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IR INTENSITY MEASUREMENTS ON GROUP VIIIB, C METAL—ALKYNE COMPLEXES

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Summary

The integrated molar absorption coefficients $\overline{A}_{\text{int}}$ of the C≡C stretching vibration of the coordinated alkynes of Rh, Ir, Ni and Pt complexes of hexafluorobutyne (HFB), tolane and hexyne have been measured. A relative scale of donor and acceptor interactions in the complexes has been calculated from the measured values of $\overline{A}_{\text{int}}$ and $\Delta(\nu^2) = \nu^2(\text{free alkyne}) - \nu^2(\text{coordinated alkyne})$. Competitive as well as synergic relations between donor and acceptor bonding have been found. The order of increasing donor and decreasing acceptor bonding has been found for the alkynes HFB → tolane → hexyne. Within the series of complexes of a given alkyne, the acceptor bond increases for the metals in the order: Pt(II) (4) < Rh(I) (4) < Ir(I) (4) < Pt(II) (5) < Ni(0) (3) < Pt(0) (3) (coordination number in parentheses) and the donor bonding increases synergically with the acceptor bonding in this series.

Introduction

The transition metal—alkyne bond has a dual nature and is usually described by the Dewar, Chatt, Duncanson bonding model [1,2] as being composed of (*i*) a bond of σ-symmetry, in which the alkyne donates π-electron density to the empty metal orbitals, and (*ii*) a bond of π-symmetry, in which the antibonding π^*-orbitals of the alkyne accept electron density from filled metal orbitals (π-backbonding). In addition, there may be a contribution from the second π and π^* orbital pair. Both donor and acceptor bonding weaken the coordinated C≡C bond and lower the C≡C stretching vibration frequency.

The C≡C stretching vibration of a coordinated alkyne is accompanied by a change in dipole moment which is perpendicular to the vibrational motion along the metal—alkyne bond. The change in the permanent dipole moment, due to the movements of the nuclear coordinates during the C≡C stretching vibration, is not likely to be of great importance, since this symmetric vibration consists

TABLE 1

ANALYTICAL DATA (Calculated values are given in parentheses)

Compound	Analysis (%)					
	C	H	N	Cl	P	F
$Pt(PPh_3)_2(HFB)$	55.0	3.7			6.9	12.5
	(55.5)	(3.4)			(7.0)	(12.9)
$Ni(PPh_3)_2(HFB)$	64.3	3.9			8.5	15.2
	(64.6)	(4.1)			(8.2)	(15.4)
$Pt(CH_3)(HBpz_3)(HFB)$	29.6	2.4	14.6			17.0
	(28.7)	(2.2)	(14.4)			(19.6)
$IrCl(PPh_3)_2(HFB)$	52.1	3.3				12.5
	(52.8)	(3.3)				(12.5)
$RhCl(PPh_3)_2(HFB)$	58.8	3.9		3.7		13.1
	(58.3)	(4.1)		(4.3)		(13.8)
$Pt(PPh_3)_2(TOL)$	66.5	4.4			7.2	
	(66.9)	(4.5)			(6.9)	
$RhCl(PCy_3)_2(TOL)$	67.7	8.2		3.7		
	(68.5)	(8.8)		(4.0)		
$IrCl(PPh_3)_2(TOL)$	64.7	4.5		3.7	6.8	
	(64.5)	(4.3)		(3.3)	(6.7)	
$RhCl(PPh_3)_2(TOL)$	70.6	4.6		3.7		
	(71.4)	(4.8)		(4.2)		
$Pt(PPh_3)_2(HEX)$	61.2	4.8			8.0	
	(62.9)	(5.0)			(7.8)	
$RhCl(PCy_3)_2(HEX)$	63.7	9.6		3.6	8.3	
	(64.7)	(9.8)		(3.5)	(8.0)	

peak, which we attribute to Fermi resonance doubling [23]. In those cases the total intensity of both absorptions has been taken.

