Vibrational spectroscopic data of metallocarbyne complexes

Nguyen Quy Dao *

Laboratoire Structures, Propriétés et Modélisation des Solides, UMR 8580 du CNRS, Ecole Centrale des Arts et Manufactures, Grande Voie des Vignes, F-92295 Châtenay-Malabry Cedex, France

This article is dedicated to Professor Dr. Ernst-Otto Fischer on the occasion of his 85th birthday

Abstract

Vibrational spectroscopic data together with electron deformation density results on Fischer's carbyne complexes are briefly reviewed in this article. The nature of the metal–carbyne bonds and modifications in the molecular structures of some carbynes as a function of temperature are presented.
© 2003 Elsevier B.V. All rights reserved.

1. Introduction

The first metallocarbyne complex was discovered by Fischer et al. [1,2] in 1973. This very reactive compound is part of a chemical class which allows numerous original syntheses [3]. In order to contribute to the understanding of their physicochemical properties, we have studied the nature of the characteristic bonds of some of the most representative of these complexes over several years. Our research work consists of structural studies involving precise X-ray and neutron diffraction and vibrational spectroscopic methods. In this paper, we would like to present a short review of this investigation.

2. General crystallographic data

Several crystallographic structures of carbyne complexes were determined and summarized in an earlier review article [4] and in different theses of the Technical University of Munich [5–9]. The $M \equiv C$ metal–carbon (carbyne) distance is short; the average bond length for $Cr \equiv C$, $Mo \equiv C$ and $W \equiv C$ (carbyne), respectively, equal to 169, 182 and 186 pm, can be considered as char-

acteristic of a $M \equiv C$ triple bond. Fig. 1 shows the molecular geometry of some archetypes of carbyne complexes of the double carbyne $[Br(CO)_4WC]_2C_6H_4$ [10] and of the metal–metal carbyne $(OC)_4CoW-(CO)_4CC_6H_5$ [11], as studied by Fischer and his co-workers.

A special feature of some of these carbynes is the orientation of the molecules inside the crystal cell. Fig. 2 shows as an example the arrangement of the molecules of the $X(CO)_4WCCH_3$ [12] series where, in the case of the bromine complex, the molecules are inclined toward one another while for the iodine complex, the molecules are all parallel to one of the crystallographic axes. This very special orientation of the molecules in the crystal cell is particularly interesting for Raman and infrared experiments as it allows the easy and precise study of the polarization effects in the crystal (especially for Raman spectrometry) and thus greatly facilitates the assignment of the observed vibrational bands.

3. Vibrational spectroscopic results

The Raman and IR spectroscopic data on carbyne complexes were first reported in 1978 [13,14]. Raman and IR vibrational spectra of $X(CO)_4MCR$ (X = Cl, Br, I; M = W, Mo, Cr; R = aryl, alkyl) were later investigated intensively. The use of deuterated isotopomers

* Tel.: +33-141-13-1105; fax: +33-141-13-1502.
E-mail address: nqdao@spms.ecp.fr (N.Q. Dao).

and the observation of the polarization effects on Raman spectra of single crystals and in solution allowed the assignments of the vibrational bands without any ambiguity. Calculations of the force fields using general-ized valence force fields (GVFF) were carried out for several of these compounds. Table 1 gives a list of the studied compounds, showing some of their character-istic vibrational wavenumbers.
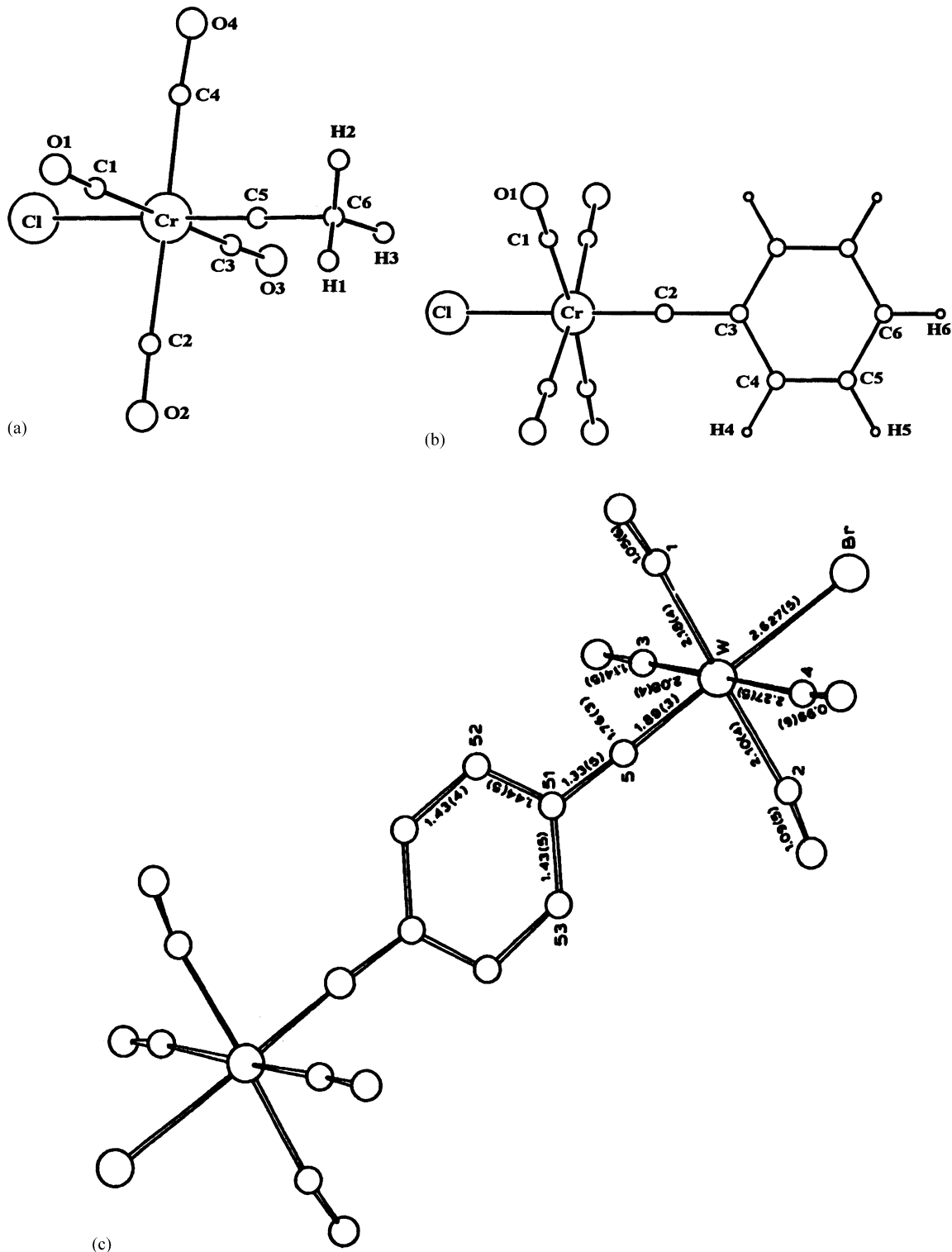

