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# SYNTHESIS AND SPECTROSCOPIC PROPERTIES OF PARTIALLY DEUTERATED DERIVATIVES OF *trans*-BROMOMETHYL(TETRACARBONYL)CARBYNECHROMIUM

NGUYEN QUY DAO*, M. JOUAN, G.P. FONSECA,

*Laboratoire de Chimie et Physico-Chimie Minèrales, Ecole Centrale des Arts et Manufactures, Grande Voie des Vignes, F 92290, Chatenay-Malabry (France)*

NGOC HOA TRAN HUY

*Laboratoire de Synthèse Organique, Ecole Polytechnique, F 91128, Palaiseau (France)*

and E.O. FISCHER

*Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstr. 4, D 8046 Garching (F.R.G.)*

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## Summary

The methyl group in methylcarbynes such as $Br(CO)_4Cr{\equiv}CR$ ($R = CH_3$) has acidic hydrogen atoms and thus it is possible by H/D exchange, to obtain a statistical mixture of the four isotopically labelled species ($R = CH_3$, $CH_2D$, $CHD_2$ and $CD_3$). The composition of several such mixtures has been determined by mass spectrometry. Another method of analysis of the isotopic composition of these mixtures, based on the spectroscopic properties of the $M{\equiv}C$ bond and involving use of Raman spectroscopy is proposed.

## Introduction

In order to study charge transfer phenomena in carbyne metal complexes of formula $X(CO)_4M{\equiv}CR$ ($X = Cl$, Br, I; $M = Cr$, W; R = alkyl or aryl groups) [1], and more particularly the charge transfer between the $M{\equiv}C$ triple bond and the rest of the molecule, by vibrational spectroscopy, partially deuterated compounds obtained in mixtures of $Br(CO)_4Cr{\equiv}CR$ ($R = CH_3$, $CH_2D$, $CHD_2$ and $CD_3$) (I) were required. We describe below the method of synthesis, the results obtained by mass spectroscopy, and the interpretation of some data in the $\nu(M{\equiv}C)$ stretching vibration region.

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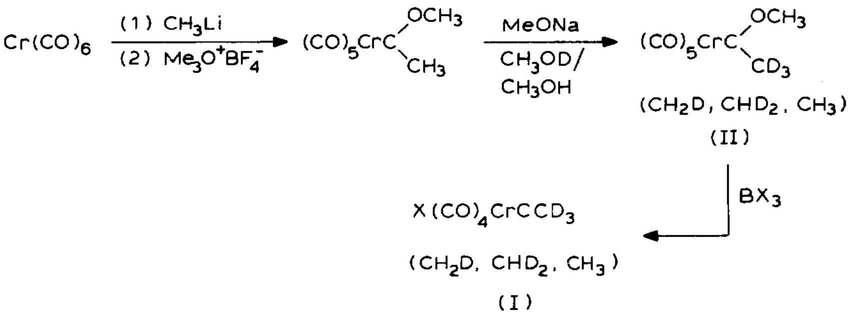
## Preparation

The reaction scheme used to obtain the isotopic mixtures I is shown in eq. 1, from which it can reasonably be concluded that the relative proportions of the various



(1)

isotopic species in I must correspond to a statistical distribution of the hydrogen and deuterium atoms.

## Mass spectroscopic results

As the carbyne complexes are very labile, we studied the corresponding carbene compounds $(CO)_5Cr{=}C(OCH_3)R$ ($R = CH_3$, $CH_2D$, $CHD_2$ and $CD_3$) (II) by mass spectroscopy. These are relatively stable precursor species from which carbyne complexes can be generated quantitatively, and they should give rise to the same proportions of the various isotopic derivatives as the corresponding carbynes. In Table 1 we show the results obtained for these carbenes by mass spectrometry and also the theoretical values for a statistical distribution (obtained using binomial formula). Comparison of these values confirms the validity of the hypothesis [2] of a statistical distribution of the hydrogen and deuterium among the compounds.

## Vibrational spectroscopy of the M≡C bond

Results analogous to those for methylcarbynetungsten complexes were expected; for the latter, determinations of the force field have shown that the $\nu(M{\equiv}C)$

TABLE 1

ISOTOPIC COMPOSITION OF CARBENES: COMPARISON OF THE RESULTS OBTAINED BY MASS SPECTROMETRY WITH THE CALCULATED STATISTICAL DISTRIBUTIONS

| | Mixture I | | Mixture II | |
|---|---|---|---|---|
| | MS | Statistical distribution (0.6H+0.4D) | MS | Statistical distribution (0.33H+0.66D) |
| $D_0$ [a] | 17(2) | 23 | 6(2) | 4 |
| $D_1$ | 38(2) | 39 | 20(2) | 22 |
| $D_2$ | 34(2) | 29 | 41(2) | 44 |
| $D_3$ | 10(2) | 9 | 33(2) | 29 |

[a] $D_0 = (CO)_5Cr{=}C(OCH_3)(CH_3)$, $D_1 = (CO)_5Cr{=}C(OCH_3)(CH_2D)$, $D_2 = (CO)_5Cr{=}C(OCH_3)(CHD_2)$, $D_3 = (CO)_5Cr{=}C(OCH_3)(CD_3)$.

stretching vibration shifts from 1354 $cm^{-1}$ for $Br(CO)_4W{\equiv}CCH_3$ to 1315 $cm^{-1}$ for $Br(CO)_4W{\equiv}CCD_3$ [3,4]. Study of I permits us to assign this vibration unambiguously to the very strong Raman line at 1343 $cm^{-1}$ for $Br(CO)_4Cr{\equiv}CCH_3$ and at 1299 $cm^{-1}$ for $Br(CO)_4Cr{\equiv}CCD_3$.

