**Table IV.** Relation between the Temperature $T_{min}$ of the Minimum of $\chi_M T$ and the Isotropic Interaction Parameter $J$ for an ABA Trinuclear Species with $S_B = {}^1/_2$ and Various Values of $S_A$ (See Text)

| $S_A$ | 1 | $^3/_2$ | 2 | $^5/_2$ |
|---|---|---|---|---|
| $kT_{min}/\|J\|$ | 0.6435 | 1.420 | 2.131 | 3.374 |

the crystal structure has been solved. Its magnetic properties display characteristic signature of this kind of polymetallic systems, namely a minimum in the $\chi_M T$ versus $T$ plot. The temperature $T_{min}$ of the minimum of $\chi_M T$ for an ACu(II)A trinuclear species with an irregular spin state structure allows a first estimation of the A–Cu interaction parameter $J$. The values of $kT_{min}/|J|$ for $S_A = 1$, $^3/_2$, 2, and $^5/_2$ are given in Table IV. These values are calculated in the approximation where the $g_A$ and $g_{Cu}$ local $g$ factors are equal and the local anisotropy of the $A$ ion is negligible. In the case of a $Ni^{II}Cu^{II}Ni^{II}$ compound, the magnetic curve is weakly contrasted, the highest and lowest values of $\chi_M T$ being close to each other (2.31 and 2.03 cm$^3$ K mol$^{-1}$ for [NiCuNi]). It follows that the parameters of the spin Hamiltonian cannot be determined without a rather large uncertainty. The $J$ value corresponding to the best fit ($J = -90.3$ cm$^{-1}$), however, is very close to that found in the binuclear species [NiCu] with the same environment for the metal ions and the same bridging network, which suggests that $J$ in [NiCuNi] is known with a fairly good accuracy. This value $J$ inspires two remarks: (i) Its magnitude confirms, if it was still necessary, the efficiency of the bisbidentate bridges such as oxamido in transmitting an antiferromagnetic interaction between magnetic centers rather far apart from each other.[23] In the present case, the average value of the Ni⋯Cu separation is 5.31 Å. (ii) The magnitude of the interaction, nevertheless, is less pronounced than that in {[Ni(Me$_6$-[14]ane-N$_4$)]$_2$Cu(pba)}(ClO$_4$)$_2$ where a $J$ value of $-124$ cm$^{-1}$ had been deduced from the magnetic susceptibility data. The crystal structure of this previously studied compound is not known. One can, however, anticipate that the copper environment is less distorted than in [NiCuNi]. As a matter of fact, the surprisingly strong distorsion of the CuN$_2$O$_2$ chromophore in [NiCuNi], from a square planar to a tetrahedral environment, could result from the asymmetry of the nickel coordination spheres, certainly more pronounced in [NiCuNi] than in {[Ni(Me$_6$-[14]ane-N$_4$)]$_2$Cu(pba)}(ClO$_4$)$_2$. If so, the weaker value of $|J|$ in [NiCuNi] would come from a less planar environment around the copper atom. It is, indeed, well established that, with this kind of compounds, the planarity of the bridging network favors the overlap of the magnetic orbitals.[23]

To conclude, we shall recall that the ferromagnetic-like polarization of high local spins owing to an antiferromagnetic interaction with a small local spin is one of the approaches that has led to the design of molecular-based compounds exhibiting a spontaneous magnetization.[24,25]

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**Supplementary Material Available:** Structure determination details (Table SI), H atom positions (Table SII), anisotropic thermal parameters (Table SIII), distances and angles in terminal ligands, anions, and H bonds (Table SIV), atom to mean-plane distances and dihedral angles (Table SV), and experimental and calculated $\chi_M T$ values for [NiCuNi] (Table SVI) (9 pages); a listing of structure factors for [NiCuNi] (24 pages). Ordering information is given on any current masthead page.

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# Infrared Frequencies and Intensities of the Vibrational Modes of Alkynes Coordinated on Metal Carbonyl Clusters

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Assignments are proposed for the main vibrational modes of an alkyne molecule coordinated to metal complexes. The modes are the C—H, CH$_3$, C≡C, and C—C stretchings and the C—H and CH$_3$ deformations of the bonded acetylene, propyne, and 2-butyne. Several model complexes are used, e.g. Co$_2$(CO)$_6$($\mu_2$,$\eta^2$-alkyne), Os$_3$(CO)$_{10}$($\mu_3$,$\eta^2$-alkyne), Co$_2$Ru($\mu_3$,$\eta^2$-alkyne), Co$_4$(CO)$_{10}$($\mu_4$,$\eta^2$-alkyne), and Co$_4$(CO)$_{10}$($\mu_4$-S)($\mu_4$,$\eta^2$-alkyne), where the alkyne coordination is schematically indicated as $\sigma_2$, $\sigma_2\pi$, $\sigma_2\pi_2$ and $\sigma_4$, respectively. The average frequency of the bands belonging to the same type of vibrations and the contribution per C–H bond to the total C–H stretching and bending intensities are evaluated and compared with the relevant values for the free alkyne. Both the frequency and intensity data provide informations on the effect induced in the alkyne (bond strengths and charge distributions) by the metal coordination and are related to the type of the metal–alkyne bond, to the nuclearity, and to the geometry of the cluster.