Fig. 1. Molecular structure of some metallocarbyne complexes. (a) Structure of **XIII**; (b) structure of **XVI**; (c) structure of **XVII**; (d) structure of **XXIII** and (e) structure of **XXV**.
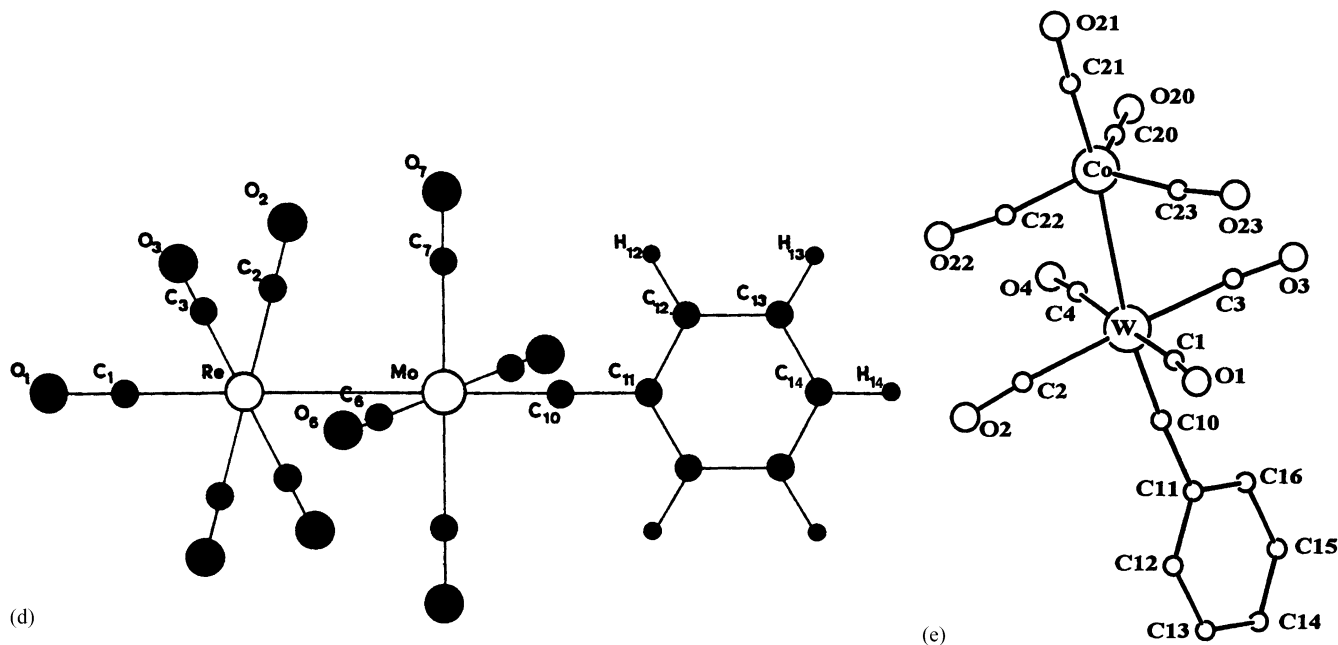
(d)

(e)

Fig. 1 (*Continued*)

3.1. Vibrational data of methylcarbynes

Figs. 3 and 4 show as an example the IR and Raman spectra of crystalline **XI**.

With the polarization effects and the deuteration of the methyl group, the $v(Cr\equiv C)$ stretching vibration is assigned to the strong peak which appears both in Raman and IR spectra in the region of 1300 cm^{-1}. For the hydrogenated methyl, this mode is situated at 1345 cm^{-1} and is strongly coupled with the $\delta_s(-CH)_3$ of the methyl group at 1280 cm^{-1}. In the case of the deuterated compounds, the wavenumber is lowered to 1295 cm^{-1}. For the tungsten series, the $v(W\equiv C)$ is higher, showing that the $W\equiv C$ bond is stronger than the $Cr\equiv C$ bond.

By careful examination of the spectra of methylcarbyne complexes with diluted isotopic mixtures [15,16] and a pure partial deuterated compound [17,18], several interesting conclusions can be drawn.

The CH stretching vibrational wavenumbers in carbynes are situated in a lower range than the classical CH ones. It is concluded that a hyperconjugation effect exists between the methyl group and the $M\equiv C$ triple bond. Moreover, two types of CH bonds of different strength of the methyl group can clearly be seen at low temperature. One type corresponds to the eclipsed position **E** of one CH bond with the *cis*-M−CO of the carbonyl group, the remaining two CH make an angle of 30° with two other M−CO bonds (Fig. 5, in plain). The difference between the two CH types is however very weak (25 cm^{-1} or 5 N m^{-1} which corresponds to a variation in bond length of 2 pm, and is much too small

to be observed even by precise X-ray diffraction experiments).

