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Molecular Orbital Studies of $^{195}Pt-^{31}P$ and $^{195}Pt-^{195}Pt$ Coupling Constants in Mononuclear and Dinuclear (Phosphine)platinum Complexes

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Nuclear spin–spin coupling constants in tris(phosphine)platinum(II) and acetylene-bridged dinuclear platinum(I) complexes have been studied in the framework of the Pople–Santry theory. The signs and the relative magnitudes of the coupling constants were satisfactorily reproduced in terms of the mutual polarizabilities of valence s orbitals. The importance of the orientation of the bridging acetylene was demonstrated for dinuclear platinum complexes. A limited number of key molecular orbitals have been pointed out for both kinds of platinum complexes, and their roles in the nuclear spin–spin coupling and the coordination bonding are discussed.

Introduction

Nuclear spin–spin coupling constants in organometallic compounds have provided valuable information not only on the coordination structures in solution but also on the metal–ligand bonding properties[1] and are usually dominated by the Fermi contact term.[2] The variations in $^1J(PtP)$ among a series of (phosphine)platinum(II) complexes were once explained qualitatively in terms of the s character of the platinum atom,[3] which is based on the mean excitation energy approximation.[4] Utilizing the extended Hückel molecular orbital (EHMO) method, Henneike showed[5] that the Pople–Santry formalism[6] is useful to elucidate the sign and magnitude of $^2J(HgH)$ of methylmercury compounds. It was demonstrated in the same formalism that the term of the mutual polarizability of valence s orbitals is most sensitive for the coupling constants of the (2-methoxyalkyl)mercury(II) compound[7] [$MeCH(OMe)CH_2HgCl$] and (ethylene)- or carbonylplatinum(II) complexes.[8] The importance of the mutual polarizability term has also been verified for the platinum–phosphorus coupling constants in (acetylene)bis(phosphine)platinum(0) complexes[9] and the phosphorus–phosphorus coupling constants in the transition-metal tris(phosphine) complexes.[10]

We have attempted here to elucidate the signs and the relative magnitudes of the platinum–phosphorus and platinum–platinum coupling constants of some tris(phosphine)platinum(II) and dinuclear platinum(I) complexes, one of which was synthesized by us recently.[11] Attempts were also made to obtain a view for trans-influence phenomena in both the nuclear spin–spin coupling and the coordination bonding by selecting some key molecular orbitals in proper model compounds.

Experimental Section

The dinuclear platinum(I) complex [$Pt_2(CO)_2(PPh_3)_2(CH_3OOCC{\equiv}CCOOCH_3)$] was prepared as described previously.[11] An analogous complex, [$Pt_2(CO)_2(PPh_3)_2(EtOOCC{\equiv}CCOOEt)$], was also prepared in the same way. Nuclear magnetic resonance spectra were measured in a dichloromethane solution (0.11 M) with use of 85% phosphoric acid and *trans*-[$PtCl_2(SMe_2)_2$] as external references for phosphorus and platinum resonances, respectively. The ^{31}P chemical shifts are given in ppm relative to the reference, where a positive sign indicates a shift to lower field. The ^{195}Pt chemical shifts are reported with use of the standard frequency of 21.4 MHz.[12] The ^{31}P and ^{195}Pt NMR spectra were recorded on JEOL FX-60 (24.20 MHz) and FX-100 (21.40 MHz) spectrometers, respectively.

Calculations

One-electron wave functions and energies were calculated according to the extended Hückel molecular orbital method, with the inclusion of a charge iterative procedure at the sensitivity of 2 eV/charge for all atoms.[13] The Slater-type functions were used as the valence atomic orbitals, and their ionization potentials were allotted to the diagonal H terms. The off-diagonal elements (resonance integrals) were evaluated by the Wolfsberg–Helmholz expression ($K = 1.75$).[14] The Slater exponents used were those proposed for platinum by Cotton and Harris[15] and for other atoms by Burns.[16]

The nuclear spin–spin coupling constant is given by eq 1–3 in Pople

$$K(AB) = (64\pi^2\beta^2/9)[S_A(0)]^2[S_B(0)]^2\pi(AB) \qquad (1)$$

$$K(AB) = 4\pi^2 J(AB)/h\gamma_A\gamma_B \qquad (2)$$

$$\pi(AB) = -4\sum_i^{\text{occ}}\sum_j^{\text{unocc}}(\epsilon_j - \epsilon_i)^{-1}C_{iS_A}C_{iS_B}C_{jS_A}C_{jS_B} \qquad (3)$$

and Santry's approximation.[6] $K(AB)$ is the reduced coupling constant, which is independent of the magnetogyric ratio γ, $[S_A(0)]^2$ is the s-electron density of the atom A at the nucleus, and $\pi(AB)$ is the mutual polarizability of the valence s orbitals of the atoms A and B. In eq 3, ϵ and C are the MO energy and the coefficient, respectively. Equation 1 indicates that the sign of $K(AB)$ is determined by $\pi(AB)$.