## Introduction

The alkynes are peculiar ligands in organometallic complexes and are known to exhibit several bonding modes, depending on the number of metal centers to which they are coordinated and on the type of the bond itself, usually known as a $\sigma$ or $\pi$ bond, according to its symmetry.[1-3]

The coordination to the metals causes the well-known structural changes in the alkyne molecules, mainly the lengthening of the triple bond and the decreasing of the bond angle, both depending on the change of the electron density in the alkyne MO's. The relationship between the two structural parameters has been recently rationalized[4] and appears, as could be reasonably expected, to be especially due to the number of metal atoms to which the alkyne is coordinated.

Together with the structural modifications, the coordinated alkyne exhibits significant changes in its vibrational pattern, among which is the well-documented decrease of the frequency of the

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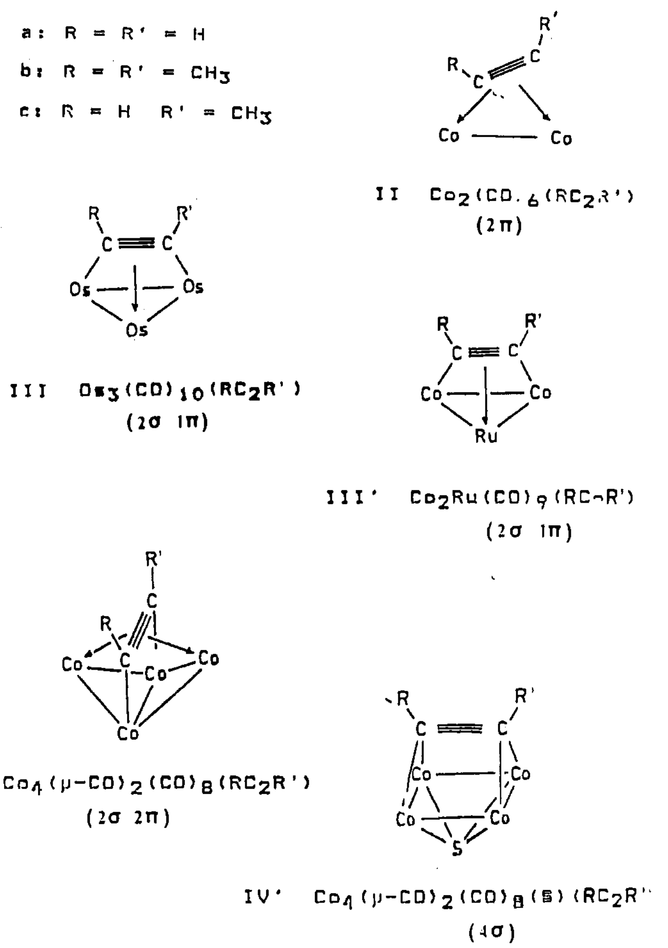

**Figure 1.** Schematic core structures of the metal–alkyne complexes (in parentheses is given the type of metal–alkyne interaction).

C≡C stretching mode, clearly related to the C≡C bond length, which was used as an index of the type both of the metal–alkyne bond[5,6] and of the adsorption of the acetylene on a metal surface.[7-10] It is expected that the effect of the coordination can be transmitted, in greater or lesser extent, to every vibrational mode of the alkyne; anyway, such a study is at present missing. As the organometallic chemistry offers several basic models, in which it is possible to change systematically the structure of the metal core and the type of the alkyne, we have selected some examples of complexes, whose schematic structures are illustrated in Figure 1, as inferred from the literature data (type II, $Co_2(CO)_6C_6H_5C_2C_6H_5$[11] and $Co_2(CO)_6(CH_3)_3CC_2C(CH_3)_3$;[12] type III, $Os_3(CO)_{10}C_6H_5C_2C_6H_5$[13] and $Os_3(CO)_{10}C_2H_5C_2C_2H_5$;[14] type III', $Co_2Ru(CO)_9C_6H_5C_2C_6H_5$ and $Co_2Ru(CO)_9HC_2tC_4H_9$;[15] type IV, $Co_4(CO)_{10}C_2H_5C_2C_2H_5$[16] and $Co_4(CO)_{10}HC_2H$;[4] type IV', $Co_4(CO)_{10}(S)HC_2C_6H_5$[17]). Close similarity in the chemical and spectroscopic properties among the members of the same series suggests that the structure is basically the same, independent of the nature of the alkyne. At the same time, we used different alkynes, RC≡CR', where (a) R = R' = H, (b) R = R' = $CH_3$, and (c) R = H and R' = $CH_3$, and we assigned the main vibrational modes of the alkyne, that is $\nu$(CH), $\nu$(C≡C), $\nu$(C—C), and $\nu(CH_3)$ stretching vibrations and the $\delta$(CH), $\delta(CH_3)$, and $\rho(CH_3)$ deformation vibrations.

An important part of this study is the analysis of the intensity of the bands assigned to the aforesaid modes. The study of the infrared intensity is often disregarded and left to the specialists in the field as a matter too difficult to handle and to be translated into simple criteria useful for nonspecialists. The problems arise from the difficulty in obtaining very accurate measurements of the absolute intensities and, above all, in calculating reliable sets of force constants and of electrooptical parameters, which can fit at the same time the frequency and the intensity values.[18] Such a calculation is very complex even with simple molecules, and it becomes absolutely prohibitive when multiatom systems are concerned. On the other hand, the intensity of a band is often a much more sensitive marker of the effect of the environment of a chemical group than is the frequency.[19]

Therefore, the study of the intensity of the infrared bands associated with the vibrational modes of an alkyne bonded to a metal cluster is appealing. The aforementioned experimental and theoretical difficulties can be partially overcome on the ground of the conclusions achieved by the careful analysis of small molecules;[21-24] that is, the intensity data can be translated into parameters transferable from one molecule to another and correlable with the molecular properties. This result may be simply obtained by measuring the integrated intensity of a whole region of the spectrum or even by measuring the ratio of appropriate bands, without the need of the accuracy usually necessary for absolute intensity values.[25]

This "simplified" use of the infrared intensities, applied to the previously reported complexes, is the other topic of the present paper.