When examining the Raman spectra of **XI** as a function of temperature (from 77 to 100 K), two temperature-dependent conformers of methylcarbyne [19] are demonstrated. The first structure corresponds to the configuration **E** described above, the second being a non-eclipsed configuration **NE** which is deduced by a rotation of 15° from the previous position around the $M\equiv C-C$ axis (Fig. 5, in dotted lines). At 77 K, a majority of **E** form is present. At 100 K, there is twice the quantity of **E** than **NE**. At 150 K, they are equal in quantity. Above 230 K, **XI** decomposes. Between the **E** and **NE** forms, there is only a difference of 7 cm^{-1} which corresponds to a coalescence lifetime of 5 ps, the same value as found for toluene and nitromethane in various solid phases [20,21].

Another interesting feature is the strong coupling between the $(M\equiv C-)$ vibration and the rest of the carbyne fragment motions. In the case of isotopically pure methylcarbyne compounds (**I**, **II**, **III**, **IV** on the one hand, and **IX**, **XII**, **XIII** on the other hand), the C_{3v} of −CH$_3$ (or −CD$_3$) groups and the C_{4v} of X(CO)$_4$MC− are both of pseudo-cylindrical symmetry. Therefore, the $v(M\equiv C)$ stretching vibration can be very strongly coupled with other symmetrical vibrational modes, especially with $\delta_s(CH3)$ deformation and with $v(\equiv C-C)$ stretching vibrations. This explains the strong decrease of the $v(M\equiv C)$ stretching vibration ($\Delta v = 50$ and 44 cm^{-1}, respectively, for the Cr and W complexes), observed for the $v(M\equiv C)$ of the deuterated compound, due to mechanical coupling. On the other hand, the
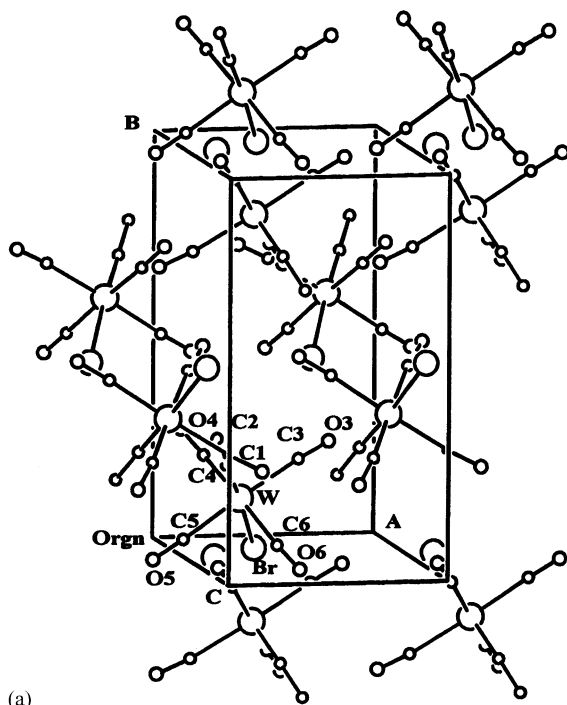
(a)
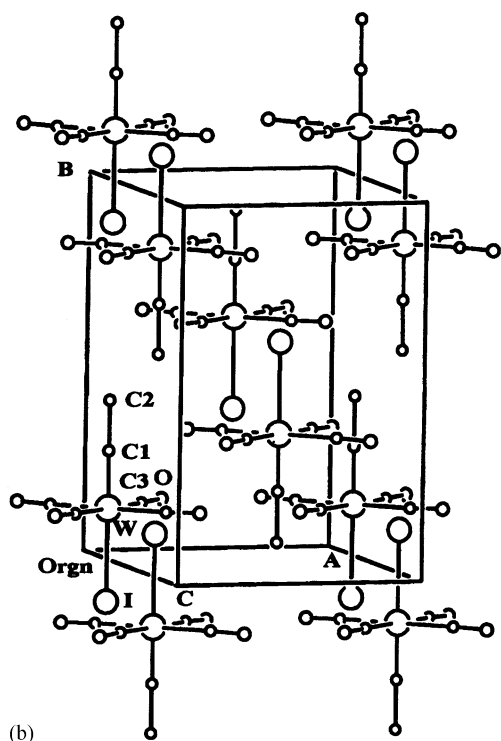
(b)

Fig. 2. Specific arrangements of the molecules in their crystal cells. Cases of **II** (a) and **IV** (b).

lower symmetry C_s of the CH_2D and CHD_2 breaks the coupling and the two peaks corresponding to $\nu(M\equiv C-)$ stretching vibrations of these two compounds are found at practically the same wavenumbers (1305–1301 cm^{-1} for the Cr complexes).

3.2. Vibrational data of phenylcarbynes

Another series of carbynes which was also thoroughly studied by IR and Raman spectroscopies is the phenylcarbynes [22]. Concerning the $\nu(M\equiv C-)$ stretching vibrations, the wavenumber $\nu(W\equiv C-Ph)$ (1373–1357 cm^{-1}) is higher than its methyl analog $\nu(W\equiv C-Me) = 1354$–1347 cm^{-1} which is in turn higher than the Cr analog $\nu(Cr\equiv C-Ph) = 1347$–1326 cm^{-1}. This is in agreement with the remarks made above for the methylcarbyne series and is comparable with the results already observed for the metal–hexacarbonyl series [23]. Concerning the carbonyl vibrations, the $\nu_E(M\text{-}4C)$ are about 50 cm^{-1} lower than in the pentacarbonyl carbene complexes. In the same way, the valence stretching vibrations of carbonyl groups are much higher in carbynes than in carbenes [24]. The M–CO bonds are much weaker here and substitution reactions can be more easily made with the carbonyl groups of carbyne complexes [25–27].