Results

The IR vibration under consideration is acceptably described by a 5-center model of C_{2v}-symmetry, comprising the central metal, the two acetylenic carbon atoms and the two substituent atom groups (Fig. 1). From the seven fundamental in-plane vibrations, four belong to the A_1 representation. With the aid of tabulated G-matrix elements [24] and estimated force constants [25,26] it is confirmed that contributions of the lower frequency vibrations to the commonly called C≡C stretching vibration in the 1700—2000 cm^{-1} region do not exceed 10%, so that approximation by a pure C≡C stretching vibration does not introduce large errors.

The integrated molar absorption coefficient $\bar{A}_{int}$ is defined as [27]:

$$\bar{A}_{int} = \int \bar{A} d\nu = 2.303(1/CL) \int_{\text{band}} \log(I_0/I_t) d\nu \qquad (1)$$

its dimension is $l\ mol^{-1}\ cm^{-2}$. $\bar{A}$ is the molar absorption coefficient in $l\ mol^{-1}\ cm^{-1}$; C is the concentration in $mol\ l^{-1}$ and L is the cell width in cm. Table 2 gives, together with some other IR data, the measured values of $\bar{A}_{int}$, with the

TABLE 2

IR INTENSITY DATA AND CALCULATED DIPOLE MOMENT CHANGES OF ALKYNE COMPLEXES

Compound	$\nu(C\equiv C)$ (cm^{-1})	$\Delta\nu(C\equiv C)$ (cm^{-1})	$(\delta\nu)_{1/2}$ (cm^{-1})	$\bar{A}_{max} \times 10^{-3}$ ($l\ mol^{-1}\ cm^{-1}$)	$\bar{A}_{int} \times 10^{-4}$ ($l\ mol^{-1}\ cm^{-2}$)	$(d\mu/dr)_{calc}$ (a.u.)	$\Delta(\nu^2)$ ($10^4\ cm^{-2}$)
Hexafluorobutyne [a]	2300						
$Pt(PPh_3)_2(HFB)$	1773	527	22	1.215	3.22(9)	0.81	215
$Ni(PPh_3)_2(HFB)$	1791	509	19	1.150	2.88(8)	0.77	208
$Pt(CH_3)(HBpz_3)(HFB)$	1862	438	17	0.748	2.31(7)	0.67	182
	1833		14.5	0.402			
$IrCl(PPh_3)_2(HFB)$	1880	441	13	0.990	2.00(6)	0.64	172
	1903			0.547			
$RhCl(PPh_3)_2(HFB)$	1921	379	15	0.822	1.61(7)	0.57	160
Diphenylacetylene [a]	2222						
$Pt(PPh_3)_2(TOL)$	1742	467	20	0.277	1.31(10)	0.52	186
	1768		20	0.277			
$RhCl(PCy_3)_2(TOL)$	1847	375	26	0.245	0.88(4)	0.42	153
$IrCl(PPh_3)_2(TOL)$	1857	365	15	0.387	0.78(5)	0.40	149
$RhCl(PPh_3)_2(TOL)$	1885	330	19	0.146	0.64(2)	0.36	136
	1898			0.171			
$[Pt(CH_3)(AsMe_3)_2(TOL)]^+$ [a,b]	2087	135		ca. 0.0		ca. 0.0	58
3-hexyne [a]	2247						
$Pt(PPh_3)_2(HEX)$	1798	449	24	0.191	0.60(4)	0.35	181
$RhCl(PCy_3)_2(HEX)$	1941	306	18	0.145	0.42(3) [c]	0.29	128
	1956(sh)						
$[Pt(CH_3)(PMe_2Ph)_2(HEX)]^+$ [a,b]	2101	146		ca. 0.0		ca. 0.0	64

[a] In Raman spectrum. [b] Data from ref. 5. [c] $RhCl(PCy_3)_2(CO)$ absorps strongly at 1947 cm^{-1}. A trace amount of this compound, although not detected in the ^{31}P NMR and IR spectra, may be present. This may increase the measured value of $\bar{A}_{int}$ of $RhCl(PCy_3)_2(HEX)$.