## Experimental Section

**Synthesis of the Complexes.** Solvents and readily available reactants were reagent grade and generally were used without further purification. Other products were purchased from Strem Chemicals ($Co_2(CO)_8$, $Os_3(CO)_{12}$), Rivoira (acetylene), P&B Research Chemicals (propyne), MSD Isotopes (methylacetylene-$d_1$), K&K (2-butyne), and Sigma Chemical ($(CH_3)_3NO$).

All the manipulations were carried out under an inert atmosphere or, when necessary, in a glovebox filled by dry nitrogen. Preparative thin-layer chromatography was conducted with Merck silica gel G 60 F-254; column chromatography, with Silica Woelm TSC. Characterization and purity of the complexes were checked by IR spectroscopy, TLC, mass spectrometry (Kratos MS 80), and elemental analysis (Mikroanalytisches Labor Pascher, Remagen-Bandorf, FRG).

The $Co_2(CO)_6RC_2R'$ compounds were prepared by reacting $Co_2(CO)_8$ and the appropriate alkyne, according to the well-known procedure.[26]

The $Os_3(CO)_{10}RC_2R'$ complexes were previously prepared and characterized.[3,14,27,28] However, the commonly used procedure, i.e. the reaction of $H_2Os_3(CO)_{10}$ with alkynes, gives a lesser yield and a more complex pattern of products than the method suggested by Tachikawa and Shapley.[29] As this method was not detailed, we describe the synthesis of $Os_3(CO)_{10}HC_2CH_3$ as a typical process for the preparation of $Os_3(CO)_{10}$alkyne complexes.

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A dichloromethane solution of 200 mg (ca. 0.214 mmol) of $Os_3(CO)_{10}(CH_3CN)_2$, prepared as previously reported,[30] was introduced into a glass vial provided with a serum cap and connected to a vacuum line. The solution was frozen and evacuated and propyne was condensed into the vial in a molar ratio of ca. 5:1 with respect to the complex. The vial was sealed and allowed to react at room temperature; small amounts of the solution withdrawn by a syringe through the serum cap were examined time to time by TLC and IR spectroscopy to test the progress of the reaction. The reaction was complete in ca. 4 h. The solution was purified by TLC (eluent: petroleum ether), and the pure compound was obtained as good orange crystals from *n*-heptane solution at −20 °C; yield 133 mg (ca. 70%). Infrared absorptions in the $\nu$(CO) region (*n*-heptane, $cm^{-1}$): 2101 m, 2061 s, 2050 s, 2024 s, 2014 m, 1999 m, 1849 m. The same procedure was used to prepare $Os_3(CO)_{10}DC_2CH_3$.

The synthesis of $Co_2Ru(CO)_9HC_2H$[15] and of $Co_4(CO)_{10}HC_2H$[4] have already been reported. The procedure to prepare and purify the new $Co_4(CO)_{10}HC_2CH_3$ and $Co_4(CO)_{10}CH_3C_2CH_3$ complexes was very close to that reported for the acetylene compound, and it is so summarized:

**$Co_4(CO)_{10}HC_2CH_3$.** Starting materials: 1 g (2.9 mmol) of $Co_2(CO)_8$ and 300 mL (room temperature, 1 atm) of gaseous propyne (ca. 12 mmol). Yield: 0.57 g (ca. 70%) of $Co_4(CO)_{10}HC_2CH_3$ (dark blue crystals). Infrared absorptions in the $\nu$(CO) region (*n*-heptane, $cm^{-1}$): 2092 m, 2052 s, 2041 m, 2036 s, 2023 w, 1996 m, 1880 m.

**$Co_4(CO)_{10}DC_2CH_3$.** Starting materials: 0.30 g of $Co_2(CO)_8$ and 100 mL (room temperature, 1 atm) of $DC_2CH_3$. Yield: 0.150 g (ca. 60%).

**$Co_4(CO)_{10}CH_3C_2CH_3$.** Starting materials: 1 g of $Co_2(CO)_8$ and 2.00 mL of liquid 2-butyne (ca. 25 mmol). Yield: 0.39 g (ca. 45%) of the complex (blue microcrystals). Infrared absorptions in the $\nu$(CO) region (*n*-heptane, $cm^{-1}$): 2090 m, 2050 s, 2039 m, 2032 s, ca. 2025 w sh, 1991 m, 1880 m.

The new complex $Co_4(CO)_{10}(S)HC_2H$ was obtained by a method similar to that briefly reported for the phenylacetylene derivative.[17] In a petroleum ether solution of $Co_3S(CO)_9$[31] (0.400 g in 100 mL), kept under CO at room temperature, a small amount of freshly sublimed $(CH_3)_3NO$ was dissolved; then gaseous acetylene was gently bubbled until the $\nu$(CO) bands of the starting compound disappeared (15–20 h). The reaction mixture contained complex IV′a as the main product, together with small amounts of $Co_2(CO)_6HC_2H$, $Co_4(CO)_{10}S_2$,[32] and $(Co_3(CO)_7S)_2S_2$.[33] The purification of the product, based on its poor solubility in hydrocarbons, consisted of the following steps: concentration of the solution and gross precipitation by freezing; working up of the solid by TLC; final crystallization from *n*-heptane. Yield: 180 mg of black microcrystals of $Co_4(CO)_{10}(S)HC_2H$ (ca. 50%). Infrared spectrum in the $\nu$(CO) region (*n*-heptane, $cm^{-1}$); 2059 s, 2048 m, 2034 s, 2021 w, 1907 m, 1890 w. Mass spectral data: main peaks at *m/e* 574 ($M^+$) and at *m/e* values corresponding to $(M - nCO)^+$ (*n* = 1–10).

