Platinum-195 Nuclear Magnetic Resonance Study of Platinum(0) Complexes containing a Series of Acetylenes

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A platinum-195 n.m.r. investigation has been performed on the acetyleneplatinum(0) complexes $[Pt(RC{\equiv}CR')(PPh_3)_2]$ (R,R′ = Ph,Ph; Ph,Me; Ph,OCOMe; Ph,H; Et,Et; Me,OCOMe; Me,Me; H,H; OCOEt,OCOEt; OCOMe,OCOMe; CF_3,CF_3; Ph,CN; $OCOCH_2CF_3$,$OCOCH_2CF_3$; Me,CN; H,CN; or CN,CN), and the results interpreted semiquantitatively based on charge-iterative extended Hückel molecular-orbital calculations. The platinum–phosphorus nuclear-spin coupling constant (3 303—3 887 Hz) is considerably sensitive to the electron-withdrawing ability of the acetylene substituents. A good correlation between this coupling constant and the calculated value of the mutual polarizability as well as the σ-bond population indicates that the substituent effect is transmitted through the σ framework of the complex. The dependence of the platinum chemical shift on the nature of the acetylene ligand is dominated by the electronic excitation energy which is in turn related to the π* level of the acetylene.

NUCLEAR magnetic resonance spectroscopy has been successfully used to investigate the structural and bonding properties of transition-metal complexes,[1] valuable information being derived from nuclear-spin coupling constants, chemical shifts, and relaxation times.[2,3] In the elucidation of the co-ordination, nuclear-spin coupling constants between the metal and the ligand atoms which both possess a nuclear spin I of $\frac{1}{2}$ are especially useful, as exemplified by the sensitive variation of ^1J(MC) in the *trans*-influence series of metal alkyl complexes.[4,5] Quantum-chemical treatments of nuclear-spin coupling constants of metal complexes have also been developed, for which the Fermi-contact interaction (between the nuclear spins and the electron spins in the valence *s* orbitals) was suggested to be a dominant factor.[6]

We have recently given reasonable *trans*-influence series of ^1J(MC) for *trans*-$[Pt(C_2H_4)LCl_2]$ [7] (L = NMe_2H, NC_5H_5, NC_5H_4Me-4, ONC_5H_5, or ONC_5H_4Me-4) and $[Hg\{CH_2C(OMe)Me_2\}X]$ [8] (X = OCOMe, Cl, Br, SCN, I, or CN). It was shown that the ligand effect was readily interpreted in terms of the mutual polarizability, π(MC), between the valence *s* electrons of the metal and carbon atoms which was calculated by the charge-iterative extended-Hückel molecular-orbital (EHMO) method in a Pople–Santry formalism.[9] It was also shown that the ^1J(MC) value reflects the σ character of the co-ordination.[8]

As for the chemical shifts of metal nuclei, the ligand-field splitting was considered to be the most important factor for cobalt(III) complexes.[10,11] On the other hand, for platinum(II) complexes it was necessary to modify the transition energies with metal–ligand covalency.[12]

We present here a systematic n.m.r. study on a series of acetyleneplatinum(0) complexes, $[Pt(RC{\equiv}CR')(PPh_3)_2]$, since no examination has so far been made of the effect of the electronic properties of d^{10} transition-metal complexes on their n.m.r. parameters.

RESULTS AND DISCUSSION

Platinum-195 and ^{31}P n.m.r. parameters for 16 kinds of acetyleneplatinum(0) complexes, $[Pt(RC{\equiv}CR')(PPh_3)_2]$, are summarized in Table 1. It can be seen that complexes of acetylenes having electron-withdrawing substituents give larger Pt–P coupling constants, although a subtle difference was found between the influences of the cyano- and methoxycarbonyl groups on the ^{195}Pt chemical shift. Changes in the ^{31}P chemical shift were rather small and generally in the opposite direction to that of the ^{195}Pt chemical shift.

TABLE 1

Platinum-195 and ^{31}P n.m.r. parameters [a] of $[Pt(RC{\equiv}CR')(PPh_3)_2]$ in CH_2Cl_2 at 25 °C

RC≡CR′	δ(^{195}Pt) [b]	δ(^{31}P) [c]	^1J(PtP)	^2J(PP) [d]
PhC≡CPh	−208.4	27.1	3 452	
PhC≡CMe	−194.2	29.5	3 377	32.4
		28.2	3 454	
PhC≡COCOMe	−176.5	26.3	3 403	22.4
		24.5	3 741	
PhC≡CH	−156.5	31.0	3 464	33.4
		27.1	3 547	
EtC≡CEt	−156.0	30.4	3 425	
MeC≡COCOMe	−148.6	27.7	3 366	28.5
		27.5	3 803	
MeC≡CMe	−141.2	31.2	3 420	
HC≡CH	−124.8	29.1	3 626	
EtOCOC≡COCOEt	−122.4	24.5	3 722	
MeOCOC≡COCOMe	−119.7	23.8	3 722	
$F_3CC{\equiv}CCF_3$	−112.2	21.0	3 595	
PhC≡CCN	−107.2	25.1	3 336	16.7
		22.9	3 772	
$CF_3CH_2OCOC{\equiv}COCO$-CH_2CF_3	−92.5	23.8	3 726	
MeC≡CCN	−64.8	26.2	3 303	23.4
		25.8	3 864	
HC≡CCN	−40.3	26.5	3 434	22.3
		25.7	3 887	
NCC≡CCN	53.4	21.3	3 696	

[a] δ ±0.3 p.p.m., J ±1 Hz. [b] The standard frequency was taken as 21.4 MHz. Positive shifts are to high frequency. [c] To high frequency of external 85% H_3PO_4. [d] Sign is opposite to that of ^1J(PtP) according to a second-order analysis of both ^{31}P and ^{195}Pt n.m.r. spectra.