3.3. Vibrational data of some other carbynes

Double carbynes **XVII**, **XVIII**, **XIX** and **XX** were also thoroughly studied [28]. The interesting feature of this compound is the influence of the carbynic fragments on the electronic distribution of the phenyl ring. Comparing this with the *para*-disubstituted benzenes and their characteristic frequencies influencing the electronic charge π of the phenyl ring, it was found, in the case of double carbynes, that π electrons are more localized in the bonds parallel to the axis of the molecule, although this effect is again too small to be observed by X-ray diffraction. Another type of carbyne which involves the metal–metal bond, **XXI**, **XXII**, **XXIII**, **XXIV**, **XXV**, is also studied [11,29]. The Re(CO)$_4$ group is found to be a weaker acceptor than the halogenide ligands. The frequency $\nu(Re-M)$ is slightly lower in the ReMPh carbyne series than in the ReM(CO)$_{10}$ series (120 cm^{-1} [30], 114, 110 cm^{-1} compared to 146, 130, 109 cm^{-1}) [31]: The triple bond M$\equiv$C weakens the *trans*-metal–metal bond. Finally, from this family of complexes where the whole series of Cr, Mo, W was synthesized and studied by IR and Raman techniques, it can be deduced that the strength of the M$\equiv$C bond in carbyne series follows the order W$\equiv$C > Mo$\equiv$C > Cr$\equiv$C.

Data on vibrational results of aminocarbynes [32,33] are also available. The following complexes X(CO)$_4$CrCNR$_2$ (X = Br, I for R = Et; X = Br for R = Me) and a cationic aminocarbyne of formula (CO)$_5$CrCNEt$_2^+$ BF$_4^-$ were studied. The (Cr)C–N vibration corresponds to a Raman line at 1600 cm^{-1} which is nearer to the C=N stretching vibration (≈ 1650 cm^{-1}) found in amides than the C–N stretching vibration (≈ 1050 cm^{-1}), and the Cr$\equiv$C(N) vibration is no longer observed at 1350 cm^{-1} but at a lower frequency (1160

Table 1
Vibrational wavenumbers of some characteristic bonds in metallocarbyne complexes (in cm^{-1})

	$\nu(M{\equiv}C)$		$\nu(C{-}R)$		$\nu(M{-}X)$		Miscellaneous		Reference number
	R	IR	R	IR	R	IR	R	IR	
$Cl(CO)_4WCCH_3$	1361	1355	556		271		1284	1273	**I**
	1353						$\delta(CH_3)$		
$Br(CO)_4WCCH_3$	1355	1352	554		≈ 175		1284	1274	**II**
	1347						$\delta(CH_3)$		
$Br(CO)_4WCCD_3$	1315	1312	529	520	≈ 175		1022	1008	**III**
							$\delta(CH_3)$		
$I(CO)_4WCCH_3$	1358	1353	554		145		1280	1280	**IV**
							$\delta(CH_3)$		
$Br(CO)_4WCC_6H_5$	1373	1368			184	180			**V**
$Br(CO)_4WCC_6D_5$	1278	1280			184	180			**VI**
$I(CO)_4WCC_6H_5$	1369	1365							**VII**
	1345	1347			145				
$I(CO)_4WCC_6D_5$	1280	1279			146				**VIII**
$Br(CO)_4CrCCH_3$	1345	1345	641	641	203	202	1267	1262	**IX**
$Br(CO)_4CrCCH_2D$	1305		630		203	202	1232	1233	**X**
	1305		626						
$Br(CO)_4CrCCHD_2$	1301		620		206	203	1011	1010	**XI**
	1300		620						
$Br(CO)_4CrCCD_3$	1295		616		206	201	992		**XII**
	1292		610						
$Cl(CO)_4CrCCH_3$		1345		640		202			**XIII**
$Br(CO)_4CrCC_6H_5$	1347	1342			182	180			**XIV**
	1326	1319							
$Br(CO)_4CrCC_6D_5$	1274	1272			180	180			**XV**
	1264	1260							
$Cl(CO)_4CrCC_6H_5$	1346	1340			246	238			**XVI**
$[Br(CO)_4WC]_2C_6H_4$	1379	1372			189	186			**XVII**
	1352	1342							
$[Br(CO)_4WC]_2C_6D_4$	1377	1365				180			**XVIII**
$[Br(CO)_4CrC]_2C_6H_4$	1352	1347			211				**XIX**
	1336								
$[Br(CO)_4CrC]_2C_6D_4$	1335	1319			202				**XX**
	1321								
$(OC)_5ReW(CO)_4CCH_3$	1355	1354	557	553			116		**XXI**
							$\nu(Re{-}W)$		
$(OC)_5ReCr(CO)_4CC_6H_5$	1344	1345							**XXII**
$(OC)_5ReMo(CO)_4CC_6H_5$	1341	1340					114		**XXIII**
							$\nu(Re{-}Mo)$		
$(OC)_5ReW(CO)_4CC_6H_5$	1368	1363					110		**XXIV**
							$\nu(Re{-}W)$		
$(OC)_4CoW(CO)_4CC_6H_5$	1372	1371							**XXV**

cm^{-1}). The bond order for $M{\equiv}C(N)$ in the metal–aminocarbyne complexes is estimated at about 2.2. The contribution of the donation of the nitrogen atom is strong in these complexes, compared to the d-electrons of the metal. The aminocarbynes are more stable than the carbyne complexes. The strength of the $M{\equiv}C(R)$ bond therefore depends greatly on the R ligands attached to the C (carbyne) atom.

3.4. GVFF of metallocarbynes

Thanks to the complete vibrational data obtained for the carbynes, GVFF of various series of carbynes are calculated [14,18,34,35]. The force constant $k(M{\equiv}C)$ can vary greatly from one complex to another. It is stronger for tungsten than for chromium and it also depends on the R ligand attached to the carbon (carbyne) (700, 680 N m^{-1} and 518, 650, 625 N m^{-1} for W and Cr carbyne complexes, respectively).