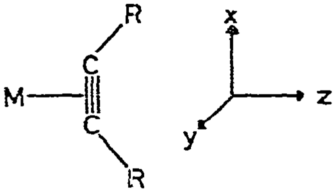

Fig. 1. Coordinate axes.

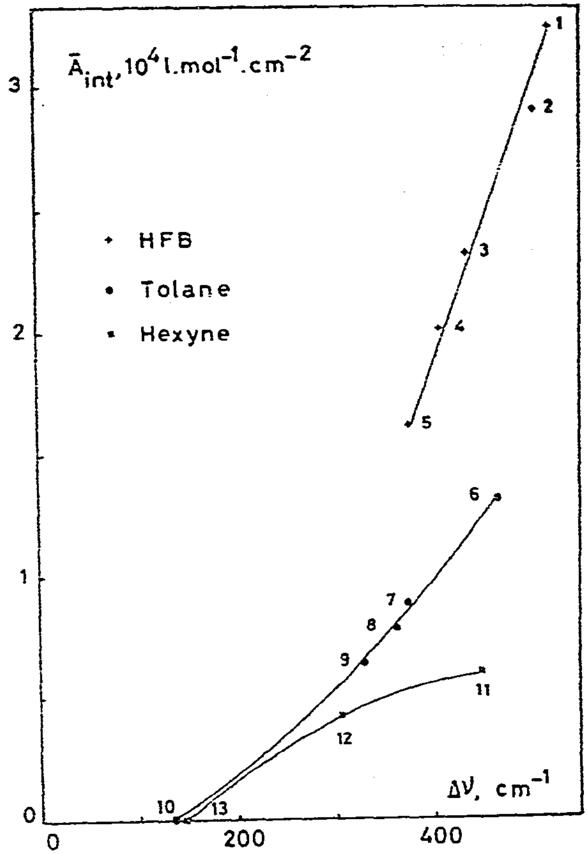

Fig. 2. $\bar{A}_{int}$ versus $\Delta\nu$. Numbering of the complexes as in Table 4.

maximum deviation in parentheses. A plot of $\bar{A}_{int}$ versus $\Delta\nu = \nu$(free alkyne) — ν(coordinated alkyne) is given in Fig. 2.

The experimental absorption coefficient $\bar{A}_{int}$ is related to molecular quantities by the expression [27]:

$$\bar{A}_{int} = 8\pi^3 N\nu|\mu_{01}|^2/(3hc \times 1000) \tag{2a}$$

where N is Avogadro's number; h is Planck's constant; c is the velocity of light, μ_{01} is the transition moment of the vibration, 0 refers to the ground state ψ_0 and 1 to the excited state ψ_1. Although the dipole moment μ is not along the carbon—carbon bond direction, the approximation [27]

$$\mu_{01} = (d\mu/dr)_{r=r_0}\langle\psi_0|r|\psi_1\rangle \tag{2b}$$

still holds, r is the C≡C distance, r_0 the equilibrium distance.

The harmonic oscillator approximation [27] for ψ_0 and ψ_1, valid for a stretching vibration, permits evaluation of $\langle\psi_0|r|\psi_1\rangle^2$. This approximation contains a systematic deviation for the complexes, which we assume to be similar for all