EHMO calculations were carried out for the model complexes [$PtH(PH_3)_3$]$^+$, [$PtCH_3(PH_3)_3$]$^+$, [$Pt_2(PH_3)_4(HC{\equiv}CH)$], and [$Pt_2(CO)_2(PH_3)_2(HC{\equiv}CH)$]. The bond distances and angles in the tris(phosphine) complexes were taken from the X-ray analyses of [$PtH(PPh_3)_3$]$(CF_3CO_2)_2H$[17] and [$PtCH_3(PMe_2C_6F_5)_3$](PF_6),[18] respectively. The Pt–H distance in the hydride complex was set as 1.6 Å, which was the sum of the covalent radii of the Pt and H. In [$Pt_2(PH_3)_4(HC{\equiv}CH)$], the geometry of [$Pt_2\{\mu\text{-}(\eta^2\text{-}PhC{\equiv}CPh)\}(\eta^2\text{-}PhC{\equiv}CPh)(PPh_3)_2$][19] was consulted for the Pt–Pt (2.905 Å) and Pt–P (2.267 Å) distances and for the angles of the P_2PtC moiety. The PH_3 ligands were placed symmetrically to the $Pt_2(HC{\equiv}CH)$ fragment. The structure of [$Pt_2(CO)_2(PH_3)_2(HC{\equiv}CH)$] was chosen so as to agree with that of [$Pt_2(CO)_2(PPh_3)_2(CH_3OOCC{\equiv}CCOOCH_3)$][11] in the corresponding parts. In the study

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Table I. Platinum-Phosphorus Coupling Constants (J(PtP)), Mutual Polarizabilities between Platinum and Phosphorus Valence s Orbitals (π(PtP)), and Valence s-Electron Densities of Phosphorus Atoms (ρ(P(s))) in Tris(phosphine)platinum(II) Complexes $[PtX(PR_3)_3]^+$

X		J(PtP), Hz	π(PtP), 10^{-3} eV^{-1}	ρ(P(s))
CH_3	$P^{c\ f}$	2822^a	1.92^c	1.406^c
	$P^{t\ g}$	1865^a	1.30^c	1.403^c
	$P^{c\ f}$	$(1.51)^e$	(1.48)	(1.00)
H	$P^{t\ g}$	2515^b	2.08^d	1.402^d
		2037^b	1.66^d	1.399^d
		(1.24)	(1.25)	(1.00)

[a] $[PtCH_3(PMe_2C_6F_5)_3](PF_6)$. [b] $[PtH(PEt_3)_3](PF_6)$. [c] $[PtCH_3(PH_3)_3]^+$. [d] $[PtH(PH_3)_3]^+$. [e] Values in parentheses are ratios of the two preceding values. [f] Phosphorus cis to X. [g] Phosphorus trans to X.

Table II. Signs of Coupling Constants and s-Orbital Mutual Polarizabilities for $[PtH(PH_3)_3]^+$

coupled nuclei	sign	π, 10^{-3} eV^{-1}	coupled nuclei	sign	π, 10^{-3} eV^{-1}
Pt-P^c	+	+2.08	P^c-H	−	−0.95
Pt-P^t	+	+1.66	P^t-H	+	+2.39
P^c-P^c	$+^a$	+0.64	Pt-H	+	+4.03
P^t-P^c	−	−0.25			

[a] Expected from analogous complexes.

for the effect of the coordinating mode of acetylene, HC≡CH was rotated so as to be perpendicular to the plane defined by the Pt, P, and C atoms.

Results and Discussion

The Mononuclear Tris(phosphine)platinum(II) Complex. Role of the Mutual Polarizability Term in the Platinum–Phosphorus Coupling Constant. The tris(tertiary phosphine)platinum(II) complexes $[PtX(PR_3)_3]^+$ are interesting, because they possess two kinds of chemically nonequivalent phosphorus atoms in a single molecule and show two different platinum–phosphorus coupling constants.[20] It was reported for $[PtCH_3(PMe_2C_6F_5)_3](PF_6)$ that the coupling constant for the phosphorus atoms cis to the methyl group, $^1J(PtP^c)$, is 1.5 times larger than for the phosphorus atom trans to the methyl group, $^1J(PtP^t)$.[18] In the case of the hydride complex $[PtH(PEt_3)_3](PF_6)$, $^1J(PtP^c)$ is 1.2 times larger than $^1J(PtP^t)$.[21] With regard to the Fermi contact terms corresponding to the two phosphorus atoms, the following features were noticed:[22] (i) the value of $[S_{Pt}(0)]^2$ is common to both of them, and (ii) the values of $[S_P(0)]^2$ would not differ so much, since the two phosphorus atoms are attached to the same platinum atom. We expected, therefore, that the observed difference of ^1J(PtP) would not be ascribed to the valence s-electron density term, ρ(P(s)) (calculated by Mulliken population analysis), but to the mutual polarizability term, π(PtP).

In order to verify this view, the values of ^1J(PtP) were compared to those of π(PtP) and ρ(P(s)) for both the methyl and hydride complexes (Table I). It is remarkable that the valence s-electron densities are little different and that the ratios of $\pi(PtP^c)/\pi(PtP^t)$ are close to those of $^1J(PtP^c)/^1J(PtP^t)$ within a few percent for both complexes.