Platinum–Phosphorus Coupling Constant.—According to Pople and Santry,[9] the nuclear spin–spin coupling constant is given by equations (1) and (2), when the Fermi-contact interaction dominates the coupling mechanism. Here γ is the gyromagnetic ratio, β is the

$$J(AB) = (16\hbar\gamma_A\gamma_B\beta^2/9)[S_A(0)]^2[S_B(0)]^2\pi(AB) \quad (1)$$

$$\pi(AB) = 4\sum_{i}^{\text{occ.}}\sum_{j}^{\text{unocc.}}(\varepsilon_i - \varepsilon_j)^{-1}C_{is_A}C_{is_B}C_{js_A}C_{js_B} \quad (2)$$

Bohr magneton, $[S(0)]^2$ is the valence *s*-orbital electron density of the atom at the nucleus, and $\pi(AB)$ is the mutual polarizability of the valence *s* orbitals of atoms A and B; the ε's are orbital energies and *C*'s are orbital coefficients.

The dominant role of the *s*-character term in the Pt–P bond was pointed out for a series of platinum(II) complexes, $[Pt(PBu_3)_2X_2]$, where the variations in $[S_{Pt}(0)]^2$ and $[S_P(0)]^2$ are considered to be unimportant.[13,14] This view is examined here for the acetyleneplatinum(0) complexes within the framework of the Pople–Santry equations. As shown in Figure 1, a fairly linear relationship was obtained between the observed coupling constant and the calculated mutual polarizability for the Pt–P bond. The unimportance of the *s*-electron density term in equation (1) for the present series of complexes was confirmed by the linear relation between $\pi(PtP)$ and the product of the mutual polarizability and the populations for the platinum and phosphorus atomic *s* orbitals (Figure 2).

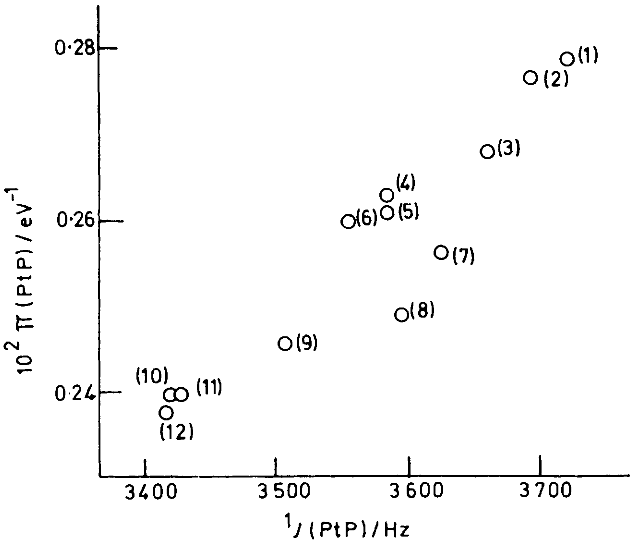

FIGURE 1 Correlation of the observed one-bond $^{195}Pt-^{31}P$ nuclear-spin coupling constant with calculated mutual polarizability for the valence *s* orbitals of platinum and phosphorus. Numbers in this and other figures correspond to complexes in Table 2

TABLE 2

Mutual polarizability, $\pi(PtP)$, of valence *s* orbitals, and platinum *s*-orbital overlap populations, in $[Pt(RC{\equiv}CR')(PPh_3)_2]$

Acetylene RC≡CR′	$10^2\,\pi(PtP)/eV^{-1}$	Overlap population Pt(*s*)–P(*s*)	Overlap population Pt(*s*)–P(p_σ)
(1) MeOCOC≡COCOMe	0.2783	0.0487	0.1784
(2) NCC≡CCN	0.2763	0.0487	0.1779
(3) HC≡CCN	0.2674	0.0474	0.1752
(4) MeC≡COCOMe	0.2628	0.0464	0.1740
(5) MeC≡CCN	0.2609	0.0464	0.1740
(6) PhC≡CCN	0.2596	0.0461	0.1729
(7) HC≡CH	0.2560	0.0459	0.1719
(8) $F_3CC{\equiv}CCF_3$	0.2482	0.0446	0.1702
(9) PhC≡CH	0.2455	0.0443	0.1691
(10) MeC≡CMe	0.2397	0.0435	0.1675
(11) EtC≡CEt	0.2396	0.0435	0.1680
(12) PhC≡CMe	0.2372	0.0432	0.1672