Using the force constants values already calculated in the normal coordinates calculations [36], a bond order equal to 1.40 can be determined for the C–C bond from the known correlation between the bond order and the force constants [37]; when using the correlation between the bond order and the interatomic distances [38,39] the C–C bond order is again estimated at 1.40. The agreement between these two values is very good. Colthup [40] has related the total electronic density of
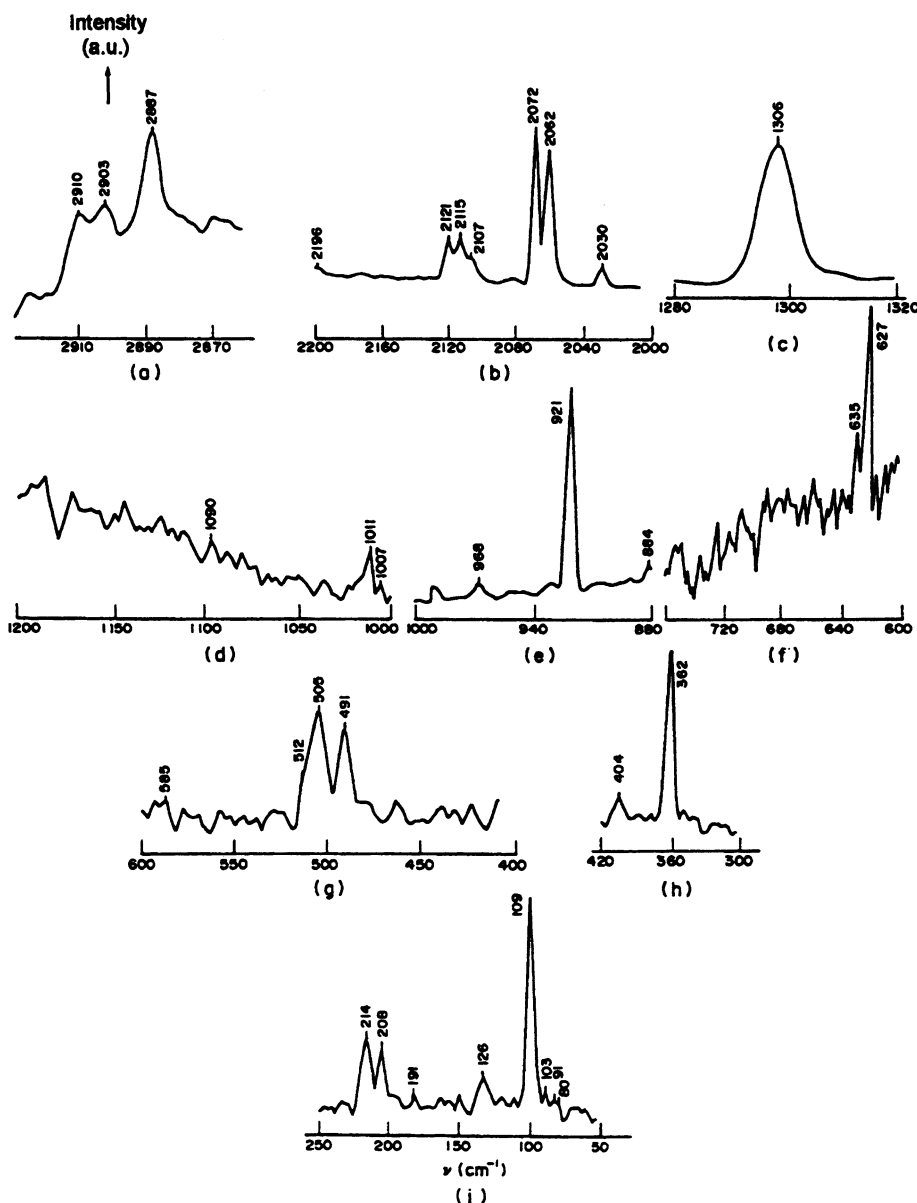
Fig. 3. Raman spectrum of **XI**.

the carbon atom of the methyl group in compounds of type CH_3-R and CD_3-R, obtained by CNDO/2 molecular orbital calculations with the deformation vibration $\delta_s(CH_3)$ and $\delta_{as}(CH_3)$, and a mean value of 1.35 can be estimated for the bond order. The methyl group is very perturbed with a negative charge on the carbon atom. This effect gives rise to a deformation of the phenyl ring approaching the conjugated mesomer form. This fact again demonstrates the conjugation and hyperconjugation effects existing in phenyl and methyl-carbynes.

A new and interesting series of carbyne complexes was studied by Manna et al. [41–44]. The general formula of this family is $M\equiv(CH)LX$ where $M = W$, $L = (PMe_3)_4$ for $X = Cl$ and $L = (dmpe^a)_2$ for $X = Cl$,

$OSiMe_3$, n-Bu, $CCSiMe_3$. Although the X-ray diffraction results give a bent $W\equiv CH$ structure, neutron diffraction for the complex $W\equiv CH(dpme-d_{12})_2Br$ [45] later established that $W\equiv CH$ is linear. Raman and IR spectra of $W\equiv CH(PMe_3)_4Cl$ and its deuterated isotopomers $W\equiv CD(PMe_3)_4Cl$ and $W\equiv CH(PMe_{3-d9})_4Cl$ show that the $v[W\equiv C(H)]$ stretching vibration is situated in a lower range (≈ 900 cm^{-1}) than for alkyl and aryl carbyne complexes. A GVFF calculation also gives a lower value (6.02 N m^{-1}) for the $W\equiv C$ vibration when compared with the value given (7.00 N m^{-1}) in the Fischer carbynes.

The force constants of the $M\equiv C$ bonds depend greatly on the R group attached to the metal–carbyne bond, independently of the influence of other *cis*-ligands

(a)