The signs of the coupling constants of the hydride complex were reported previously[21] except $^2J(P^cP^c)$, for which a positive sign is expected from the analogous complexes $[PtCl(PMe_3)_3](BF_4)$ (+414 Hz) or $[PtBr(PMe_3)_3](NO_3)$ (+415 Hz).[23] The calculated mutual polarizability terms have reproduced all the signs of these coupling constants, ensuring the adequacy of the present approach (Table II).

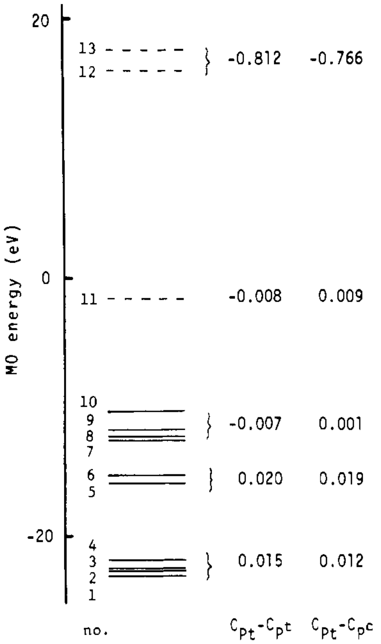

Figure 1. Product of valence s-orbital coefficients in significant occupied and unoccupied MO's of $[PtCH_3(PH_3)_3]^+$.

Table III. Term of the s-Coefficient Double Product over Energy Separation, $C_{iPt}C_{iP}C_{jPt}C_{jP}/(\epsilon_j - \epsilon_i)$ (10^{-4} eV^{-1}), for Various Types of Transitions

	occ → unocc(ψ_{11})		occ → unocc(ψ_{12} + ψ_{13})	
occ MO	Pt-P^t	Pt-P^c	Pt-P^t	Pt-P^c
ψ_1-ψ_4	−0.06	−0.05	−2.15	−1.62
ψ_5-ψ_6	−0.12	−0.12	−3.29	−2.94
ψ_7-ψ_{10}	+0.06	−0.01	+1.25	−0.17
total	−0.12	−0.18	−4.19	−4.73

Characterization of Constituent Molecular Orbitals. For the elucidation of the difference between $\pi(PtP^c)$ and $\pi(PtP^t)$ of $[PtCH_3(PH_3)_3]^+$ in detail, the characteristics of the constituent molecular orbitals are analyzed.

In Figure 1, the energy levels and the s-coefficient products are given for all the molecular orbitals with nonzero s coefficients on both the platinum and phosphorus atoms. From the examination of the orbital coefficients, the occupied molecular orbitals are classified into the following three groups: (i) ψ_1–ψ_4 (mainly contributed from the phosphorus s orbitals, accompanying a small contribution of the platinum s orbital), (ii) ψ_5–ψ_6 (contributed from both the platinum s orbital and the phosphorus s and p orbitals), and (iii) ψ_7–ψ_{10} (contributed from various σ-type orbitals, which are schematically shown in Figure 2).

The product $C_{iPt}C_{iP}C_{jPt}C_{jP}/(\epsilon_j - \epsilon_i)$, which constitutes the mutual polarizability term (eq 3), is shown for various kinds of transitions in Table III. Although the unoccupied ψ_{11} molecular orbital gives the smallest transition energy among the unoccupied molecular orbitals, the product terms due to ψ_{11} exert little influence. Because ψ_{11} consists of the platinum d_σ and phosphorus p_σ orbitals in an antibonding mode, their s-orbital coefficients are small. It is apparent that the transitions from the occupied ψ_1–ψ_6 molecular orbitals to the unoccupied ψ_{12} and ψ_{13} molecular orbitals contribute signif-

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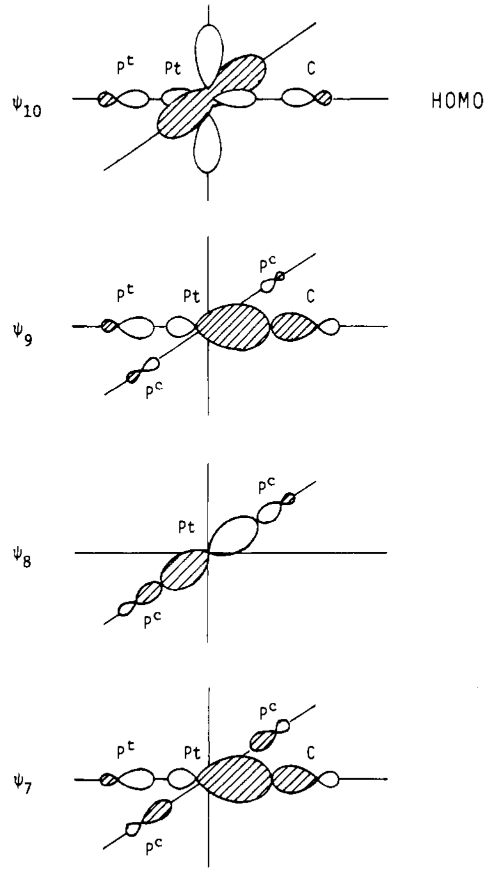