TABLE 3

ORBITAL CORRELATIONS FOR THE METAL—ALKYNE FRAGMENT IN C_{2v}-SYMMETRY

Representation	Interaction type	Metal orbitals	Alkyne orbitals
A_1	σ donor	d_{z^2}, $d_{x^2-y^2}$, s, p_z	σ, π_z
B_2	π donor	d_{yz}, p_y	π_y
B_1	π acceptor	d_{xz}, p_x	σ^*, π_z^*
A_2	δ acceptor	d_{xy}	π_y^*

$$N_b^{i2} = (2 + 2S^i_{CC})^{-1} \qquad N_a^{i2} = (2 - 2S^i_{CC})^{-1} \tag{5}$$

where $S^i_{CC} = \langle\varphi^i_1|\varphi^i_2\rangle$. The normalization constants N^i_b and N^i_a differ in the sign of S^i_{CC}, and we shall show that this has far-reaching consequences. The p_π orbitals at a carbon—carbon distance of 1.25 Å have $S_{CC} = 0.33$, which leads to the values $N_\pi{}^2 = 3/8$ and $N_{\pi^*}{}^2 = 3/4$, and a ratio $(N_{\pi^*}/N_\pi)^2 = 2$. We take the diagonal term of φ^i_1 in the Hamiltonian matrix as a reference: $\langle\varphi^i_1|H|\varphi^i_1\rangle = 1$. With the use of the Wolfsberg-Helmholz approximation [28] $H_{kl} = \frac{1}{2}KS_{kl}(H_{kk} + H_{ll})$ for the off-diagonal terms, this results in diagonal terms E^i_b and E^i_a for the χ^i_b and χ^i_a orbitals of:

$$E^i_b = 2(1 + KS^i_{CC})N_b^{i2} \qquad E^i_a = 2(1-KS^i_{CC})N_a^{i2} \tag{6}$$

Filled M.O.'s of the metal—alkyne complex take the general form:

$$\psi^i_{don} = C^i_M\chi^i_M + C^i_b\chi^i_b \qquad \psi^j_{acc} = C^j_M\chi^j_M + C^j_a\chi^j_a \tag{7}$$

ψ^i_{don} and ψ^j_{acc} describe the alkyne-to-metal donor and alkyne-from-metal acceptor interactions respectively. From here on, i refers to filled M.O.'s of the complex containing an alkyne orbital filled in the free alkyne, and j to filled M.O.'s containing an alkyne orbital empty in the free alkyne. Eqs. 4 and 7 combine to give an expression for the coefficients of the carbon atomic orbitals in the filled M.O.'s of the complex:

$$C^i_1 = C^i_2 = C^i_b N^i_b \qquad C^j_1 = C^j_2 = C^j_a N^j_a \tag{8}$$

$\Sigma_i\, 2(1 - C_b^{i2})$ is the amount of charge donated from alkyne orbitals to metal orbitals, and $\Sigma_j\, 2C_a^{j2}$ the amount of charge accepted from metal orbitals into alkyne orbitals. We define a measure of the alkyne-to-metal donor interaction strength as:

$$(\text{don}) = \sum_i 2(1 - C_b^{i2}) \tag{9a}$$

and a measure of the alkyne-from-metal acceptor interaction strength:

$$(\text{acc}) = \sum_j 2C_a^{j2} \tag{9b}$$

The frequency differences

ν^2 is proportional to the force constant f_{CC} of the CC stretching vibration.

f_{CC} is related to the carbon coefficients of the doubly filled M.O.'s by [29,30]:

$$f_{\mathrm{CC}} = \mathrm{a}\sum_{k} 2C_1^k C_2^k + \mathrm{b} = \mathrm{a}\sum_{k} 2C_1^{k^2} + \mathrm{b} = \mathrm{aP}_{\mathrm{CC}} + \mathrm{b} \tag{10}$$

The summation k runs over all filled M.O.'s; P_{CC} is the carbon—carbon bond order, and a and b are constants. So is a′ in:

$$\Delta f_{\mathrm{CC}}(:)\Delta(\nu^2) = \mathrm{a}'\Delta \mathrm{P}_{\mathrm{CC}} \tag{11}$$