The variation of the relative intensities of the two bands is in good agreement with the relative proportions of these compounds in the mixtures. There should also be present two other bands corresponding to the $\nu(M{\equiv}C)$ stretching vibration for the compounds $Br(CO)_4Cr{\equiv}CCH_2D$ and $Br(CO)_4Cr{\equiv}CHD_2$ present in I. In fact, only one band appears at 1305 $cm^{-1}$ (Fig. 1). This is particularly interesting because it proves the existence of coupling between the $\nu(M{\equiv}C)$ stretching vibration and the vibrations of the methyl group. In the case of the isotopically pure compounds, the $C_{3v}$ symmetry of the $CH_3$ (or $CD_3$) groups gives rise to an important coupling between the $\nu(M{\equiv}C)$ stretching vibration of the $Br(CO)_4M{\equiv}C$ group of quasicylindrical $C_{4v}$ symmetry, the stretching $\nu({\equiv}C{-}C)$ and the symmetric deformation $\delta_s(CH_3)$ (or $\delta_s(CD_3)$). This phenomenon partially explains the substantial lowering of the $\nu(M{\equiv}C)$ frequency (44 $cm^{-1}$) observed upon deuteration. Conversely, the lower symmetry of $CH_2D$ and $CHD_2$ groups ($C_s$ symmetry) does not favour coupling with the rest of the molecule. The fact that the two corresponding $\nu(M{\equiv}C)$ frequencies are superimposed shows that the coupling is negligible in this case.

In the light of these observations, it is interesting to compare the Raman intensities for the different species with the proportions found by mass spectrometry. Table 2 shows that there is a good agreement between the results given by the two

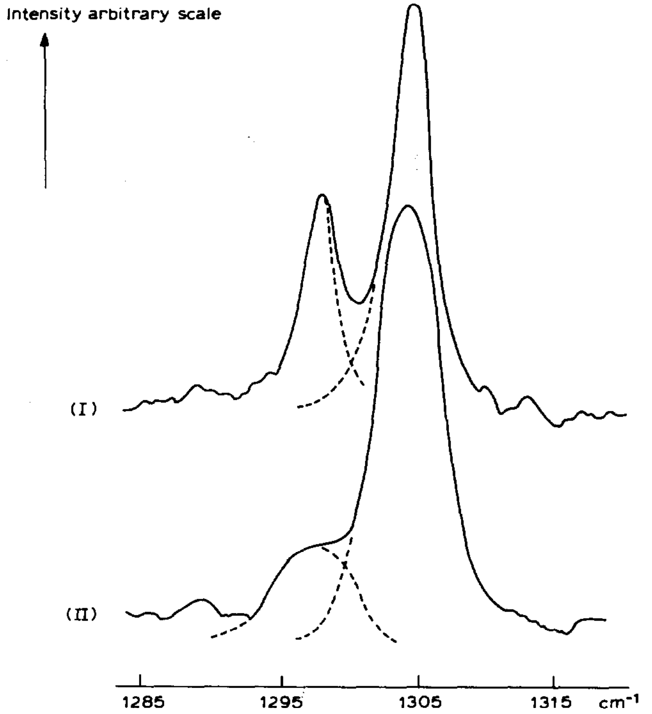


Fig. 1. The $\nu(M{\equiv}C)$ stretching vibration region (Number of accumulations 64 (I), 9 (II); $\nu_0$ 6328 Å, resolution 1 $cm^{-1}$).

TABLE 2

COMPARISON OF PROPORTIONS OF ISOTOPICALLY LABELLED SPECIES OBTAINED BY MASS SPECTROMETRY AND RAMAN SPECTROMETRY

| Mixture | MS $\frac{CD_3}{CHD_2+CH_2D}$ | Raman (Ratio of the intensities measured at the peak maxima) |
|---|---|---|
| I | 0.54 | 0.52 |
| II | 0.13 | 0.15 |

methods. In our future research studies, we intend to use Raman data directly for measuring the degree of deuteration of the partially deuterated methylcarbynes.

## Experimental

### *Synthesis*

All preparations were carried out under $N_2$ using water-free solvents saturated with nitrogen. Carbyne complexes were kept and studied at low temperature.

### *Preparation of II*

The carbene compounds were prepared as previously described [5] from $Cr(CO)_6$,$LiCH_3$ and $(CH_3)_3OBF_4$.

The deuteration involved use of the acidic properties of the hydrogens of the methyl group of the carbene compounds. Thus a solution of 6 g (0.024 mol) of $(CO)_5CrC(OCH_3)CH_3$ in about 10 cm$^3$ of a $CH_3OD/CH_3OH$ in the presence of MeONa was stirred for 10 min at room temperature. The solvent was evaporated off and the carbene was purified by chromatography on silica gel (eluent: pentane/ $CH_2Cl_2$). Recrystallisation from pentane at −78°C gave 4 g of carbene (yield 80%).

Two isotopic mixtures of methanol were used; viz.: (a) Mixture I: 9.5 cm$^3$ $CH_3OD$ + 0,5 cm$^3$ $CH_3OH$; (b) Mixture II: 7.5 cm$^3$ $CH_3OD$ + 2.5 cm$^3$ $CH_3OH$.

### *Preparation of the carbynes*

Carbynes were prepared as previously described [6]. The partially deuterated methyl group is incorporated intact in the carbyne complexes.

### *Mass spectrometry*

The mass spectra were obtained with a VG. ZAB. 2F. spectrometer.

### *Raman spectrometry*

The spectra were recorded on a DILOR RT130 Raman spectrometer with a of 25 mW He-Ne laser.

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