(b)
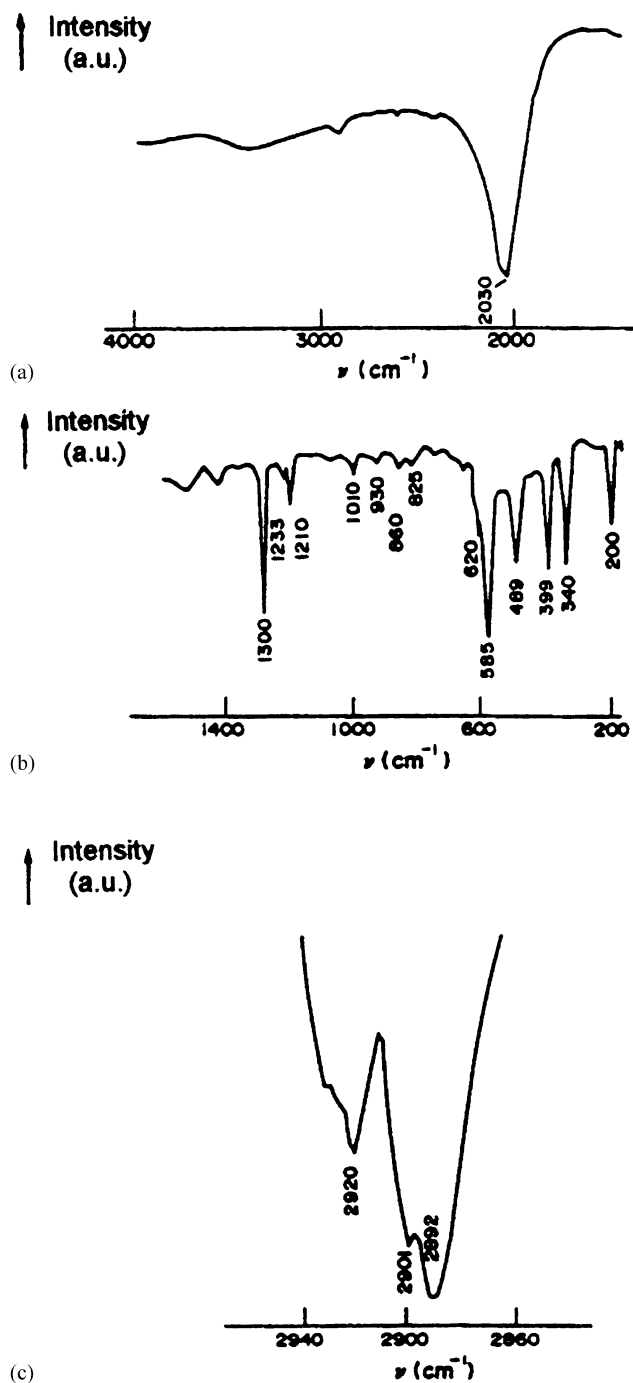

(c)

Fig. 4. IR spectrum of **XI**.

Fig. 5. Difference of the CH bonds in methylcarbynes. Conformers **E** (in full line) and **NE** (in dotted line).

orkers [46,47]. The X–X maps obtained at 100 K by these authors provided information of interest concerning the distribution of electron density around the metal and along the metal≡carbyne triple bond. A further refinement [48] using Hansen and Coppens' [49] multipole models produced additional quantitative information, especially concerning the metal orbital populations. Table 2 gives the comparison of the chromium d-orbital populations obtained by multipole model maps and the theoretical ones. The population of the d-orbitals facing the carbyne (d_{z^2}, d_{xz}, d_{yz}) display relatively small deviations from isotropy compared to the population of metal d-orbitals facing the carbonyl ligands. A balance of the populations of the metal and carbon orbitals involved in the Cr≡C bond reflects the more homopolar character of the metal–carbyne interactions compared to the metal–carbonyl ones. A theoretical deformation density map computed with

Table 2
Populations (e) of the metal d-orbitals and the ab initio CASSF calculations and net atomic charges (e) from ab initio calculations

	$Cl(CO)_4CrCCH_3$ multipolar refinement		$Cl(CO)_4CrCCH_3$ ab initio (CASSCF/6) [a]	
	Population	%	Population	%
d_{z^2}	0.8(4)	15	0.73	14
$d_{xz} + d_{yz}$	2.6(4)	47	2.28	44
$d_{x^2-y^2}$	0.6(4)	12	0.43	8
d_{xy}	1.5(4)	27	1.72	33
Total	5.60(8)		5.16	
Cr			+0.33	
CCO			+0.23	
O			−0.37	
$C_{CrC(carbyne)}$			−0.32	
C_{Me}			−0.45	
H_{Me}			+0.17	
Cl			−0.40	

[a] For CASSCF/6, the active space is limited to six MOs populated with six electrons describing the CrC (carbyne) triple bond.

linked to the metal, as can also be seen in the aminocarbynes series cited above.

4. Electron deformation density of some carbyne complexes

The electron density deformation of two representative metal–carbyne complexes **XIII** and **XVI** were studied. **XIII** was first examined by Krüger and cow-
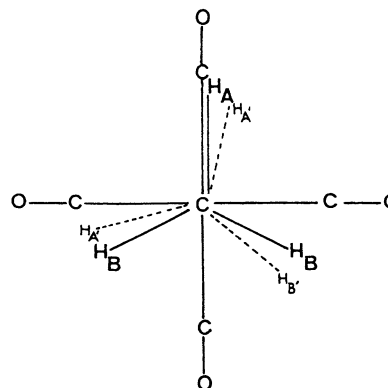
respect to the Cl(CO)$_4$Cr and CCH$_3$ fragments shows that the formation of the triple bond increases the density by about 0.1 e Å^{-3} along the C–C(H$_3$) bond, and this additional accumulation extends over the π-bonding regions. A hyperconjugation effect is therefore suggested on the basis of the observation of the experimental deformation density. This is in good agreement with the conclusions obtained from the force field determination of the X(CO)$_4$MCCH$_3$ series (X = Cl, Br, I; M = Cr, W) and its partially deuterated isotopomers.

Another electron density deformation study was completed for **XVI** [50–52] using precise neutron [53] and X-ray diffraction data at 100 K. Multipolar models were necessary for the refinements in this case as the structure is non-centric. An examination of the dynamic and static deformation density maps along the Cr≡C–C axis in two planes, one containing and the other perpendicular to the phenyl ring (Fig. 6), shows that the electronic density is not distributed isotropically around the symmetry axis. The accumulation between Cr and the carbynic carbon appears slightly more extended in the plane containing the phenyl. Similarly, an opposite tendency is observed for the accumulation located along the C–C (phenyl) bond, which appears broader in the plane perpendicular to the phenyl. This loss of cylindrical symmetry is again attributed to the conjugation effect of the phenyl ring with the Cr≡C bond.