From the various equations, $\Delta(\nu^2)$ is calculated:

$$\Delta(\nu^2) = \mathrm{a}'\Big[\sum_{i} 2(1 - C_{\mathrm{b}}^{i2})N_{\mathrm{b}}^{i2} + \sum_{j} 2C_{\mathrm{a}}^{j2}N_{\mathrm{a}}^{j2}\Big] \tag{12}$$

Under the assumption that the contribution of the alkyne π and π^* orbitals to the metal—alkyne interaction dominate those of the σ and σ^* orbitals, the substitution of N_{b}^i by N_π and N_{a}^j by N_{π^*} is a reasonable simplification for eq. 12 which then becomes by the use of eq. 9 (α is a proportionality constant):

$$\Delta(\nu^2) = \alpha[(\mathrm{don}) + (N_{\pi^*}/N_\pi)^2(\mathrm{acc})] \tag{13}$$

This equation emphasizes that the acceptor interactions have a greater weight in the lowering of the frequency of the carbon—carbon stretching vibration than the donor interactions, and that this is largely due to the differences in normalization constants ($(N_{\pi^*}/N_\pi)^2 = 2$).

The dipole moment derivative

The carbon—carbon stretching vibration of the coordinated alkyne belongs to the A_1 representation in C_{2v}-symmetry. Consequently, the dipole moment and its derivative are equal to their component along the M—C_2 axis (z-axis in Fig. 1):

$$\mu = \mu_z = 2e\bar{z} = 2e\Big[\sum_{i}\langle\psi_{\mathrm{don}}^i|z|\psi_{\mathrm{don}}^i\rangle + \sum_{j}\langle\psi_{\mathrm{acc}}^j|z|\psi_{\mathrm{acc}}^j\rangle\Big] = \sum_{i}\mu_i + \sum_{j}\mu_j \tag{14}$$

with i and j as formerly defined. On the basis of the atomic orbitals, the overlaps S_{kl} are the only geometry-dependent quantities and thus:

$$\mathrm{d}\mu_i/\mathrm{d}r = \sum_{k,l}(\partial\mu_i/\partial S_{kl})(\mathrm{d}S_{kl}/\mathrm{d}r) \tag{15}$$

and similarly for $\mathrm{d}\mu_j/\mathrm{d}r$. On the basis of the symmetry-adapted orbitals the geometry-dependent quantities are:

$$S_{\mathrm{Mb}}^{kl} = \langle\chi_{\mathrm{M}}^k|\chi_{\mathrm{b}}^l\rangle; \qquad S_{\mathrm{Ma}}^{mn} = \langle\chi_{\mathrm{M}}^m|\chi_{\mathrm{a}}^n\rangle; \qquad E_{\mathrm{b}}^l \text{ and } E_{\mathrm{a}}^n$$

(where E_{b}^l and E_{a}^n are functions of S_{CC}^l and S_{CC}^n respectively) and 15 can be rewritten as:

$$\mathrm{d}\mu_i/\mathrm{d}r = \sum_{l}(\partial\mu_i/\partial E_{\mathrm{b}}^l)(\mathrm{d}E_{\mathrm{b}}^l/\mathrm{d}S_{\mathrm{CC}}^l)(\mathrm{d}S_{\mathrm{CC}}^l/\mathrm{d}r) + \sum_{k,l}(\partial\mu_i/\partial S_{\mathrm{Mb}}^{kl})(\mathrm{d}S_{\mathrm{Mb}}^{kl}/\mathrm{d}r) \tag{16}$$

and similarly for $\mathrm{d}\mu_j/\mathrm{d}r$. Eq. 16 states that the dipole moment change during the vibration arises from a change in the energy of the alkyne orbitals and a change in the metal—alkyne overlap. Approximate calculations with the use of Mulliken's expression [31] $\mu_i = C_{\mathrm{M}}^{i2} - C_{\mathrm{b}}^{i2}$ reveal that the second group of terms in eq. 16 is always about 10% of, and has the same sign as, the first group of terms. Under the assumption that the contributions of the alkyne π and π^* orbitals to the metal—alkyne interaction dominate over those of the σ and σ^* orbitals, one E-term remains in each representation and eq. 16 reduces to:

$$\mathrm{d}\mu_i/\mathrm{d}r \simeq (\partial\mu_i/\partial E^i_\mathrm{b})(\mathrm{d}E^i_\mathrm{b}/\mathrm{d}S^i_\mathrm{CC})(\mathrm{d}S^i_\mathrm{CC}/\mathrm{d}r) \tag{17}$$

and similarly for $\mathrm{d}\mu_j/\mathrm{d}r$. A slightly different but comparable expression is given in ref. 11. The result, expressed in eq. 17, is that the dominant contribution to the dipole moment change during the vibration originates from the change in energy of the alkyne orbitals caused by the change of the carbon—carbon distance. $\partial\mu_i/\partial E^i_\mathrm{b}$ and $\partial\mu_j/\partial E^j_\mathrm{a}$ are independent of the geometry. In the parametrized calculations, it turned out that they were reasonable proportional to $1 - C^{i^2}_\mathrm{b}$ and $C^{j^2}_\mathrm{a}$ with the same proportionality constant k:

$$\partial\mu_i/\partial E^i_\mathrm{b} \simeq \mathrm{k}(1 - C^{i^2}_\mathrm{b}) \qquad \partial\mu_j/\partial E^j_\mathrm{a} \simeq \mathrm{k}C^{j^2}_\mathrm{a} \tag{18}$$

From eqns. 5 and 6 it is calculated that:

$$\mathrm{d}E^i_\mathrm{b}/\mathrm{d}S^i_\mathrm{CC} = 4(K-1){N_\mathrm{b}}^4 = 4(K-1){N_\pi}^4 \, \mathrm{d}E^j_\mathrm{a}/\mathrm{d}S^j_\mathrm{CC} = 4(1-K){N_\mathrm{a}}^4 = 4(1-K){N_{\pi^*}}^4 \tag{19}$$

For all π and π^* orbitals $S^i_\mathrm{CC} = S^j_\mathrm{CC} = S_\mathrm{CC}$. Substitution of 18 and 19 in 17 leads, after summation over the four irreducible representations, to the simplified expression for $\mathrm{d}\mu/\mathrm{d}r$:

$$\mathrm{d}\mu/\mathrm{d}r \simeq 4\mathrm{k}(K-1){N_\pi}^4(\mathrm{d}S_\mathrm{CC}/\mathrm{d}r)[\sum_i (1 - C^{i^2}_\mathrm{b}) - (N_{\pi^*}/N_\pi)^4 \sum_j {C^{j}_\mathrm{a}}^2] \tag{20}$$

With the substitutions 9a and 9b and β as a proportionality constant, we get the expression:

$$\mathrm{d}\mu/\mathrm{d}r \simeq \beta[(\mathrm{don}) - (N_{\pi^*}/N_\pi)^4(\mathrm{acc})] \tag{21}$$

This expression shows that the ratio between the contributions of (don) and (acc) to $\mathrm{d}\mu/\mathrm{d}r$ is unaffected by the value of the Wolfsberg-Helmholz parameter K, although according to eq. 20 $\mathrm{d}\mu/\mathrm{d}r$ itself is strongly dependent on this parameter.

Eq. 21 emphasizes that the acceptor interactions have an about four times greater weight in the dipole moment change during the carbon—carbon stretching vibration than the donor interactions, and that this is determined by the differences in normalization constants.