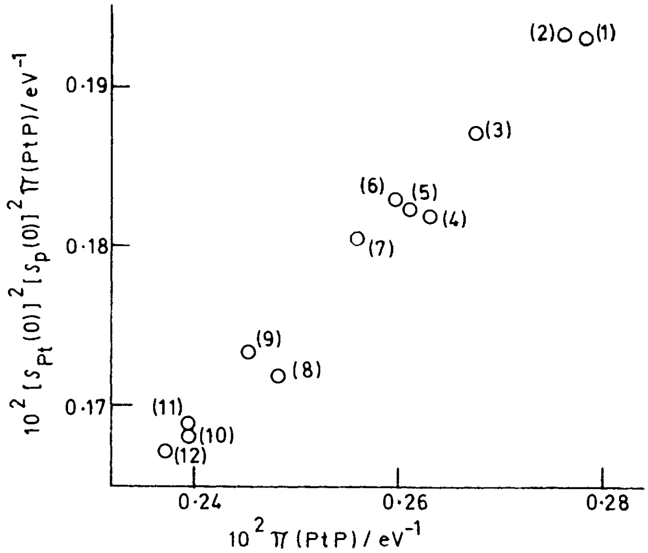

FIGURE 2 Plot of the products of mutual polarizability [$\pi(PtP)$] and atomic *s*-orbital populations {$[S(0)]^2$} of platinum and phosphorus against $\pi(PtP)$ for $[Pt(RC{\equiv}CR')(PPh_3)_2]$

In order further to examine the molecular parameter $\pi(PtP)$ in the context of the nature of the bonding, the values of $\pi(PtP)$ were compared with the overlap populations between *s* orbitals of Pt and P (Table 2). Evidently both the mutual polarizability and the overlap population between the valence *s* orbitals of these atoms are larger for acetylene complexes with electron-withdrawing groups. A similar relationship was observed for the overlap populations between the Pt(*s*)–P(*s*) and Pt(*s*)–P(p_σ) orbital pairs, which in turn leads to a linear relation between $\pi(PtP)$ and the Pt(*s*)–P(σ) overlap population (Figure 3). These relationships are interesting in the context of the suggestion by Mason and

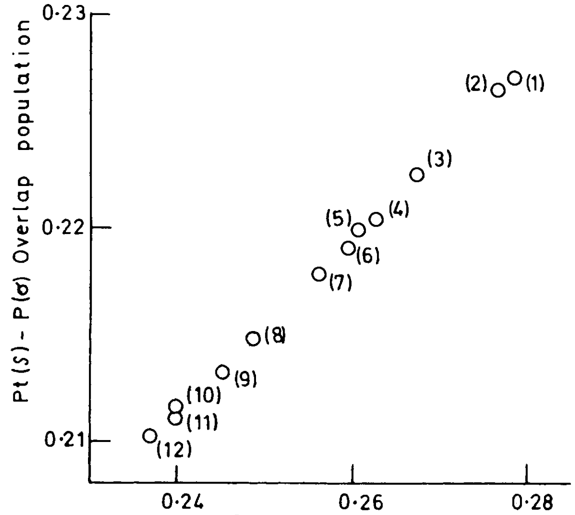

FIGURE 3 Plot of overlap population between platinum 6*s* and phosphorus σ orbitals against $\pi(PtP)$ for $[Pt(RC{\equiv}CR')(PPh_3)_2]$. The phosphorus σ orbital is composed of *s* and p_σ orbitals

Meek[15] that σ-electron effects are relatively important in co-ordination of a phosphine to a metal, particularly with reference to the Pt–P coupling constants.

A similar correlation of π(PtP) with the Pt–P total overlap population is shown in Figure 4, which was derived on the basis that the Pt 6*p* orbital contributes to the overlap population in the same manner as the Pt 6*s* orbital, and that the contribution of the Pt 5*d* orbital is comparatively small in each case. The σ contribution to the total overlap population amounted to 95—96%. Thus the σ-bond framework of the present complexes is important not only in transmitting the influence of the acetylene substituents to the platinum–phosphine bond but also in determining the strength of this co-ordination bond.

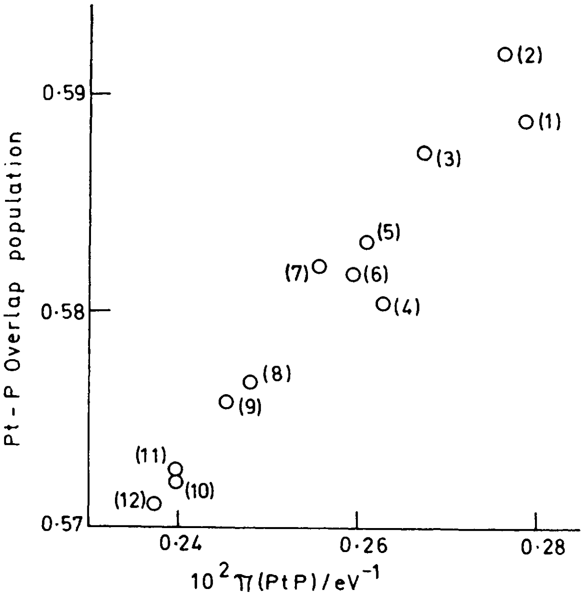

FIGURE 4 Plot of platinum–phosphorus overlap population against π(PtP) for [Pt(RC≡CR′)(PPh$_3$)$_2$]. Contributions from both σ and π bonding are included in the overlap population