**Infrared Measurements.** The spectra were recorded by a Perkin-Elmer (Model 580B) IR grating spectrophotometer. The Computer Data Station (Model 3600) permitted us to make all the spectral data manipulations and the band intensity measurements with the PE580 software provided.

## Results and Discussion

**(1) Assignment of the Vibrational Modes.** The infrared bands of the coordinated alkynes were assigned by observation of the frequency changes due to the isotopic substitution and the intensity changes due to the lowering of temperature and by comparison with spectra of other alkyne compounds and the free ligands.[34] The assignments are almost always straightforward: small couplings cannot be excluded, but they do not have practical significance on the analysis of the data (see later).

**(a) Acetylene Complexes.** The spectra of IIa,[35] IIIa,[36] and IVa[4] were previously reported. We completely agree with the proposed assignments, except that concerning the C–H deformation modes in IIa, which, according to the $C_{2v}$ symmetry, are expected to give rise to three IR bands, two deformations in the plane of the acetylene, $\delta$(CH), and one deformation out of the plane, $\gamma$(CH). Iwashita assigned two modes only, presumably $\delta$(CH); we are inclined to assign the missing $\gamma$(CH) mode to the absorption at 605 $cm^{-1}$, shifted by deuterium labeling to 561 $cm^{-1}$, previously reported as Co–acetylene stretching.

**Table I.** Frequency Values ($cm^{-1}$) of the Vibrational Modes of the Free and Coordinated Acetylene

| assignt | $HC_2H$[a] | IIa[b] | IIIa[c] | III′[a] | IVa[d] | IV′a |
|---|---|---|---|---|---|---|
| $\nu$(C—H) | 3374 R | 3116 m | 2996 w | 2984 m | 3020 vw | 2951 w |
| | 3287 IR | 3086 m | 2945 m | 2965 mw | 2993 vw | 2919 m |
| $\nu$(C≡C) | 1974 R | 1403 s | 1301 m | 1354 m | 1199 m | 1384 m |
| $\delta$(C—H) | 729 IR[e] | 894 s | 1035 m | 1008 m | 1120 m | 1193 w |
| | | 768 s | 978 w | 930 m | 983 ms | 1063 m |
| $\gamma$(C—H) | 912 R[e] | 605 m | 848 s | 787 m | 922 w | 894 m |
| | | f | f | f | 837 m | 645 w |

[a] From ref 34. [b] From ref 35. [c] From ref 36. [d] From ref 37. [e] The modes are both doubly degenerate, one component being related to the $\delta$ mode and the other one to the $\gamma$ mode of the coordinated acetylene. [f] Not observed.

**Table II.** Frequency Values ($cm^{-1}$) of the Vibrational Modes of the Free and Coordinated 2-Butyne

| assignt | $CH_3C_2CH_3$[a] | IIb[b] | IIIb | IVb |
|---|---|---|---|---|
| $\nu(CH_3)$ | 2975 IR | 2970 s | 2979 w | 2954 w |
| | 2961 R | 2963 s | 2939 s | 2918 m |
| | 2920 R | 2910 s | 2900 s | |
| $\nu$(C≡C) | 2313 R | 1633 w | 1390 mw | c |
| $\delta(CH_3)$ | 1468 IR | 1460 m | 1444 m | 1435 m,br |
| | 1447 R | 1445 m | 1430 w | |
| | | 1432 s | | |
| | 1380 IR | 1383 w | 1373 m | 1376 m |
| | 1379 R | 1368 m | 1360 mw | 1363 m |
| $\nu$(C—C) | 1126 IR | 1130 m | 1131 vw | 1088 w |
| | 697 R | 770 m | 894 w | 822 w,br |
| $\rho(CH_3)$ | 1050 IR | 1065 m | 1066 m | 1048 m |
| | 1029 R | 1045 s | 1052 s | 1036 m |
| | | 1017 s | 1012 s | 1016 w |

[a] From ref 34. [b] From ref 37. [c] Not observed.

The assignment for III′a is easily recognized by comparison with that of IIIa: in this case too, one $\gamma$(CH) mode is not observed, probably being obscured by the strong M–C–O modes below 600 $cm^{-1}$.

The spectrum of the complex IV′a shows two bands in the 3000–2900-$cm^{-1}$ region, clearly belonging to the $\nu$(CH) modes. The C≡C stretch appears as a medium-intenstiy band at 1384 $cm^{-1}$ and the four C—H bending modes are recognized in the four medium–weak bands in the 1200–600-$cm^{-1}$ region, which increase their intensity on cooling. The out-of-plane $a_2$ mode is expected to be strictly IR inactive in a formal $C_{2v}$ symmetry, but can have some intensity in the solid-state spectrum, as occurs with complex IVa.[4]

For the sake of clarity, all the data are reported in Table I.