Figure 2. Schematic representation of the HOMO and occupied MO's with the high energy level for $[PtCH_3(PH_3)_3]^+$.

icantly to both $\pi(PtP^c)$ and $\pi(PtP^t)$. Both the ψ_{12} and ψ_{13} molecular orbitals are antibonding σ orbitals and have large s-orbital coefficients on both the platinum and phosphorus atoms. Thus, the positive signs of $^1J(PtP)$ were derived from the contribution of these large negative double s-coefficient products, $C_{i\mathrm{Pt}}C_{i\mathrm{P}}C_{j\mathrm{Pt}}C_{j\mathrm{P}}$ ($i = 1$–6, $j = 12$ and 13). On the other hand, the difference between $\pi(PtP^c)$ and $\pi(PtP^t)$ is ascribed to the transition from the occupied ψ_7–ψ_{10} orbitals to the unoccupied ψ_{12} and ψ_{13} orbitals; it is evident that the $\pi(PtP)$ value for the Pt–P^t pair is reduced in magnitude considerably by the largest positive contribution of +1.25, whereas the absolute value for the Pt–P^c pair is rather increased by the negative contribution (−0.17).

The importance of the ψ_7 and ψ_9 molecular orbitals is to be noted in clarifying the distinctions between P^c and P^t. In the first place, the difference in sign between the product terms (+1.25 vs. −0.17) was derived principally from them. It is reasonable because the s_{Pt}–s_{P^c} overlaps in these orbitals are in phase, whereas the s_{Pt}–s_{P^t} overlaps are out of phase (cf. Figure 2). Secondly, the difference in the trans influence between the methyl and phosphine ligands to the trans phosphorus atoms becomes interpretative, since the strong s–s interaction of the Pt–C pair is transmitted mainly through these orbitals to the Pt–P^t pair. The unique and significant negative contribution of the ψ_7–ψ_{10} orbitals to the Pt(s)–P^t(s) orbital bond population, shown in Table IV, is actually made up from the ψ_7 and ψ_9 orbitals.

The s_{Pt}–s_{P^c} bond population (32.60×10^{-3}) being larger than that of s_{Pt}–s_{P^t} (22.16×10^{-3}) was in parallel with the large σ_{Pt}–σ_{P^c} bond population (0.526) compared to that of σ_{Pt}–σ_{P^t} (0.507). Therefore, the higher trans influence of the methyl ligand than of the phosphine ligand,[24] reflected in the platinum–phosphorus coupling constants, is well accounted for on the ground of the high σ-donating ability of the methyl group.[25] The parallelism between the metal–ligand coupling constant and the σ-bond strength, pointed out by Shustrovich[26] with his perturbation approach, is thus able to be described by the key molecular orbitals, i.e., the ψ_7 and ψ_9 orbitals, which transmit the trans influence via an sp hybrid orbital of the platinum atom.

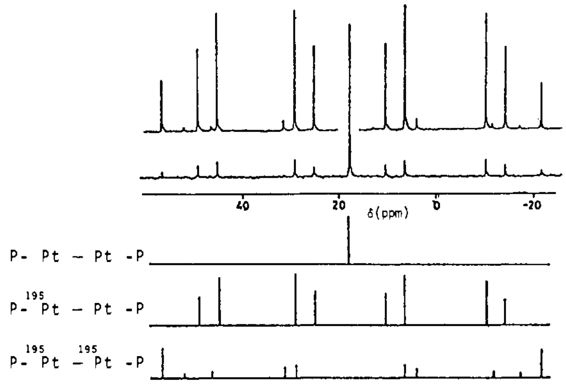
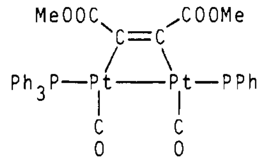


Figure 3. $^{31}P\{^1H\}$ NMR spectrum of $[Pt_2(CO)_2(PPh_3)_2(CH_3OOCC{\equiv}CCOOCH_3)]$ and its analyses based on the superposition of three kinds of spin systems.

Table IV. Items of Pt(s)–P(s) Orbital Bond Population for $[PtCH_3(PH_3)_3]^+$

occ MO	10^3Pt–P^t	10^3Pt–P^c
ψ_1–ψ_4	10.96	12.67
ψ_5–ψ_6	18.87	19.32
ψ_7–ψ_{10}	−7.67	0.61
total	22.16	32.60

The Dinuclear Platinum(I) Complex. Spectrum Analysis and Determination of Nuclear Spin–Spin Coupling Constants. The covalently bonded dinuclear platinum(I) complex $[Pt_2(CO)_2(PPh_3)_2(CH_3OOCC{\equiv}CCOOCH_3)]$ (**1**), synthesized recently,[11] has the collinear carbon–carbon bond of the acetylene ligand to the Pt–Pt axis. Not only these carbon and platinum atoms but also the other coordinating atoms are placed on the same plane.