5. Conclusion

This article presents some structural data of metallo-carbynes obtained by vibrational spectroscopy and structural diffraction methods which helped to explain
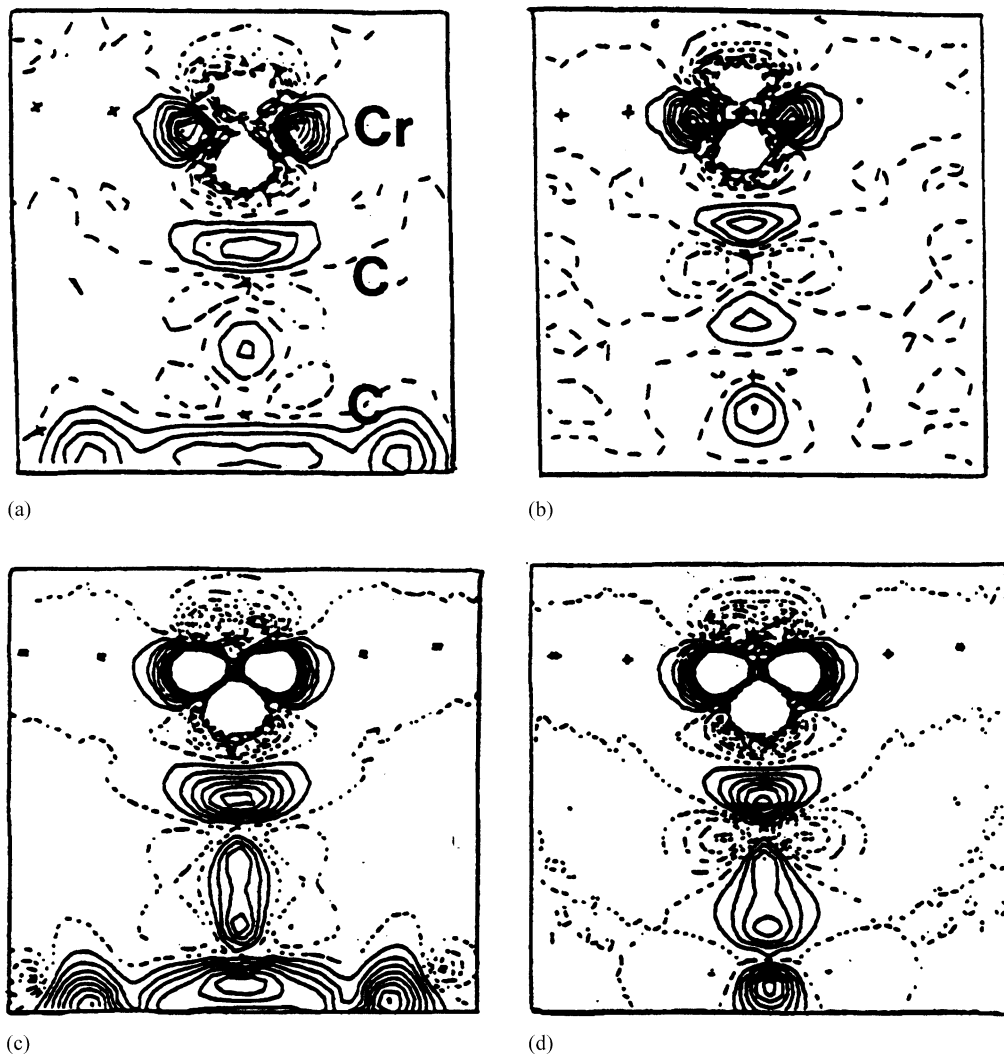

Fig. 6. Conjugation effect in **XVI**. (a) X–M experimental deformation map in the plane containing the phenyl ring; (b) X–M experimental deformation map in the plane perpendicular to the phenyl ring; (c) static deformation map in the plane containing the phenyl ring and (d) static deformation map in the plane perpendicular to the phenyl ring (contours: 0.1 e Å^{-3}).

some physicochemical properties of these compounds. Other experimental studies still need to be done including an examination of Jorgensen's [54] hypothesis on the influence of the hard and soft ligands on the geometry of the M≡C–R bonds.

Acknowledgements

References

[1] (a) E.O. Fischer, G. Kreis, C.G. Kreiter, J. Müller, G. Huttner, H. Lorenz, Angew. Chem. 85 (1973) 618;
(b) E.O. Fischer, G. Kreis, C.G. Kreiter, J. Müller, G. Huttner, H. Lorenz, Angew. Chem. Int. Ed. Engl. 12 (1973) 564.

[2] E.O. Fischer, Angew. Chem. 86 (1974) 651.

[3] (a) See for example: H. Fischer, P. Hofmann, F.R. Kreissl, R.R. Schrock, U. Schubert, K. Weiss (Eds.), Carbyne Complexes, VCH, New York, 1988.;
(b) F.R. Kreissl (Ed.), Transition Metal Carbyne Complexes, Kluwer Academic Publishers, NATO ASI Series, C, Vol. 392, 1992.

[4] G. Huttner, A. Franck, E.O. Fischer, Israel J. Chem. 15 (1976) 133.

[5] H. Lorenz, Dissertation, Technischen Universität München, 1974.

[6] W. Gartzke, Dissertation, Technischen Universität München, 1974.

[7] A. Franck, Dissertation, Technischen Universität München, 1978.

[8] D. Neugebauer, Dissertation, Technischen Universität München, 1979.

[9] P. Friedrich, Dissertation, Technischen Universität München, 1980.

[10] W. Röll, Dissertation, Technischen Universität München, 1981.

[11] E.O. Fischer, P. Friedrich, T.L. Lindner, D. Neugebauer, F.R. Kreissl, W. Uedelhoven, N.Q. Dao, G. Huttner, J. Organomet. Chem. 247 (1983) 219.

[12] D. Neugebauer, E.O. Ficher, N.Q. Dao, U. Schubert, J. Organomet. Chem. 153 (1978) C41.

[13] (a) E.O. Fischer, N.Q. Dao, W.R. Wagner, Angew. Chem. 90 (1978) 51;
(b) E.O. Fischer, N.Q. Dao, W.R. Wagner, Angew. Chem. Int. Ed. Engl. 17 (1978) 50.

[14] N.Q. Dao, E.O. Fischer, W.R. Wagner, D. Neugebauer, Chem. Ber. 112 (1979) 2552.

[15] N.Q. Dao, M. Jouan, G.P. Fonseca, N.H. Tran Huy, E.O. Fischer, J. Organomet. Chem. 287 (1985) 215.