**(b) 2-Butyne Complexes.** The band frequencies and assignments are reported in Table II. The C≡C stretching is expected in the 1400–1300-$cm^{-1}$ region for the IIIb and IVb complexes. The spectrum of IIIb shows three bands in this region, two of which are assignable to the $CH_3$ antisymmetric deformation modes (cf. with IIb): considering the relative intensity and frequency, the $\nu$(C≡C) mode is probably the absorption at 1390 $cm^{-1}$. Two bands only, $\delta(CH_3)$, appear in the IVb spectrum and presumably cover the weak $\nu$(C≡C) absorption.

**(c) Propyne Complexes.** The absorptions due to the propyne vibrations for IIc compound were previously reported and correctly assigned on the basis of the comparison with the spectra of the deuterated compound and of the free ligand.[37] Table III reports the frequencies and the proposed assignments for the bands of IIIc and of IVc, together with those of the isomers with the deuterated propyne $DC_2CH_3$. The assignments are generally straightforward, and the isotopic shift of the CH modes is in the

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**Table III.** Frequency Values (cm$^{-1}$) of the Vibrational Modes of the Free and Coordinated $HC_2CH_3$ and $DC_2CH_3$ (D)

| assignt | $HC_2CH_3$[a] | IIb[b] | IIb(D)[b] | IIIb | IIIb(D) | IVb | IVb(D) |
|---|---|---|---|---|---|---|---|
| ν(C—H) | 3429 IR | 3100 m | 2320 m | 2974 w | *c* | 2963 w | *c* |
| ν($CH_3$) | 2994 IR | 2960 m | 2960 m | 2953 s | 2942 m | 2921 m | 2921 m |
| | 2971 R | 2942 m | 2940 m | 2905 m | 2921 m | 2852 w | 2854 w |
| | 2941 R | 2903 s | 2903 s | | 2905 m | | |
| ν(C≡C) | 2142 R | 1550 m | 1525 m | 1357 m | 1345 m | 1305 m | 1295 w |
| δ($CH_3$) | 1448 R | 1440 m | 1440 m,sh | 1429 m,br | 1430 w,br | 1437 m,br | 1436 s |
| | | 1430 s | 1430 m | | | | |
| | 1382 IR | 1366 m | 1366 m | 1366 s | 1366 m | 1372 m | 1372 m |
| ρ($CH_3$) | 1041 IR | 1054 s | 1054 s | 1064 s | 1116 m | 1054 w | 1066 s |
| | 1035 R | 1010 s | 1010 s | 1018 s | 1019 m | 1018 s | 1026 m |
| δ(C—H) | 643 IR | 840 s | 697 m | 1174 m | 979 m | 1105 m | 830 s |
| | 643 R | 777 s | 607 m | 911 w | 713 s | 874 m | 674 m |
| ν(C—C) | 926 IR | 939 m | 923 m | 963 m | 964 m | 915 m | 910 m |

[a] From ref 34. [b] From ref 37. [c] Not observed.

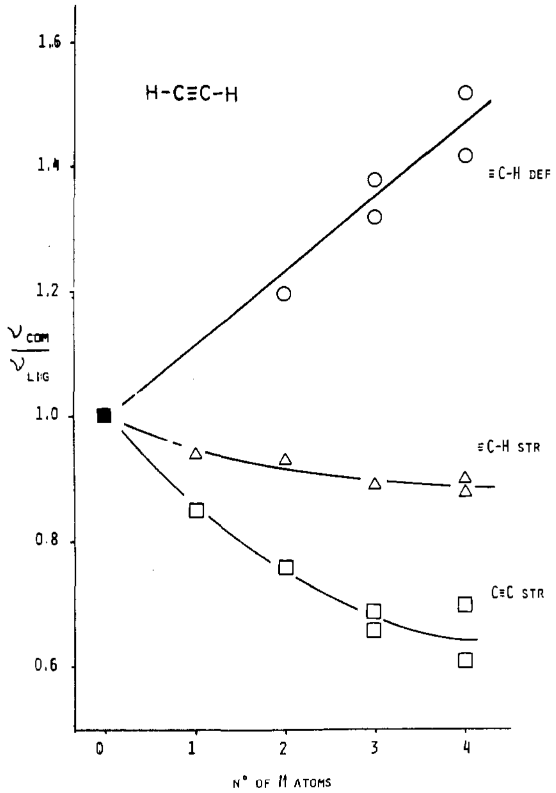

**Figure 2.** Average frequencies of the main vibrational modes of the coordinated acetylene related to those of the free acetylene vs the nuclearity of the complexes.

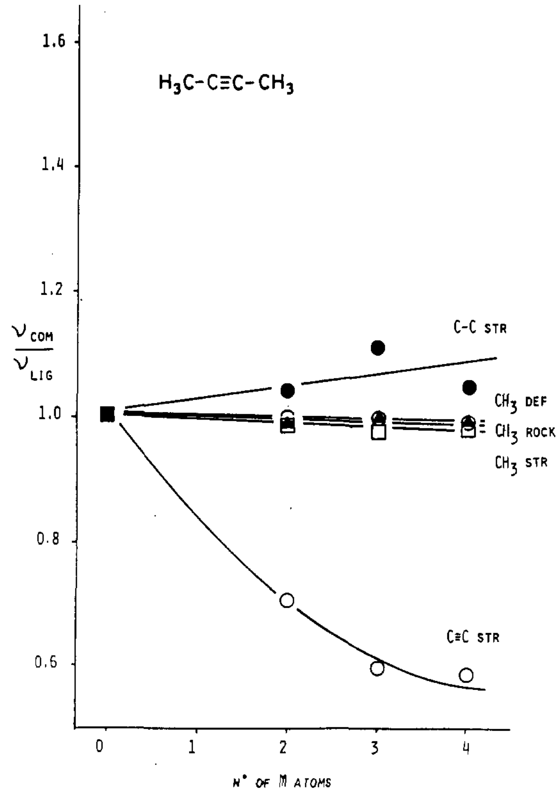

**Figure 3.** Average frequencies of the main vibrational modes of the coordinated 2-butyne related to those of the free 2-butyne vs the nuclearity of the complexes.