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Figures 3 and 4 show the ^{31}P and ^{195}Pt NMR spectra of **1**, respectively. Since the ^{195}Pt nuclei exhibit magnetic nonequivalence in relation to the phosphorus nucleus, these spectra are to be analyzed in the second order. Because of the limited natural abundance of ^{195}Pt (33.8%), the present dinuclear complex is a mixture of the following three magnetic isomers: the isomer of 44% abundance with two $I = 0$ nuclei, the isomer of 45% with both $I = 0$ and $I = {}^1/_2$ nuclei, and the isomer of 11% with two $I = {}^1/_2$ nuclei. In correspondence to these magnetic isomers, the ^{31}P NMR spectrum is composed of a singlet due to the A_2 spin system, 8 signals due to the AA′ part of the AA′X spin system, and 10 signals due to the AA′ part of the AA′XX′ spin system, respectively. The dinuclear platinum(II) complex $[Pt_2I_4(PBu_3)_2]$[27] has the same spin

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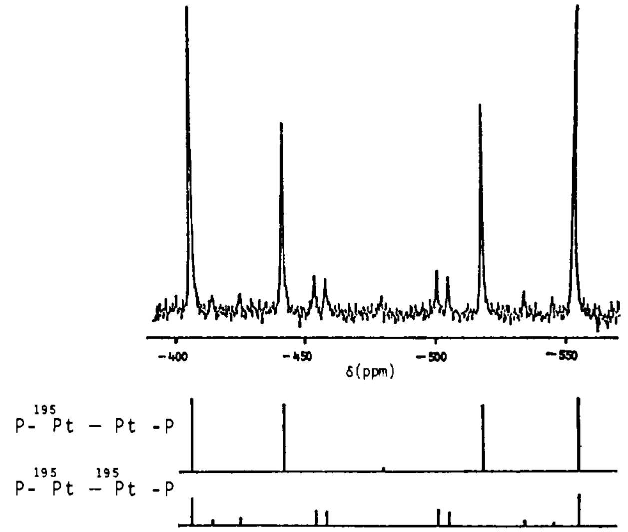

Figure 4. $^{195}Pt\{^1H\}$ NMR spectrum of $[Pt_2(CO)_2(PPh_3)_2(CH_3OOCC{\equiv}CCOOCH_3)]$ and its analyses based on the superposition of two kinds of spin systems.

Table V. ^{31}P and ^{195}Pt NMR Parameters of $[Pt_2(CO)_2(PPh_3)_2(ROOCC{\equiv}CCOOR)]$

R	δ(Pt)	δ(P)	^1J(PtP), Hz	^1J(PtPt), Hz	^2J(PtP), Hz	^3J(PP), Hz
Me	−479.4	19.5	+2409	+786	+783	+163
Et	−478.9	19.5	+2421	+785	+782	+163

systems as **1** and exhibits 19 peaks in its ^{31}P NMR spectrum as expected. The spectrum simulation has reproduced not only the positions but also the intensities of the peaks by superposing these spin systems (Figure 3). In the spectrum of **1**, 17 peaks appeared (Figure 3), as the two signals of the AA′X and AA′XX′ spin systems are incidentally overlapped with each other.

The same nuclear spin–spin coupling constants, determined by the ^{31}P NMR analysis, were obtained from the ^{195}Pt NMR spectrum, consisting of the X part of the AA′X spin system (5 signals) and the XX′ part of the AA′XX′ spin system (10 signals). Because of the overlapping of the two of them, 13 peaks were observed. From the spectrum analyses, it was also concluded that the signs of J(AX) and J(AX′) or of J(XX′) and J(AA′) were the same.

The detour-route contribution in the nuclear spin–spin coupling constants, i.e., ^3J(PtCCPt) or ^5J(PPtCCPtP), appears unimportant, because the magnitudes of J(PtPt) and J(PP) in the dinuclear platinum(I) complex with no bridging ligands $[Pt_2Cl_2(CO)_2(PPh_3)_2]$ (**2**)[28] are similar to those of **1** (Table VI). Since positive signs were reported for both ^1J(PtPt) and ^1J(PtP) in some covalently bonded dinuclear complexes,[28] it is quite conceivable that the signs of ^1J(PtPt) and ^1J(PtP) of **1** are also positive. Consequently, the signs of ^2J(PtP) and ^3J(PP) are expected to be positive. In Table V the observed NMR parameters are summarized.

