NOTIZEN

^{13}C NMR Spectroscopic Study of Pentacarbonylacetonitrilemetal(0) Complexes of the Group 6 B Elements

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The complexes $M(CO)_5(CH_3CN)$ (M: Cr, Mo, W) were obtained from the substitution of THF in $M(CO)_5(THF)$ which has been generated by photolysis of $M(CO)_6$ in THF and characterized by using IR, ^1H NMR and ^{13}C NMR spectroscopies. The acetonitrile ligand is found to be N-bonded to the $M(CO)_5$-moiety with a local C_{4v}-symmetry. The effect of the acetonitrile ligand on the metal-carbonyl bonding was discussed in terms of ^{13}C NMR chemical shifts.

Introduction

The photochemical or thermal substitution of hexacarbonylmetal(0) molecules with acetonitrile gives the complexes $M(CO)_{6-n}(CH_3CN)_n$ (M: Cr, Mo, W; $n = 1, 2, 3$) which have been known for more than three decades [1] and widely used as starting materials in the preparation of many carbonyl-metal derivatives [2]. Particularly $M(CO)_5(CH_3CN)$ has proven to be a useful $M(CO)_5$ transfer reagent for the synthesis of $M(CO)_5L$ complexes where L is either a donor ligand like a trialkylphosphine or an acceptor ligand like an olefin [3]. Eventhough the $M(CO)_5(CH_3CN)$ complexes have enough stability to be purified by using column chromatography [4], the acetonitrile ligand is regarded as a good leaving group when compared to the carbonyl group [5]. Unexpectedly, however, we noticed that there have been no reports on the ^{13}C NMR chemical shifts of these complexes which could provide more information about the bonding. As users of the $M(CO)_5(CH_3CN)$ complexes [6] we decided to isolate these complexes and record their ^{13}C NMR spectra which we would like to report in this letter.

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The $M(CO)_5(CH_3CN)$ complexes were obtained from $M(CO)_5(THF)$ [7] and acetonitrile in THF.

$$M(CO)_5(THF) + CH_3CN \rightarrow M(CO)_5(CH_3CN) + THF$$

M: Cr, Mo, W;
THF: Tetrahydrofuran

Experimental

All reactions and manipulations were carried out either in vacuum or under a dry and deoxygenated nitrogen atmosphere. Solvents were distilled after refluxing over metallic sodium or phosphorus pentoxide under nitrogen for three to four days and stored until use.

Hexacarbonylchromium(0), hexacarbonylmolybdenum(0) and hexacarbonyltungsten(0) were purchased from Ventron GmbH, Germany, and used without any further purification. The photochemical reactions and other treatment of the organometallic compounds such as purification and crystallization were followed by IR-spectra taken at appropriate time intervals.

NMR spectra were recorded on a Bruker AC-80 spectrometer (80.131 MHz for ^1H and 20.149 MHz for ^{13}C). TMS was used as the internal reference for ^1H and ^{13}C NMR chemical shifts. Infrared spectra were recorded from *n*-hexane solution on a Perkin-Elmer 1430 instrument. Elemental analyses were carried out on a HP 185 CHN analyzer. $M(CO)_5(THF)$, (M: Cr, Mo, W) were prepared according to the procedure described in literature [7]. The $M(CO)_5(CH_3CN)$ complexes were prepared by stirring of $M(CO)_5(THF)$ with excess acetonitrile in THF at room temperature for one day and purified by recrystallization from *n*-hexane solution. They have been identified by comparing their IR and ^1H NMR spectra with the values reported in the literature [4].

Results and Discussion

In the $M(CO)_5(CH_3CN)$ complexes the acetonitrile ligand is bonded to the $M(CO)_5$-moiety through its nitrogen atom. The IR and ^1H NMR spectroscopic data of the complexes (Table I) are in good agreement with the results reported previously [1, 3, 4]. The ^{13}C NMR spectra of the complexes exhibit two signals of the relative intensities 1:4 for the carbonyl ligands providing additional evidence for the existence of the $M(CO)_5$-moiety

Table I. IR CO stretching frequencies (νCO in cm^{-1}, from *n*-hexane), ^1H and ^{13}C NMR chemical shifts (δ ppm, rel. to TMS, benzene-d_6) of free acetonitrile and its $M(CO)_5(CH_3CN)$ complexes.

		CH_3CN	$Cr(CO)_5(CH_3CN)$	$Mo(CO)_5(CH_3CN)$	$W(CO)_5(CH_3CN)$
IR	νCO		2074	2077	2076
			1943	1946	1938
			1908	1907	1906
^1H NMR	CH_3	1.85	2.25	2.35	2.35
^{13}C NMR	CH_3	1.00	3.36	2.22	3.25
	CN	116.88	127.13	122.19	123.32
	CO(*cis*)		213.87	203.29	196.49
	CO(*trans*)		219.39	214.97	199.33

with a local C_{4v}-symmetry in the complexes as elucidated from the IR observation.

The replacement of one carbonyl ligand in $M(CO)_6$ with acetonitrile causes deshielding of the carbon atom of the remaining CO groups as observed for similar complexes [8]. It is well known that this deshielding reflects the enhancement of the metal→carbonyl π-back bonding upon CO-substitution with a ligand, which is a stronger σ donor but a weaker π acceptor than carbon monoxide. The carbonyl group *trans* to the acetonitrile ligand shows a larger down-field shift than the *cis* ones indicating that the deshielding effect of the acetonitrile ligand on the carbonyl carbon is largest if the ligands are *trans* to each other [9].

In the ^{13}C NMR spectra of the complexes one observes two more signals for the nitrile and methyl carbons of the acetonitrile ligand. Both of these signals show down-field shifts compared to those of the free acetonitrile molecule (Table I). It is interesting to note that this coordination shift decreases in the order Cr > W > Mo. This can be related to the relative strength of the metal→acetonitrile bond. The $Mo(CO)_5(CH_3CN)$ complex, which shows the smallest coordination shift in the ^{13}C NMR signal of the nitrile carbon is expected to be the most labile complex among the three. Indeed the experimental observations show that the molybdenum complex is the least stable one.

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