl iodides and trimethylsilylacetylene in the presence of copper(I) iodide and tetrakis-(triphenylphosphine)palladium(0) [14] as described in [15]. An analogous reaction was reported to give derivatives of η^6-phenylacetylenetricarbonylchromium complexes with a very high yield when starting from η-^{6}chlorobenzenetricarbonylchromium [16]. Unfortunately we were unable to reproduce such good results. In our attempts to synthesize complex **1** by that method, the yields of the desired product did not exceed 30% and simultaneously η^6-benzenetricarbonylchromium and 1,4-bis(trimethylsilyl)-1,3-butadiyne [17] were separated from the reaction mixture in comparable amounts.

The earlier proposed methods of the synthesis of complex **1** were very inefficient [18].

Finally, it appeared that complexes **1**–**5** could be synthesized by the standard method [19], i.e. by heating a ligand with $\mathrm{Cr(CO)_6}$ in dibutyl ether and THF. Complexes **6**–**8** were obtained by hydrolysis of their trimethylsilyl derivatives [18]. The reaction products were contaminated with some amounts of free ligands (TLC, ^{13}C NMR) which were not removed.

^{13}C NMR data of the compounds investigated are listed in Table 4. Spectra of samples of ~ 10% w/v solutions in $\mathrm{CDCl_3}$ were recorded on a Varian XL-VXR-300 spectrometer (operating at 75.4 MHz). The central line of the $\mathrm{CDCl_3}$ triplet (77.0 ppm) was used as an internal standard. The recording conditions ensured that the signal-to-noise ratio would be higher than 3 for the weakest signal, and the digital resolution would be better than 0.015 ppm.

The signals of the ring carbons were assigned assuming additivity of the substituent increments of the chemical shifts [20] and taking into account low intensities of quaternary carbon signals. The signals of the acetylenic carbons were distinguished from each other on the basis of the proton coupled ^{13}C spectra.

IR spectra of 0.1 mol/l solutions in $\mathrm{CCl_4}$/HMPT (9:1) samples were determined with a SPECORD M80 spectrometer using a 0.063 mm $\mathrm{KRS_5}$ cell. All measurements were taken at room temperature.

Acknowledgments

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