A scale of donor and acceptor interactions

Eqs. 13 and 21 permit an evaluation of the measured frequencies and intensities in a relative scale of donor and acceptor interaction strengths. For the elimination of the proportionality constants α and β, we have arbitrarily chosen the donor and acceptor interaction strengths of $\mathrm{Pt(PPh_3)_2(HFB)}$ (the complex with the largest frequency difference and the largest intensity) to be equal, and to have the reference value 1. With the use of these reference values and of the value $(N_{\pi^*}/N_\pi)^2 = 2$, a relative scale of donor and acceptor interaction strengths is calculated from the measured values (Table 4). The results are presented graphically in Fig. 4. Because of the simplifications involved in the model and because

TABLE 4

CALCULATED RELATIVE DONOR AND ACCEPTOR INTERACTION STRENGTHS IN ALKYNE COMPLEXES

No.	Compound	(acc)	(don)
1	$Pt(PPh_3)_2(HFB)$	1 [a]	1 [a]
2	$Ni(PPh_3)_2(HFB)$	0.96	0.98
3	$Pt(CH_3)(HBpz)_3(HFB)$	0.84	0.87
4	$IrCl(PPh_3)_2(HFB)$	0.80	0.81
5	$RhCl(PPh_3)_2(HFB)$	0.72	0.78
6	$Pt(PPh_3)_2(TOL)$	0.75	1.08
7	$RhCl(PCy_3)_2(TOL)$	0.61	0.90
8	$IrCl(PPh_3)_2(TOL)$	0.59	0.89
9	$RhCl(PPh_3)_2(TOL)$	0.54	0.82
10	$[Pt(CH_3)(AsMe_3)_2(TOL)]^+$	0.14	0.54
11	$Pt(PPh_3)_2(HEX)$	0.64	1.24
12	$RhCl(PCy_3)_2(HEX)$	0.48	0.84
13	$[Pt(CH_3)(PMe_2Ph)_2(HEX)]^+$	0.15	0.59

[a] Taken as reference value.

of the necessarily arbitrary ratio of the reference value, these scales should be considered separately. The acceptor scale is rather insensitive to the chosen acceptor to donor ratio in the reference complex, because of the larger coefficients of (acc) than of (don) in eqs. 13 and 21; however, this is not so for the donor scale.

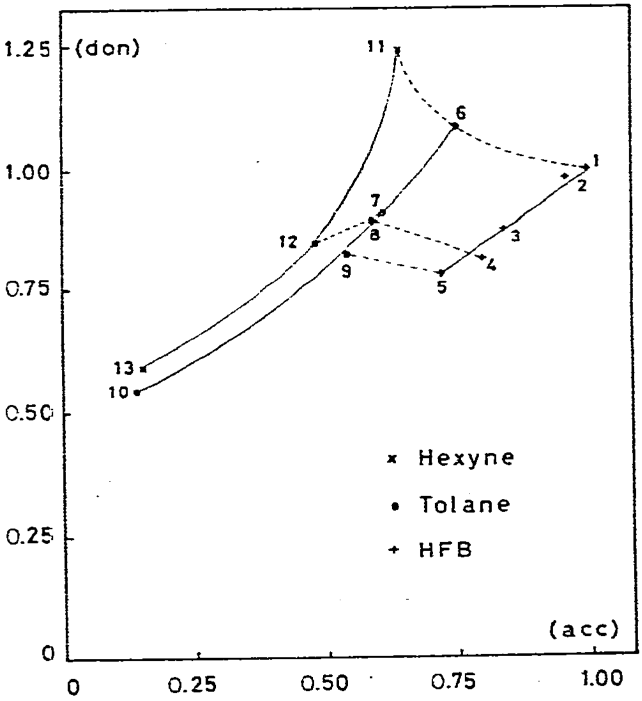

Fig. 4. (don) versus (acc) in metal—alkyne complexes. Numbering of the complexes as in Table 4.

The donor scale only allows comparison of complexes with the same alkyne ligand; for complexes with the same metal substrate but with different alkynes the donor scale only indicates trends.