With regard to the co-ordination between platinum and acetylenic carbon atoms, substantial information can be obtained from the variation in the atomic orbital populations (Table 3). The total atomic orbital populations of platinum and carbon as well as the C(*s*) atomic orbital populations were all smaller for the complexes of acetylene with electron-withdrawing groups. It should be noted that the mutual influence of acetylene and phosphine ligands was clearly exhibited in the reverse correlation between the two overlap populations for the Pt(*s*)–P(σ) and Pt(*s*)–C(σ) orbital pairs (Figure 5). Thus, in the σ framework of the present complexes the acetylene and phosphine ligands compete for stronger bonding to platinum when in mutually *trans* positions.[16]

TABLE 3

Mutual polarizability, π(PtP), of valence *s* orbitals, and atomic orbital populations of platinum and carbon atoms, in [Pt(RC≡CR′)(PPh$_3$)$_2$]

		Atomic orbital population			
acetylene, RC≡CR′	10^2 π(PtP)/ eV^{-1}	Pt (*s*)	Pt (total)	C (*s*)	C (total)
(1)	0.2783	0.493	10.153	1.185	4.058
(2)	0.2763	0.498	10.132	1.187	4.033
(3)	0.2674	0.497	10.180	1.215	4.144
(4)	0.2628	0.490	10.240	1.207	4.120
(5)	0.2609	0.496	10.215	1.209	4.105
(6)	0.2596	0.494	10.239	1.214	4.119
(7)	0.2560	0.500	10.220	1.241	4.288
(8)	0.2482	0.490	10.258	1.165	4.115
(9)	0.2455	0.499	10.285	1.240	4.265
(10)	0.2397	0.496	10.313	1.226	4.221
(11)	0.2396	0.496	10.330	1.230	4.222
(12)	0.2372	0.497	10.327	1.232	4.222

Platinum Chemical Shift.—It has been established that the magnetic shielding of metal nuclei is determined mainly by the paramagnetic term.[17] With regard to platinum(II) complexes of D_{4h} symmetry, the expression (3) has been given by Dean and Green,[18] where $\Delta E_A =$

$$\sigma_p = -(16/3)\beta^2 \langle r^{-3}\rangle C_{a_{1g}}{}^2(2C_{a_{2g}}{}^2\Delta E_A{}^{-1} + C_{e_g}{}^2\Delta E_E{}^{-1}) \quad (3)$$

$E(^1A_{2g}) - E(^1A_{1g})$, $\Delta E_E = E(^1E_g) - E(^1A_{1g})$, and $C_{a_{1g}}$, $C_{a_{2g}}$, and C_{e_g} are the platinum *d*-orbital coefficients of the molecular orbitals. Accordingly, the platinum chemical shift is affected by: (1) the asymmetry of the electronic distribution within the valence 5*d* orbital of the platinum atom; (2) the mean inverse cube of the distance between these electrons and the platinum nucleus; and (3) the inverse of the energy separations between the ground and excited states for these electrons.[19] An elegant interpretation was proposed[12] for the platinum(II) complexes, [PtLX$_3$]$^-$ (X = Cl, Br, or I; L = NMe$_3$, PMe$_3$, AsMe$_3$, SMe$_2$, *etc.*), where the reciprocal transition energy is modified by constants, characteristic of the respective ligands, which reflect the covalency of the metal–ligand bonds.

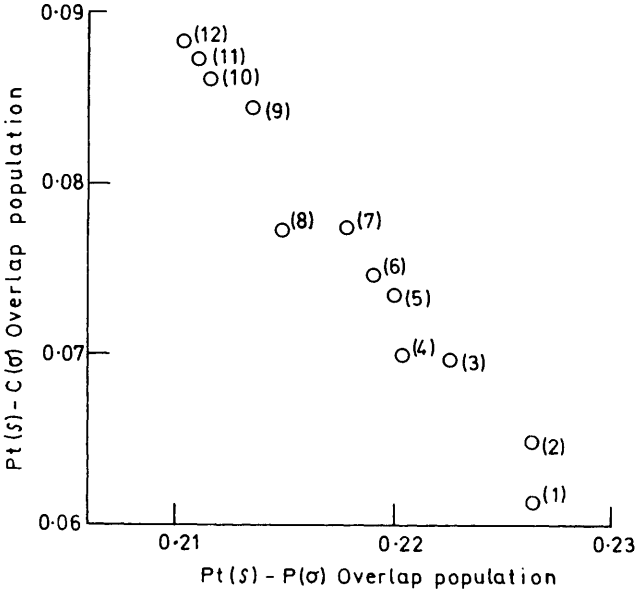

FIGURE 5 Correlation of Pt(*s*)–P(σ) overlap population with Pt(*s*)–C(σ) overlap population for [Pt(RC≡CR′)(PPh$_3$)$_2$]. The σ orbitals are composed of *s* and p_σ orbitals

With regard to zerovalent platinum (d^{10}) complexes, the paramagnetic contribution becomes significant only when the 5*d* shell is not completely filled. Such an electronic configuration was supported by molecular-orbital calculations on the present platinum(0) complexes.