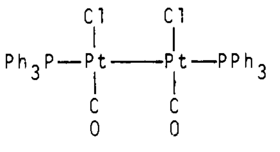

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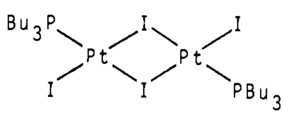
Table VI. Nuclear Spin-Spin Coupling Constants of Some Dinuclear Platinum Complexes

complex	^1J(PtP), Hz	J(PtPt), Hz	J(PtP), Hz	J(PP), Hz	ref
$[Pt_2I_4(PBu_3)_2]$	+3528	380	−26	5	27
$[Pt_2(PMe_3)_4(PhC{\equiv}CPh)]$	+3340	470	−83	15, 10	28
$[Pt_2Cl_2(CO)_2(PPh_3)_2]$	+2190	760	+491	233	28

It is to be noted that the values of ^1J(PtPt), ^2J(PtP), and ^3J(PP) of **1** and **2** are larger than those of the halogen-bridged dinuclear complex $[Pt_2I_4(PBu_3)_2]$[27] (**3**) or the acetylene-bridged dinuclear complex $[Pt_2(PMe_3)_4(PhC{\equiv}CPh)]$[28] (**4**), where the carbon–carbon bond of the acetylene ligand is coordinated perpendicularly to the Pt–Pt axis (Table VI).



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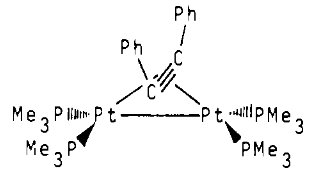

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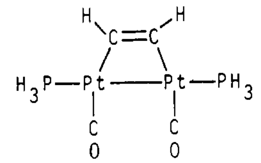
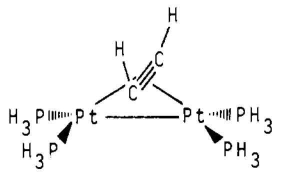
Influence of the Bridging Mode of the Acetylene Ligand on Nuclear Spin–Spin Coupling Constants. The differences in molecular geometries between **1** and **4** are evident as follows: (i) the Pt–Pt bond length of **1** (2.636 Å)[11] is significantly shorter than that of **4** (2.905 Å)[19], (ii) the bond angle of the P–Pt–Pt fragment is essentially linear for **1** but about 120° for **4**, and (iii) the parallel orientation of the acetylene ligand to the Pt–Pt axis constitutes di-σ bonding in **1**, whereas its perpendicular orientation realizes μ bridging in **4**. The observed values of reduced coupling constants and the mutual polarizabilties calculated for $[Pt_2(CO)_2(PH_3)_2(HC{\equiv}CH)]$ (**5**) and $[Pt_2(PH_3)_4(HC{\equiv}CH)]$ (**6**) are summarized in Table VII.



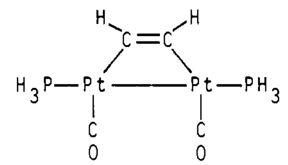
l(PtPt) = 2.636 Å
5



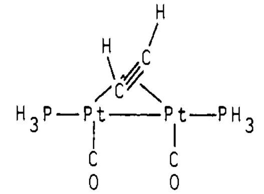
l(PtPt) = 2.905 Å
6

Satisfactory reproduction was demonstrated for the signs of the nine coupling constants and the trend of the larger ^1J(PtPt) and smaller ^1J(PtP) values of **1** than those of **4**.

So as to elucidate the influence of the molecular geometries, we have made calculations on two virtual model complexes, **7** and **8** (Table VII). The geometry of **7** differs from that of **5** only in the Pt–Pt bond length (2.905 Å), which is the same value as in **6**. The geometry of **8** is common to **5** except for the perpendicular (μ-bridging) orientation of acetylene to the Pt–Pt axis in **8** against the parallel (di-σ-bonding) one in **5**. Since the $^1\pi$(PtP) value of **7** is close to that of **5**, it is not so sensitive to the difference in the Pt–Pt bond length. The two μ-bridging model complexes, **6** and **8**, are quite different with



l(PtPt) = 2.905 Å
7



l(PtPt) = 2.636 Å
8

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Table VII. Reduced Coupling Constants and Mutual Polarizabilities for Dinuclear Platinum Complexes

complex	orientation	l(PtPt), Å		Pt–P	Pt–Pt	P–Pt–Pt	P–Pt–Pt–P
$[Pt_2(CO)_2(PPh_3)_2(CH_3OOCC{\equiv}CCOOCH_3)]$ (1)	di-σ	2.636	K^a	+253.8	+154.5	+82.50	+9.21
$[Pt_2(CO)_2(PH_3)_2(HC{\equiv}CH)]$ (5)	di-σ	2.636	π^b	+20.40	+7.441	+1.477	+0.32
$[Pt_2(CO)_2(PH_3)_2(HC{\equiv}CH)]$ (7)	di-σ	2.905	π^b	+22.10	+12.39	+4.078	+0.95
$[Pt_2(PMe_3)_4(PhC{\equiv}CPh)]$ (4)	μ	2.905	K^a	+351.9	+92.4	−8.74	+0.85, +0.57
$[Pt_2(PH_3)_4(HC{\equiv}CH)]$ (6)	μ	2.905	π^b	+31.02	+0.656	−0.030	+0.073,[c] +0.071[d]
$[Pt_2(CO)_2(PH_3)_2(HC{\equiv}CH)]$ (8)	μ	2.636	π^b	+31.30	+2.297	−0.431	+0.57

[a] Units in nm^{-3}. [b] Units in 10^{-4} eV^{-1}. [c] Value for phosphorus atoms in the trans position. [d] Value for phosphorus in the cis position.