expected range ($\nu_H/\nu_D$ = 1.30–1.35). Apparently surprising is the upward shift of one $CH_3$ rocking mode in the deuterated derivatives of IIIc and IVc. Presumably, the "true" frequency of this mode is that of the D complex; in the H complex, the coupling with the close δ(CH) mode pushes the frequency down. The absence of this effect in the IIc spectrum, where the two modes are far away, supports the suggestion.

**(2) Coordination Effect on the Frequencies of the Alkyne Modes.** A careful inspection of the data in Tables I–III allows us to observe the trends in the frequency variation of the alkyne modes, when one moves from the free alkyne to the alkyne in a different coordinating environment. The C≡C stretching is on this basis very significant. The well-known decrease of frequency as a consequence of the coordination can be clearly related to the number of the metal atoms to which the alkyne is coordinated, independent of the type of alkyne itself. Therefore, the ν(C≡C) roughly varies in the following order: free alkyne > $Co_2$ > $Os_3$ ≈ $Co_2Ru$ > $Co_4$. A similar order is not easily associated with other modes, for the following reasons: first, each gives rise to more than one spectral feature; second, a variety of molecular symmetries are involved, and the corresponding band correlations are not always unique or determined; finally, the actual frequencies can be sensitive to accidental coupling with other modes. Nevertheless, if an average over the frequencies of the relevant modes is considered, the above effects either become irrelevant or become of reduced importance, and general trends may be easily recognized, with respect to the nuclearity of the metal cluster. Figures 2–4 summarize the results: to compare the different modes, the frequency values are referred to those of the free alkyne.[38]

The plots clearly confirm the aforesaid observations on the ν(C≡C) value, which in turn is related to the C≡C length:[4] both essentially depend on the number of the coordinating metal atoms.

The modes associated with the alkynic C-H show interesting effects. The C—H stretching has similar, but less evident behavior of the ν(C≡C) whereas the C—H bending exhibits the greatest variation, showing an increase up to ca. 60% of the reference value.

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(38) Figure 1 also reports the values related to the acetylene bonded to a single metal atom. Since at present no detailed vibrational study on M($HC_2H$) complexes has been reported, the data are referred to the Ni($HC_2H$) species formed in low-temperature matrices.[39] Other similar Cu, Pd, or Pt species have close values.[40]

(39) Ozin, G. A.; McIntosh, D. F.; Power, W. J.; Messmer, R. P. *Inorg. Chem.* **1981**, *20*, 1782.

(40) Zoellner, R. W.; Klabunde, K. J. *Chem. Rev.* **1984**, *84*, 545.

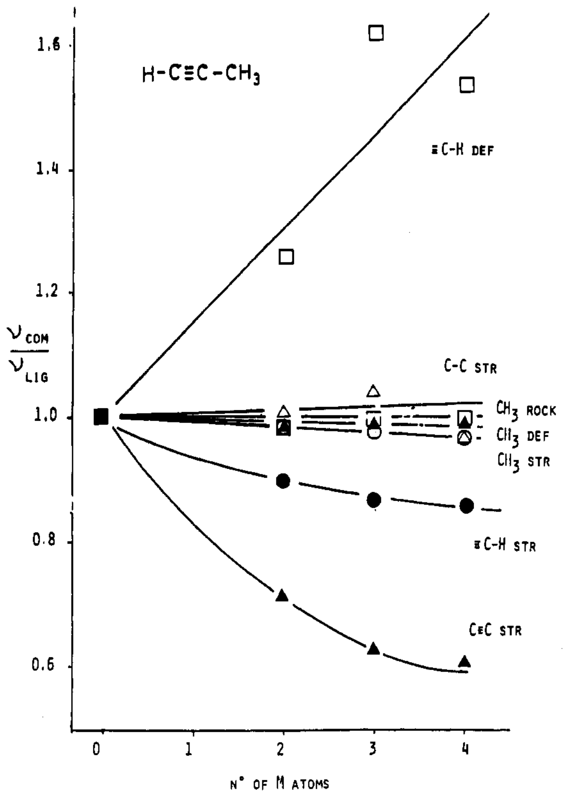

**Figure 4.** Average frequencies of the main vibrational modes of the coordinated propyne related to those of the free propyne vs the nuclearity of the complexes.

A corresponding increase of the C–C–H bending force constant should be the main reason for this behavior:[41] this in turn could be ascribed to the increasing repulsion between H and R of the HC≡CR system and/or between H and the π-density on the C≡C bond, which are closer and closer as the coordination number increases. The sensitivity of the frequency of this mode to the type of coordination, together with the high intensity of the corresponding bands, suggests its use as a vibrational marker of the extent of the alkyne coordination to the metal clusters, one that is much better than the commonly observed ν(C≡C) mode, which is in turn less sensitive and less intense.

The frequencies of the other modes do not show any change because of the coordination, except perhaps the ν(≡C—C) frequency, which slightly increases passing from the free to the tetracoordinated alkyne.