In the case of [Pt(NCC≡CCN)(PPh_3)$_2$], the highest occupied molecular orbital (h.o.m.o.) (−9.90 eV) † was lower than the corresponding *d* orbital of the Pt(PH_3)$_2$ fragment (−9.30 eV) due to weak *d*–*p* mixing, accompanying an increase in the energy of the vacant *p* orbital (Figure 6). The *d*–*p* mixing also caused the Pt $d_{x^2-y^2}$ orbital coefficient of the h.o.m.o. to decrease from 0.996 in the fragment to 0.916 in the complex. The same behaviour was observed for all the other complexes, where the dominant atomic orbital in the h.o.m.o. was either Pt($d_{x^2-y^2}$) or Pt(d_{xz}). Since the coefficients of these *d* orbitals were calculated to be 0.90—0.95 for the present platinum(0) complexes, it is apparent that the h.o.m.o. has significant metal *d* character.

The lowest unoccupied molecular orbital (l.u.m.o.) (−8.17 eV), a δ-type antibonding molecular orbital of [Pt(NCC≡CCN)(PPh_3)$_2$], comprises the acetylene $\pi_\perp$* and the Pt(d_{yz}) orbitals, the latter giving the character of the *d*–*d* transition. The second lowest unoccupied m.o., comprised of both the acetylene $\pi_\parallel$* and the platinum d_{xy} orbitals, was relatively high in energy (−6.40 eV). These orbitals are shown schematically in Figure 7. Besides the two m.o.s mentioned above, there are some vacant orbitals of higher energy which possess metal *d* character through *d*–*p* mixing. However, the *d* coefficient is very small, and the corresponding Δ*E* value is quite large. For example, a vacant m.o. (−5.41 eV) is mainly composed of metal p_z with a small d_{xz} character (0.06). These features of the unoccupied orbitals were the same for all the other complexes.

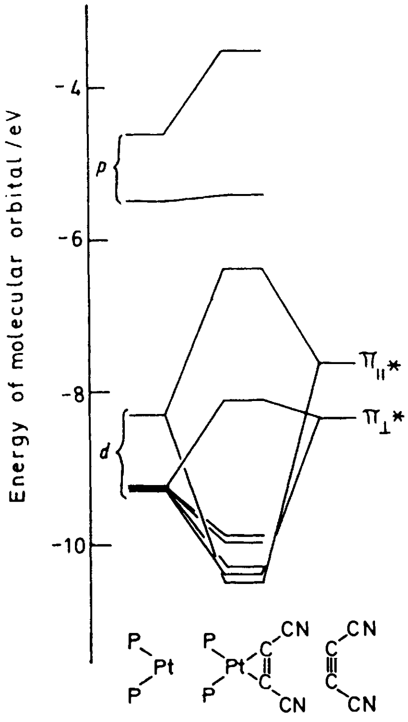

Figure 6 Orbital-interaction diagram for [Pt(NCC≡CCN)(PH_3)$_2$] built up from the orbitals of Pt(PH_3)$_2$ and *cis*-bent NCC≡CCN fragments

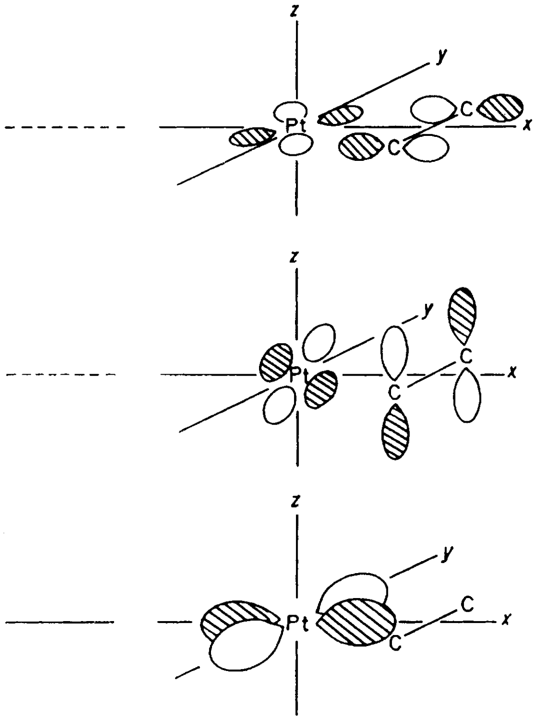

Figure 7 Schematic representation of the calculated h.o.m.o. (——) and l.u.m.o.s (– – –) of [Pt(NCC≡CCN)(PPh_3)$_2$]. The 5*d* atomic orbital coefficient of the h.o.m.o. was slightly less than unity. The lobe size of each atomic orbital is drawn in accordance with the magnitude of the calculated orbital coefficient

The contribution of the orbitals in the higher-energy region can be neglected. Hence the *d*–*d* component in the h.o.m.o.–l.u.m.o. excitation, which is magnetic-dipole allowed,[20] is expected to contribute significantly to the paramagnetic shielding.