Discussion

With respect to acceptor interactions, the complexes behave largely as expected, but with respect to donor interactions there are some unexpected trends. Electronegative substituents on the alkyne should increase its acceptor properties at the expense of its donor properties [12,32] and this is found to be so: the order of decreasing acceptor and increasing donor interaction strength for a given metal is: (dashed lines in Fig. 4):

hexafluorobutyne → tolane → hexyne

The metal centers show the expected order for backbonding, but not for bonding. Three-coordinated platinum(0) is the better and four-coordinated platinum(II) the poorer backbonding metal. In agreement with the increase of metal basicity going down a group [33], platinum(0) is a better backbonding metal than nickel(0), and iridium(I) than rhodium(I) when the same ligands are present. Also, rhodium(I) is a better backbonding metal with PCy$_3$ than with the less basic PPh$_3$ as a ligand. The position of five-coordinated platinum(II) on the scale confirms the aptness of trigonal bipyramidal d^8-complexes for backbonding towards ligands in the equatorial plane [34] and is a further justification of the division of metal olefin and acetylene complexes into class S (square planar + octahedral) and class T (trigonal + trigonal bipyramidal complexes) as given by Hartley [35]. Unexpectedly, for a given alkyne and varying metal center (full lines in Fig. 4), the donor interactions increase smoothly with the acceptor interactions and not at their expense. Schematically, the results can be presented as follows:

$d^8(4)$, M(II)	$d^8(4)$, M(I)	$d^8(5)$, M(II)	$d^{10}(3)$, M(0)
platinum(II)	rhodium(I)		
	iridium(I)	platinum(II)	nickel(0)
			platinum(0)

→ ↓ increasing acceptor and donor bonding

This related increase of donor and acceptor interactions, keeping the same alkyne and changing the metal, needs further comment. It is tempting to ascribe this to the synergic mechanism, which can be described as follows: the mere presence of a π-bond strengthens the σ-bond by shortening the bond distance, and because the π-bond is an acceptor bond, this effect is reinforced by an increased positive charge on the metal and an increased negative charge on the ligand, which makes the metal—ligand combination more apt for σ-bonding; a similar influence of the σ-bond on the π-bond is possible [36]. In our results, the donor interactions follow the acceptor interactions. Within the scope of the synergic mechanism, the results can be interpreted only if it is assumed that the influence of the π-bond on the σ-bond dominates over the influence of the σ-bond on the π-bond. The expected decrease in donor bonding going from hexyne to tolane to hexafluorobutyne should then be reduced but not wiped out by the increased acceptor bonding.

That changes in the acceptor bond dominate changes in the total metal—alkyne bond supports the results of our theoretical analysis that the acceptor bond has the greater influence in the frequency shift and the intensity of the carbon—carbon stretching vibration. In discussions of the metal—alkene and metal—alkyne bond of Group VIII metals, changes in the π-character of these bonds has often been assumed a dominant influence on the various bonding characteristics, and this is supported here by our results.

This does, however, not imply that the acceptor bond must be stronger than the donor bond. Although in Table 4 the acceptor-to-donor ratio depends on the chosen reference, this is not so for the four-coordinated platinum(II)-complexes, where the zero intensity of the C≡C stretching vibration gives directly from eq. 21 the ratio (acc) : (don) = 20 : 80. It is interesting to compare this with the results of some molecular orbital calculations on $[PtCl_3(C_2H_4)]^+$, a comparable square planar platinum(II)—alkene complex. In the calculations are given the metal—alkyne donor and acceptor overlap populations rather than the changes in alkyne orbital occupation, used by us and defined in eq. 9, but these quantities are readily comparable measures for the metal-h^2 ligand interaction. An early extended Hückel calculation [37] and a CNDO-type calculation [38] gave almost equal π and σ overlap populations, but a later extended Hückel calculation [39] and a recent SCF-Xα-SW calculation [40] gave a π to σ overlap population ratio of about 31 : 69 and 25 : 75 respectively. Our results agree qualitatively with the latter two calculations, and confirm that for four-coordinated platinum(II) π-backbonding is relatively weak.

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