As the stretching frequency of a bond is usually related to the relative strength and/or bond order, in an alkyne, which moves from the free molecule to coordination to two, three, and four metal atoms, the C≡C and the ≡C—H bond strength are regularly reduced. The increasing π-electron density, pushed by the metals into an alkyne antibonding MO, should be the main source of the reduced bond strength. The effect on the C–H bond seems to be similar to the interaction of the oxygen lone pair with the antibonding MO of the C–H unit in the aldehydes;[42,43] this is reflected in the chemical reactivity of the aldehydic C–H, which parallels the easy isotopic exchange of acetylenic hydrogen in IVa.[4]

**(3) Intensity of the Bands.** The knowledge of the charge distribution in a molecule has been improved by the interpretation of the infrared intensity as a function of the so-called electro-optical parameters (EOP), which are the bond dipole moment and its variation during the vibrational displacement.[18] The infrared intensity can be expressed also as function of the electric charge and of the charge flux, i.e. the variation of the charge during a vibration (ECCF parameters), which are uniquely related to EOP's and have a more evident physical meaning, because they correlate very well with other bond properties, such as length, energy, order, stretching force constant, etc.[44,45] A lot of work was performed in the last 10 years, mainly on the C–H bond, to calculate the charge on H atoms, $q^\circ_H$, and the charge flux, $CF(R_i)$, where $R_i$ is any vibrational coordinate.[18,20-24,44,45] The results show that the intensity of any C–H mode can be parametrized into ECCF values, which, in turn, can be easily transferred from one molecule to another. The following relationships hold:

**Table IV.** Values of the Ratio between the Total IR Deformation Intensity and the Total IR Stretching Intensity for CH and $CH_3$ Groups

| complex | $R$(CH) | $R$($CH_3$) |
|---|---|---|
| IIa | 8.2 | |
| IIIa | 1.3 | |
| III'a | 1.3 | |
| IVa | 16 | |
| IV'a | 0.7 | |
| $HC_2H$ | 2.52 | |
| IIb | | 0.26 |
| IIIb | | 0.84 |
| IVb | | 1.5 |
| $CH_3C_2CH_3$ | | 0.34 |
| IIc | 3.2 | 0.40 |
| IIIc | 6.8 | 0.54 |
| IVc | 6.6 | 2.4 |
| $HC_2CH_3$ | 1.94 | 0.60 |

$$I(CH_{str}) \propto [q^\circ_H + CF(CH_{str})]^2 \qquad (1a)$$

$$I(CH_{bend}) \propto [q^\circ_H + CF(CH_{bend})]^2 \qquad (1b)$$

Moreover, it was demonstrated[20] that qualitative or semiquantitative information on ECCF parameters can be obtained if the total C–H stretching or C–H bending intensities per C–H bond are used instead of a single isolated band. This allows the use of intensity information in the case of complex systems where detailed assignments, are not possible or absolute intensities cannot be measured or reliable force fields are not available. Finally, even simply the ratio $R = \sum I(CH_{bend})/\sum I(CH_{str})$ seems to be a very sensitive indicator of the charge distribution in the various C–H bonds: a plot of $R$ vs $q^\circ_H$ was successfully used to obtain an estimate of the charge value in molecules where detailed calculations are not possible.[25]

The present organometallic complexes are an example of such systems, and only the R values can be reliably measured. They are collected in Table IV for the ≡C—H and the $CH_3$ groups: the slight ambiguities in the assignments (see point 1) do not have significant effect.

The $R$ values for the $CH_3$ groups of the coordinated alkynes are not far from those of the free alkynes, except for IVb and IVc complexes, whose values are about 4 times higher. As a consequence, if the relationship between $R$ and $q^\circ_H$ holds,[25] the charge on the hydrogen atoms of the $CH_3$ groups in the $Co_4$ butterfly complexes has reached the values typical of an aromatic or an olefinic hydrogen, but this modification of the bonding is not reflected in parallel changes of the frequency of the $CH_3$ modes.

The most dramatic change concerns the relative intensities associated with the acetylenic C–H modes. The complexes IIa, IIc, IIIc, IVa, and IVc (see Table IV) are characterized by high $R$ values, which are due, since the C–H bending intensities are "normal",[46] to the very low values of the C–H stretching intensities. Considering the eq 1a, this may be a consequence either of

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(41) The G matrix elements do not vary significantly from free linear acetylene to coordinated folded acetylene; moreover, the greatest structural modification, i.e. the change of the C≡C—H (α) angle, should cause a decrease of the bending frequency, as G elements depend on −cos α.

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(43) McKean, D. C.; Duncan, J. L.; Batt, L. *Spectrochim. Acta, Part A* **1973**, 1037.

(44) Gussoni, M.; Jona, P.; Zerbi, G. *J. Chem. Phys.* **1983**, *78*, 6802.

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(46) The values of the total absolute intensity of the $CH_3$ deformation modes measured on $Co_2(CO)_6CH_3C_2CH_3$ and $Co_2(CO)_6HC_2CH_3$ in $CCl_4$ solution are approximately $4.0 \times 10^5$ and $6.2 \times 10^5$ cm mol$^{-1}$ per CH bond, respectively. Cf. the values of 2-butyne ($5.30 \times 10^5$ cm mol$^{-1}$ per CH bond) and of propyne ($6.45 \times 10^5$ cm mol$^{-1}$ per CH bond) 23.

near-zero values of both charge and charge flux during the stretching or of close values and opposite signs of the two parameters. The first hypothesis must be discarded because reasonable C–H deformation intensities require $q°_H$ values far from zero, the charge flux on deformation being negligible[44,45] (eq 1b), so the second hypothesis should be the preferred one. The meaning of $CF(CH_{str})$ having large values and opposite sign with respect to $q°_H$ is that the hydrogen atom of the C–H group has a high deformable charge, which tends to release during the stretching, reaching neutrality at the dissociation limit: in other words, the ≡C—H bond of the coordinated terminal alkynes dissociates into neutral atoms and not into ions. Among the free hydrocarbons, the alkanes and alkenes have high deformable charges, whereas on the alkynes the charge is practically fixed. This is further support for the model of the coordinated alkynes, which are supposed to be similar to olefins or to saturated hydrocarbons.