Since the Pt *d* character is dominant in the h.o.m.o. and the acetylene $\pi_\perp$* character is considerably larger than the Pt(d_{yz}) character in the l.u.m.o., the corresponding electron transition is essentially a metal-to-ligand charge transfer (m.l.c.t.). It is therefore important to examine the correlation between the platinum chemical shift and the electronic absorption for the present complexes. Figure 8 shows the electronic absorption spectra of [Pt(NCC≡CCN)(PPh_3)$_2$] and [Pt(EtC≡CEt)(PPh_3)$_2$] in dichloromethane solutions. A weak band at 340 nm and a strong band in the high-energy region were observed for the former, whereas a strong peak with a shoulder in the high-energy region, but no low-energy band, was obtained for the latter. The band at 340 nm can be assigned to a platinum-to-acetylene c.t. as follows. (1) Its molar absorption coefficient (ε = 1 200 dm^3 mol^{-1} cm^{-1}) is appropriate for a m.l.c.t. transition.[21] (2) The absorp-

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† Throughout this paper: 1 eV ≈ 1.60 × 10^{-19} J.

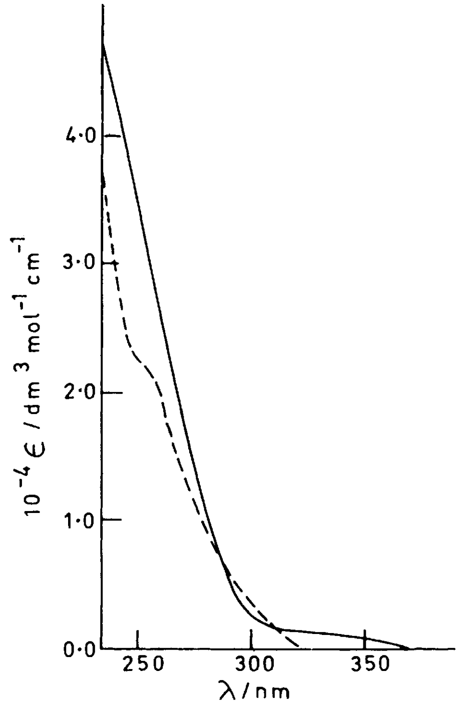

FIGURE 8 Electronic absorption spectra of [Pt(NCC≡CCN)-$(PPh_3)_2$] (——) (4.22 × 10^{-4} mol dm^{-3}) and [Pt(EtC≡CEt)-$(PPh_3)_2$] (– – –) (1.13 × 10^{-5} mol dm^{-3}) in CH_2Cl_2 at 25 °C

tion band was dependent on the polarity of the solvent (see below), as found for the m.l.c.t. band of [Pt(C_2H_4)-$(PPh_3)_2$].[22] (3) The appearance of the low-energy region around 340 nm was dependent on the nature of the acetylene ligand; no absorption was noticeable for the complexes with acetylenes such as MeOCOC≡COCOMe, $F_3CC{\equiv}CCF_3$, EtC≡CEt, and HC≡CH, and a rather large low-energy tail on the strong absorption band appeared for the complexes with HC≡CCN and MeC≡CCN. The strong high-energy absorption, commonly observed for these complexes, is assigned to either an m.l.c.t. band from platinum to the PPh_3 ligand[23] or a π–π* transition localized on the benzene ring of the PPh_3 ligand.[22]

The π* levels of NCC≡CCN, HC≡CCN, and HC≡CH were evaluated as −7.47, −6.83, and −6.27 eV, respectively, based on photoelectron[24] and electronic absorption[25] spectra. Thus the acetylene–cyanide conjugation is evidently sufficient to lower the acetylene π* level. We consider that this feature is the reason why the c.t. band of [Pt(NCC≡CCN)$(PPh_3)_2$] was observed only as a low-energy peak. With regard to MeOCOC≡COCOMe, the π* level is estimated to be higher than −6.54 eV on the basis of photoelectron spectroscopic data[26] and the fact that no electronic absorption is exhibited in the low-energy region (< 250 nm; measured in n-hexane). The electron-withdrawing ability of the cyano- and methoxycarbonyl groups is thus different.

The dependence of the peak position on the solvent polarity was examined for the c.t. band of [Pt(NCC≡CCN)$(PPh_3)_2$] in the mixed solvents CCl_4–CH_2Cl_2 and MeOH–CH_2Cl_2. As expected,[22] the more polar the solvent the lower is the energy of the peak maximum (Table 4). Platinum-195 n.m.r. spectra were recorded for the same solutions. It is seen from Table 4 that the more polar the solvent the more downfield is the ^{195}Pt resonance. Figure 9 shows the relation between the platinum chemical shift and the reciprocal of the electronic transition energy. The observed linearity indicates the importance of the h.o.m.o.–l.u.m.o. separation.