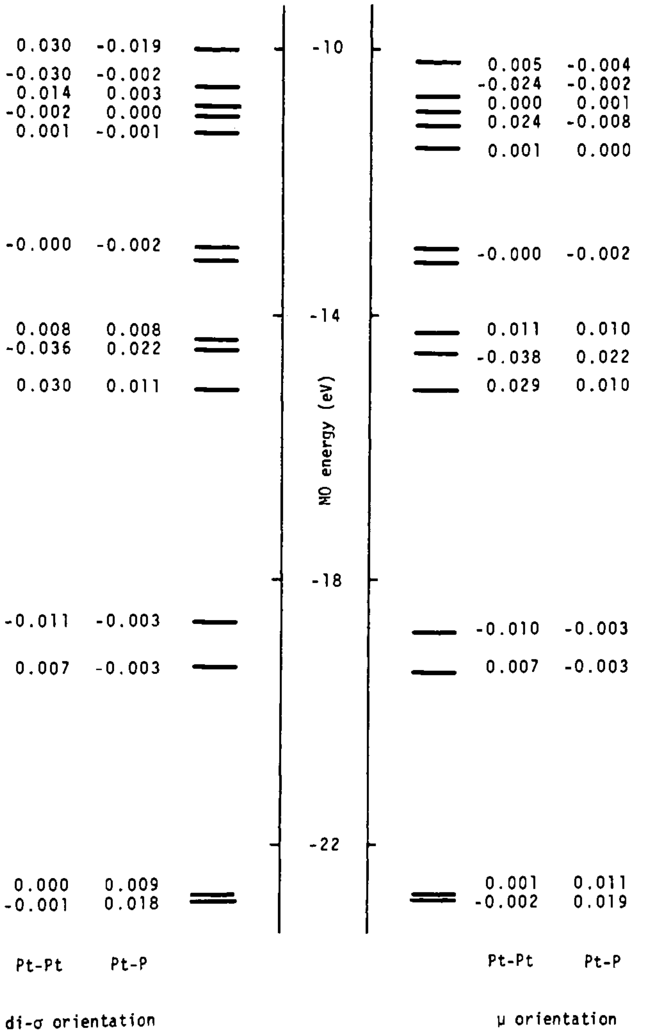

Figure 5. Product of valence s-orbital coefficients in occupied MO's for Pt–Pt and Pt–P atomic pairs of $[Pt_2(CO)_2(PH_3)_2(HC{\equiv}CH)]$.

respect to the geometry of the dinuclear skeleton, but their $^1\pi$(PtP) values are very similar. It is therefore of interest to inspect from the molecular orbital viewpoint why the difference in $^1\pi$(PtP) arises between **5** and **8**.

Figure 5 shows the energy levels of the occupied molecular orbitals of **5** (di-σ orientation) and **8** (μ orientation) together with the s-coefficient products of the Pt–P and Pt–Pt pairs. From the bottom up to the top, most of the occupied molecular orbitals exhibit similar s-coefficient products. Key orbitals can be pointed out, however, which explains the difference between **5** and **8**; that is, the highest occupied molecular orbitals. Their magnitudes of the s-coefficient products for the di-σ complex (0.030, −0.019) are several times larger than those for the μ complex (0.005, −0.004).

The orbital lobes of the HOMO's are depicted schematically in Figure 6. The σ bonds between the two platinum atoms and between the platinum and acetylene carbon atoms are found in the HOMO of **5**, with the in-phase overlap of the platinum s orbital, which, in turn, brings about an out-of-phase overlap between s_{Pt} and s_P, just as in the case of the mononuclear complex (Figure 2). The large positive s-coefficient products for s_{Pt}–s_{Pt} (0.030) and the negative value for s_{Pt}–s_P (−0.019) (Figure 5) reflect these features.

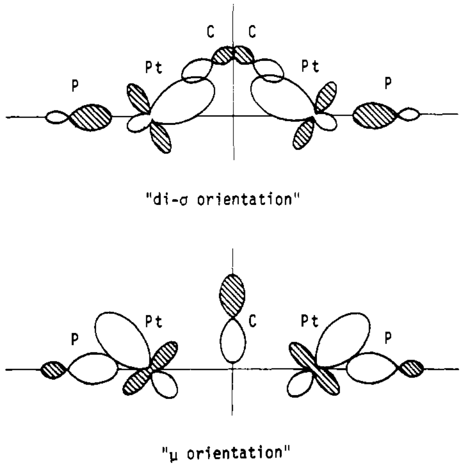

Figure 6. Schematic representation of the HOMO for $[Pt_2(CO)_2(PH_3)_2(HC{\equiv}CH)]$.

In the HOMO of the μ complex, on the other hand, the π orbital of the coordinated acetylene is set intersecting the platinum–platinum bond in an antibonding phase with respect to the platinum AO's. As appeared in the s-coefficient products, both the bonding overlap of s_{Pt}–s_{Pt} (0.005) and the antibonding overlap of s_{Pt}–s_P (−0.004) are markedly reduced in this configuration. Therefore, the Pt–Pt σ bonding is weakened but the Pt–P σ bonding is strengthened, compared with those formed in the HOMO of the di-σ complex.