Even if the intensity value does not resolve the ambiguity of the sign of the charge on H atom (eq 1a), it seems likely that the charge is positive, as in the free alkynes. At the same time, the charge on the C alkynic atom should be negative because of the aforementioned relationship between the signs of charge and charge flux. As the negative charge on C atoms is mainly released by the π-back-donation from the metals, the greater the $q°_C$ and, consequently, the $q°_H$ values, the greater the π-effect. So we expect the greatest π-back-donation and the greatest $q°_H$ with IVa and IVc complexes, because the π-effect increases as the number of the coordinating metals increases, and the lowest ones with complex IV′a, because its structure implies the lowest degree of π-interaction between the alkyne and the metal cluster. From Table IV, the *R*(CH) values suggest $q°_H$ values in the following order: IVa > IIa > free $HC_2H$ > IIIa ≈ III′a > IV′a for acetylene complexes; IVc ≈ IIIc > IIc > free $HC_2CH_3$ for propyne complexes. This roughly parallels the expected order of the M-to-alkyne π-donation.

The $M_3$ complexes require further comments. Their structures, usually indicated as $M_3(\parallel)$alkyne with the C≡C axis parallel to an M—M bond, implies a low level of π-back-donation from metals to the alkyne, so the charge order for the acetylene complexes is reasonable. The $Os_3$ propyne compound, according to its *R* value, appears to have greater $q°_H$, which in turn suggests greater π-back-donation. In the $M_3$(alkyne) complexes the π-effect is increased if the structure moves from the $M_3(\parallel)$ to the $M_3(\perp)$; therefore, the *R* value of the $Os_3$(propyne) complex is suggestive of a deformation of the symmetric structure, with $HC_2CH_3$ moiety slightly rotated, such that the C≡C axis is no longer parallel to the Os—Os bond. Such a slightly distorted structure has already been reported for $Os_3H_2(CHCOC_2H_5)(CO)_9$[47] and for $Os_3(CO)_9(C_2H_5C_2C_2H_5)P(C_6H_5)_3$[14] and was ascribed to the asymmetric π-donation from the $OC_2H_5$ group or to the steric demands of the phosphine ligand.

Very good agreement was reported on simple molecules between the $q°_H$ values derived from experimental infrared intensities and those computed by quantum-mechanical calculations, suggesting agreement between the IR charge and the Mullikan electron population.[48] The agreement, however, is only evident if both parameters are the result of very sophisticated calculations (NCA on absolute intensities and "ab initio" MO analysis). Comparison is meaningless in our case because the Mullikan charges on C and H reported for alkyne–metal cluster complexes are approximate and one dependent on the calculation procedure. However, in agreement with the previous suggestion, MO analysis on model compounds such as $Co_2(CO)_6HC_2H$,[49] $Co_2(CO)_6(CH_3)_3CC_2C(CH_3)_3$,[12] $Fe_3(CO)_9HC_2H$,[50] and $Co_4(CO)_{10}HC_2H$[51] stressed the importance of the π-back-donation from metal to alkyne, suggesting carbanionic character for the ligand.

In conclusion, comparative analysis of the IR vibrational properties (frequencies and intensities) of the alkynes coordinated to metal clusters can suggest the following points.

(a) The C≡C and the ≡C—H bonds are greatly affected by the coordination, whereas slight effects or no effect is observed on the other bonds of the alkyne.

(b) The charge on the acetylenic H is positive and that on acetylenic C is negative and both mainly depend on the metal-to-alkyne π-back-donation.

(c) The ≡C—H bond has prevailing covalent character, and it is expected to dissociate into neutral atoms.

(d) The charge distribution on the coordinated alkyne molecule affects the group bonded to the alkynic carbon atoms.

(e) Both frequency and intensity of the IR bands offer some insight into structure predictions.

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# The Chemistry of Iron–Alkene Ions with Chlorobenzene

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The chemistry of $Fe^+$–alkene ions with chlorobenzene is studied in the gas phase by laser-desorption Fourier transform mass spectrometry. The reaction between $Fe^+$–ethylene and chlorobenzene occurs via initial insertion of $Fe^+$ into the Cl–C bond, followed by ethylene migratory insertion into the $Fe^+$–phenyl bond. Subsequent β-hydrogen abstraction and HCl elimination completes the reaction. In the case of $Fe^+$–propene, a remarkable selectivity governing the migratory insertion step is present, resulting in the formation of $Fe^+$–β-methylstyrene.

Recent studies on transition-metal ions in the gas phase have provided a great deal of insight into their reaction mechanisms, kinetics, and thermochemistry.(1) Attachment of one or more ligands to such a transition-metal center can have little or major effects on the reactivity of the metal ion center. This depends on the nature of the ligand and the interaction between the metal center and the ligand, as well as on the neutral reacting species selected for the reaction process.(2),(3) Thus, results obtained from

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