The calculated values of this separation for the present complexes were compared with the position of the m.l.c.t. band and the platinum chemical shift. The above three-group classification of the acetylene ligands with reference to the position of the m.l.c.t. band was well reproduced; the energy separation was large for [Pt-

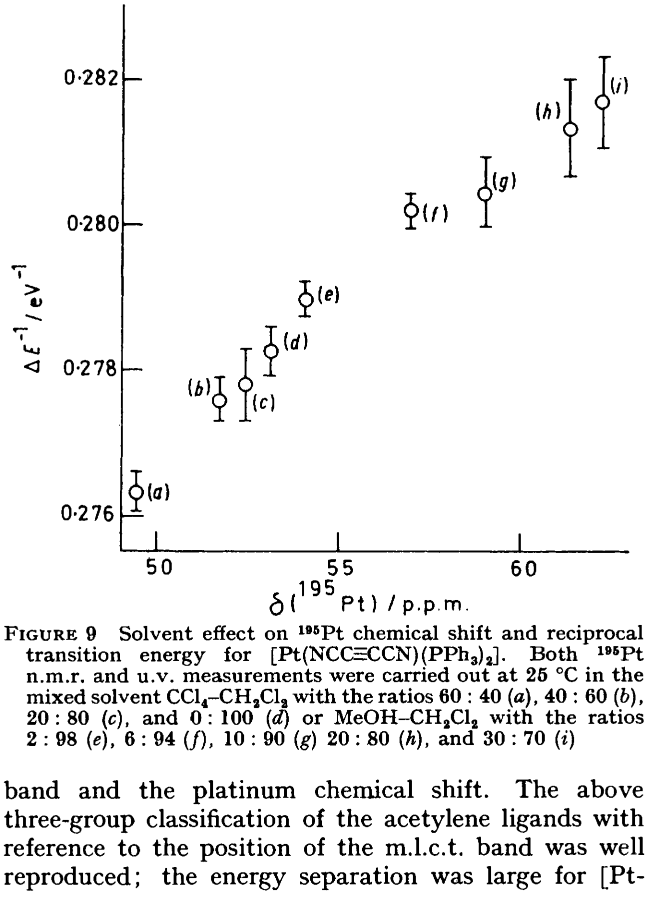

FIGURE 9 Solvent effect on ^{195}Pt chemical shift and reciprocal transition energy for [Pt(NCC≡CCN)$(PPh_3)_2$]. Both ^{195}Pt n.m.r. and u.v. measurements were carried out at 25 °C in the mixed solvent CCl_4–CH_2Cl_2 with the ratios 60 : 40 (*a*), 40 : 60 (*b*), 20 : 80 (*c*), and 0 : 100 (*d*) or MeOH–CH_2Cl_2 with the ratios 2 : 98 (*e*), 6 : 94 (*f*), 10 : 90 (*g*) 20 : 80 (*h*), and 30 : 70 (*i*)

TABLE 4

Solvent effect on the *d*(Pt)–π*(NCC≡CCN) transition band and the platinum chemical shift of [Pt(NCC≡CCN)$(PPh_3)_2$]

Ratio of solvents	CCl_4 : CH_2Cl_2				MeOH : CH_2Cl_2				
	60 : 40	40 : 60	20 : 80	0 : 100	2 : 98	6 : 94	10 : 90	20 : 80	30 : 70
λ_{max}/nm [a]	342.4	344.4	344.8	344.9	345.8	347.2	347.8	349.3	349.5
δ(^{195}Pt) [b]	49.4	51.7	52.4	53.1	54.0	56.9	59.0	61.3	62.2

[a] The error limits are shown as bars in Figure 9. Concentration: 8.55 × 10^{-4} mol dm^{-3} at 25 °C. [b] ±0.2 p.p.m., 0.1 mol dm^{-3} at 25 °C.

(MeOCOC≡COCOMe)$(PPh_3)_2$] or [Pt(MeC≡CMe)$(PPh_3)_2$], medium for [Pt(MeC≡CCN)$(PPh_3)_2$], and small for [Pt(NCC≡CCN)$(PPh_3)_2$]. The importance of the electronic excitation energy in determining the chemical shift was further supported by a correlation observed between the platinum chemical shift and the reciprocal of the h.o.m.o.–l.u.m.o. energy difference (Figure 10).

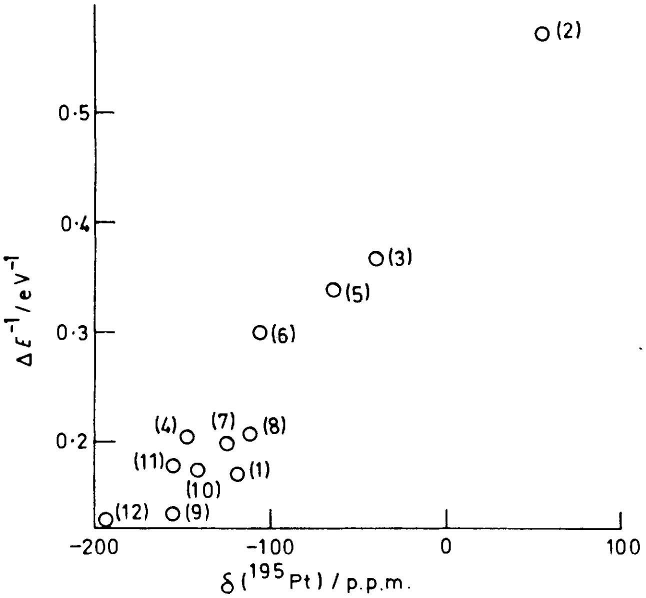

FIGURE 10 Correlation of ^{195}Pt chemical shift with reciprocal h.o.m.o.–l.u.m.o. energy separation for [Pt(RC≡CR′)$(PPh_3)_2$]

The electron-density term $\langle r^{-3}\rangle$ may contribute to the magnetic shielding of the platinum nucleus. The total atomic orbital populations of the platinum and the acetylenic carbon atoms in the complexes with cyano- and methoxycarbonyl groups were indeed small (Table 3), but marked low-field shifts were only noticed for the former. The role of the electron-density term is thus unimportant compared to the energy-separation term, as far as the platinum chemical shifts of the present complexes are concerned.