Since most unoccupied molecular orbitals exhibited antibonding overlaps for both the Pt–Pt and the Pt–P s-orbital paris, the positive Pt–Pt s-coefficient product in the HOMO should contribute to an increase in the $^1\pi$(PtPt) value and the negative Pt–P s-coefficient product to a decrease in $^1\pi$(PtP), respectively.

The orientation of the bridging acetylene ligand strongly affects the HOMO characteristics, which were shown to govern the relative magnitudes of $^1\pi$(PtPt) and $^1\pi$(PtP). The observed trend of ^1J(PtPt) and ^1J(PtP) in the two types of dinuclear platinum acetylene complexes is thus well interpreted by the key orbitals.

We consider that the trans influence of the platinum atom is high, as the Pt–Cl lengths in $[Pt_2Cl_4(CO)_2]^{2-}$[29] and $[Pt_2Cl_2(\mu\text{-}Ph_2PCH_2PPh_2)]$[30] are close to the upper limit among the square-planar Pt(II) complexes. The present calculation seems to be appropriate in demonstrating how the trans in-

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Inorg. Chem. **1981**, *20*, 4413–4415 **4413**

fluence of platinum atoms is sensitive to the mode of acetylene bridging.

A few calculations have been accumulated so far on the electronic structures of acetylene-bridged dinuclear complexes.[31-34] Recently, the reactivity of an acetylene-bridged dinuclear nickel complex toward dihydrogen was interpreted in terms of the lobe shape of some molecular orbitals.[35] The present approach of elucidating the characteristics of key orbitals, on the basis of the nuclear spin–spin coupling constants will, therefore, not only assist the interpretation of bonding properties but also provide a practical clue to the design of orbital-controlled reactions.[36]

Registry No. **1**, 72207-39-7; **4**, 79084-40-5; **5**, 79084-41-6; **6**, 79084-42-7; **8**, 79084-43-8; $Pt_2(CO)_2(PPh_3)_2(EtOOCC{\equiv}CCOOEt)$, 79084-44-9; $[PtCH_3(PH_3)_3]^+$, 79084-45-0; $[PtH(PH_3)_3]^+$, 79084-46-1.

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Vibronic Structure of Square-Planar Complexes. Some Evidence of Odd Mode Progressions

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Recent theoretical work contends that progressions in odd modes, rather than in totally symmetric modes, comprise the band structure in electronic transitions of metal complexes. Evidence supporting this hypothesis is provided by the luminescence spectrum of $[Pt(bpy)Cl_2]$ and by reexamination of luminescence data on $PtCl_4^{2-}$.

Introduction

It is fairly generally acknowledged that the structure of spectral bands due to electronic transitions, of transition-metal complexes as well as other molecules, results from vibronic progressions in one or more normal modes which are totally symmetric or at least totally symmetric in the point group of the final state.[1,2] There is indeed an impressive amount of evidence, experimental[3-11] and theoretical,[8,12-14] for this assumption. The experimental evidence includes some very careful spectroscopic work on metal complexes doped in host crystals at low temperatures, in which the vibronic components are quite distinct, and in which the individual progression frequencies may be determined. This work has supported well the statement above.

In a recent paper by Hollebone,[15] however, the group theoretical foundations of this hypothesis have been called into question. Hollebone has contended that it is incorrect, or, at least, insufficient, to analyze the vibronic problem in terms of the static symmetry of the molecule in its equilibrium position. In the equilibrium position, a d–d transition is forbidden. The transition must therefore occur from a nonequilibrium position, in which the molecule has a lower symmetry, and consequently the problem becomes a dynamic one in which displacements (in initial as well as final states) along all the normal coordinates are considered, and the Born–Oppenheimer approximation is explicitly rejected.

The continuous group of three-dimensional harmonic motions may be taken to be SU(3), the group of unitary, unimodular 3 × 3 matrices.[15] Electronic wavefunctions may be formulated in terms of the group SU(2), which corresponds to the labeling of wavefunctions according to the free ion terms from which they are derived. The appropriate group in which to classify vibronic wavefunctions should then be SU(2) × SU(3), or SU(6). This is restricted by Hollebone to SU(3).[15]

Within this framework, the operative principle is an octupole selection rule for the total wavefunction (dipole and quadrupole interactions are forbidden), i.e., the quantum number associated with the representation in SU(3) of the wavefunctions in question must change by 3 (actually 3 mod 4) during a transition from one state to another. This may be expressed as

$$|\Delta L| + |\Delta S| + |\Delta V| = 3 \tag{1}$$

In this equation, S and L are the normal spin and orbital angular momentum quantum numbers, and V is a quantum number (not to be confused with v, the number of excited vibrational quanta) determined from the SU(3) representation of the vibrational part of the wavefunction. V may be obtained by inspection as the number of nodes associated with a spatial representation of a particular normal mode. For example, the ν_4 asymmetric stretch of a planar AB_4 molecule, as with an

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