[16] N.Q. Dao, H. Février, M. Jouan, N.H. Tran Huy, E.O. Fischer, D. Neugebauer, J. Organomet. Chem. 241 (1982) C53.

[17] N.Q. Dao, G.P. Foulet-Fonseca, M. Jouan, E.O. Fischer, H. Fischer, J. Schmid, C. R. Acad. Sci. Paris 307 (II) (1988) 245.

[18] G.P. Foulet-Fonseca, M. Jouan, N.Q. Dao, H. Fischer, J. Schmid, E.O. Fischer, Spectrochim. Acta A 46 (1990) 339.

[19] G.P. Foulet-Fonseca, N.Q. Dao, M. Jouan, H. Fischer, J. Schmid, ICORS XI, in: Proceedings of the International Conference on Raman Spectroscopy, London, 1988, p. 2010.

[20] D. Cavagnat, M. Fesquer, J. Phys. Chem. 90 (1986) 3289.

[21] D. Cavagnat, J. Lascombe, J. Phys. C 18 (1985) 6457.

[22] N.Q. Dao, E.O. Fischer, C. Kappenstein, Nouv. J. Chim. 4 (1980) 85.

[23] L.H. Jones, Spectrochim. Acta 19 (1963) 329.

[24] M.Y. Darensbourg, D.J. Darensbourg, Inorg. Chem. 9 (1970) 32.

[25] E.O. Fischer, U. Schubert, J. Organomet. Chem. 100 (1975) 59.

[26] A. Ruhs, Dissertation, Technischen Universität München, 1977.

[27] (a) E.O. Fischer, P. Friedrich, Angew. Chem. 91 (1979) 345;
(b) E.O. Fischer, P. Friedrich, Angew. Chem. Int. Ed. Engl. 18 (1979) 327.

[28] N.Q. Dao, H. Février, M. Jouan, E.O. Fischer, W. Röll, J. Organomet. Chem. 275 (1984) 191.

[29] N.Q. Dao, E.O. Fischer, T.L. Lindner, J. Organomet. Chem. 209 (1981) 323.

[30] E.O. Fischer, T.L. Lindner, F.R. Kreissl, P. Braunstein, Chem. Ber. 110 (1977) 3139.

[31] J.R. Johnson, D.M. Duggan, W.M. Risen, Jr., Inorg. Chem. 14 (1975) 1053.

[32] E.O. Fischer, N.Q. Dao, ICORS VI, in: Proceedings of the International Conference on Raman Spectroscopy, Bangalore, India, 1978, p. 72.

[33] N.Q. Dao, I. Cabello, H. Février, E.O. Fischer, M. Jouan, in: J. Lascombe, P.V. Huong (Eds.), Raman Spectroscopy, Linear and Nonlinear, Wiley Heydon Ltd, 1982, p. 645.

[34] H. Février, Thèse de Docteur-Ingénieur, Université Paris XIII, 1982.

[35] N.Q. Dao, H. Février, M. Jouan, E.O. Fischer, Nouv. J. Chim. 7 (1983) 719.

[36] G.P. Fonseca, M. Jouan, N.Q. Dao, N.H. Tran Huy, E.O. Fischer, J. Chim. Phys. 87 (1990) 13.

[37] F.A. Cotton, Inorg. Chem. 3 (1964) 703.

[38] L. Pauling, The Nature of the Chemical Bond, Cornell University Press, Ithaca, NY, 1940.

[39] C.A. Coulson, Proc. R. Soc. A 169 (1939) 419.

[40] N.B. Colthup, Appl. Spectrosc. 34 (1964) 1.

[41] J. Manna, Ph.D. Thesis, University of Pittsburgh, 1995.

[42] J. Manna, S.J. Geib, M.D. Hopkins, J. Am. Chem. Soc. 114 (1992) 9199.

[43] J. Manna, L.A. Mlinar, R.J. Kuk, R.F. Dallinger, S.J. Geib, M.D. Hopkins, in: F.R. Kreissl (Ed.), Transition Metal Carbyne Complexes, Kluwer Academic Publishers, The Netherlands, 1993, pp. 75–77.

[44] J. Manna, R.F. Dallinger, V.M. Miskowski, M.D. Hopkins, J. Phys. Chem. B 104 (2000) 10928.

[45] C. Menoret, A. Spasojevic-de Biré, N.Q. Dao, A. Cousson, J.-M. Kiat, J.D. Manna, M.D. Hopkins, J. Chem. Soc. Dalton Trans. (2002) 1.

[46] R. Goddard, C. Krüger, in: P. Coppens, M.B. Hall (Eds.), Electron Distribution and the Chemical Bond, Plenum Press, New York, 1982, pp. 297–330.

[47] C. Krüger, R. Goddard, K.H. Claus, Z. Naturforsch. B 38 (1983) 1431.

[48] A. Spasojevic-de Biré, N.Q. Dao, A. Strich, C. Thieffry, M. Bénard, Inorg. Chem. 29 (1990) 4908.

[49] N.K. Hansen, P. Coppens, Acta Crystallogr. A 34 (1978) 909.

[50] N.Q. Dao, A. Spasojevic-de Biré, E.O. Fischer, P.J. Becker, C. R. Acad. Sci. Paris 307 (II) (1988) 341.

[51] A. Spasojevic-de Biré, N.Q. Dao, P.J. Becker, M. Bénard, A. Strich, Cl. Thieffry, N. Hansen, C. Lecomte, in: G.A. Jeffrey, J.F. Piniella (Eds.), The Applications of Charge Density Research to Chemistry and Drug Design, Plenum Press, New York, 1991, p. 385.

[52] A. Spasojevic-de Biré, N.Q. Dao, E.O. Fischer, N.K. Hansen, Inorg. Chem. 32 (1993) 5354.

[53] N.Q. Dao, D. Neugebauer, H. Février, E.O. Fischer, P.J. Becker, J. Pannetier, Nouv. J. Chim. 6 (1982) 359.

[54] K.A. Jorgensen, J. Organomet. Chem. 478 (1994) 9.