It is now evident that in these complexes the electronic properties affect the n.m.r. parameters in different ways: the Pt–P coupling constant is sensitive to the electron distribution in the σ-bond framework of the complex, whereas the platinum chemical shift is predominantly influenced by the position of the acetylene π* level. In addition, the subtle differences between the electron-withdrawing groups seems to have been disclosed: the cyano-group influences both the σ framework of the complex and the π*-orbital energy of the ligand, whereas the methoxycarbonyl group affects the σ-electron distribution only.

EXPERIMENTAL

The acetyleneplatinum(0) complexes, [Pt(RC≡CR′)$(PPh_3)_2$] (R,R′ = Ph,Ph; Ph,Me; Ph,OCOMe; Ph,H; Et,Et; Me,OCOMe; Me,Me; H,H; OCOEt,OCOEt; OCOMe,OCOMe; CF_3,CF_3; Ph,CN; $OCOCH_2CF_3$,$OCOCH_2CF_3$; Me,CN; H,CN; or CN,CN), were prepared from *cis*-dichlorobis(phosphine)platinum(II) [27] or tetrakis(phosphine)platinum(0) [27,28] according to the established methods, and identified by m.p., i.r., and ^1H n.m.r. spectroscopy, and elemental analysis. The ^{195}Pt and ^{31}P n.m.r. spectra were recorded on JEOL FX-100 (21.28 MHz) and FX-60 (24.20 MHz) spectrometers, with *trans*-[Pt$(SMe_2)_2Cl_2$] (0.3 mol dm^{-3} $CDCl_3$ solution) [17] and triphenylphosphine (15% $CDCl_3$ solution) respectively as external references. The ^{195}Pt chemical shifts are reported by use of the standard frequency of 21.4 MHz,[17] and the ^{31}P chemical shifts are given relative to 85% H_3PO_4 using the conversion $\delta(PPh_3) = \delta(H_3PO_4) + 4.64$ p.p.m. (high frequencies being taken as positive). The n.m.r. measurements were made in dichloromethane solution (0.2—0.3 mol dm^{-3}) except otherwise noted.

The electronic absorption spectra were recorded on a Shimazu UV-365 spectrophotometer. When the solvent effects on the low-energy band and ^{195}Pt chemical shifts were examined, the NCC≡CCN complex was dissolved in the mixed solvents to give precise concentrations of 8.55×10^{-4} and 1.00×10^{-1} mol dm^{-3}, respectively. For shoulders, the peak maximum was determined from the point of inflection in the first-order differentiation of the spectrum by using a built-in data processor.

Calculations.—Orbital coefficients and energies of one-electron wavefunctions were calculated according to the extended-Hückel molecular-orbital method,[29] including a charge-iteration procedure at a sensitivity of 2 eV per charge.[30] Slater-type functions were used as the valence atomic orbitals and their ionization potentials were allotted to the diagonal H terms. As for off-diagonal H terms, the Wolfsberg–Helmholz approximation ($K = 1.75$) was adopted. The Slater exponents used were those proposed for platinum by Cotton and Harris [31] and for other atoms by Burns.[32]

The bond distances and angles in the Pt(RC≡CR′)P_2 moiety were taken from the X-ray analysis of [Pt(PhC≡CPh)$(PPh_3)_2$].[33] Although the line joining the two co-ordinated carbon atoms is slightly inclined (14°) to the plane composed of the Pt and the two P atoms, a simplification was made for the purpose of higher local symmetry so that five atoms of this moiety were placed on a plane.[34] Since structural data are lacking for most of the complexes, we adopted this geometry for all the complexes investigated. The molecular parameters of [Pt(F_3CC≡CCF_3)$(PPh_3)_2$], calculated from its own geometry,[35] were scarcely different from those of the simplified Pt(RC≡CR′)P_2 geometry; *e.g.* the deviation of the mutual polarizabilities was only 2%. Even for the complexes with unsymmetrical acetylenes, the averaged values for the two co-ordinated atoms in this geometry were almost the same as those in the actual geometry,[36] as confirmed for [Pt(PhC≡CMe)$(PPh_3)_2$].

The geometry of the acetylene substituent was taken either from the analogous complexes of [Pt(RC≡CR′)$(PPh_3)_2$] (R,R′ = Ph,Me; [36] Ph,Ph; [33] or CF_3,CF_3 [35]) and [Pd(RC≡CR′)$(PPh_3)_2$] (R = R′ = OCOMe [37]) or from the free molecule (R = R′ = H, Et, or CN). For the sake of simplicity in calculation, PPh_3 was replaced by PH_3.

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