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SIGN AND MAGNITUDE OF ONE-BOND $^{195}Pt-^{13}C$ COUPLING CONSTANTS IN Pt(II)-OLEFIN AND -CARBONYL COMPLEXES

Takao IWAYANAGI and Yasukazu SAITO*

The Institute of Industrial Science,
The University of Tokyo, Roppongi, Minato-ku, Tokyo 106

The positive sign of $^1J(Pt-C)$ in $[Pt(C_2H_4)Cl_3]^-$ has been determined by the double resonance experiments, although both positive and negative signs are inferred for Pt(II)-cyclooctadiene π-complexes. The small magnitude of $^1J(Pt-C)$ in $[Pt(C_2H_4)Cl_3]^-$ compared with $[Pt(CO)Cl_3]^-$ has been interpreted in terms of the s orbital coefficients of Pt and C.

The nuclear spin-spin coupling constants in metal complexes,[1] especially their signs,[2] have attracted wide interest in recent years. As for the directly bonded $^{195}Pt-^{13}C$ coupling constants, no attempt at sign determination has hitherto been made, although both positive and negative signs are inferred for two kinds of π-bonded carbons (*cis* to Me and *trans* to Me) in the Pt(cod)MeX complexes (cod = cyclooctadiene).[3] In the present study, the sign of $^1J(Pt-C)$ for a Pt(II)-ethylene π-complex has been obtained experimentally for the first time and the magnitude of $^1J(Pt-C)$ for the ethylene complex has been compared with that of $^1J(Pt-C)$ for a carbonyl complex quantum chemically within the framework of the Pople and Santry theory.[4]

The double resonance technique using a $^{13}C-\{^1H\}$ selective decoupling is useful for deciding the relative signs of $^nJ(M\text{--}C)$ and $^{n+1}J(M\text{--}C\text{-}H)$.[5] Since the value of $^2J(Pt-C-H)$ including the sign is -60.6 Hz for *trans*-$[Pt(C_2H_4)Cl_2(py)]$ (py = pyridine), obtained by pmr experiments in a nematic solvent,[6] the absolute sign of $^1J(Pt-C)$: 167 Hz can be determined by this technique. The Zeise's anion, $[(n\text{-}Bu)_4N]^+[Pt(C_2H_4)Cl_3]^-$ ($^1J(Pt-C)$: 192 Hz, $^2J(Pt-C-H)$: 64.3 Hz), was chosen here because of the advantage of spectrum simplicity. The magnitudes of $^1J(Pt-C)$ and $^2J(Pt-C-H)$ for a series of *trans*-$[Pt(C_2H_4)Cl_2X]$ were reported previously.[7]

Cmr spectra of $[(n\text{-}Bu)_4N]^+[Pt(C_2H_4)Cl_3]^-$ ($CDCl_3$ solution: $\delta(\underline{C}_2H_4)$ = 67.2 ppm from TMS, $^1J(Pt-C)$ = 192 Hz) and $[(n\text{-}Bu)_4N]^+[Pt(CO)Cl_3]^-$ ($CDCl_3$ solution: $\delta(\underline{C}O)$ = 151.4 ppm from TMS, $^1J(Pt-C)$ = 1757 Hz) were measured on a JEOL PFT-100 spectrometer at 25.03 MHz. The relative sign of $^1J(Pt-C)$ and $^2J(Pt-C-H)$ for $[(n\text{-}Bu)_4N]^+[Pt(C_2H_4)Cl_3]^-$ in

$CDCl_3$ solution was determined by the ^{13}C-{^1H} selective decoupling experiments.[5] The irradiating and observing frequencies were monitored by a TAKEDA RIKEN TR-550 frequency counter.

Irradiation of the low-field portion of the proton spectrum enhanced selectively the upfield platinum satellite of the ^{13}C resonance of the ethylene carbon of $[(n\text{-}Bu)_4N]^+[Pt(C_2H_4)Cl_3]^-$ in $CDCl_3$ solution and *vice versa*, showing that the sign of ^1J(Pt-C) was opposite to ^2J(Pt-C-H) (negative). Therefore, the sign of ^1J(Pt-C) with the magnitude of 192 Hz for the ethylene π-coordination in $[Pt(C_2H_4)Cl_3]^-$ is positive.

Table 1 summarizes the magnitudes of ^1J(Pt-C) for various organoplatinum(II) complexes, *trans*-$[PtLClQ_2]$ (L = carbon-ligand). It is to be noted that the influence of the ligand X *trans* to the carbon-ligand L on ^1J(Pt-C) has been reported to be quite large (*trans* infulence[1]; L = C_2H_4,[7] Me^-,[8] Ph^-,[9] and CO[10]). Chlorine ion was chosen as the common *trans* ligand X for comparison. The dominance of the Fermi contact mechanism in the one-bond ^{195}Pt-^{13}C coupling was suggested by the linear relationship between ^1J(Pt-C) and ^2J(Pt-C-H) for a series of *trans*-$[PtMeXQ_2]$ (Q = $AsMe_3$ or PMe_2Ph) passing almost through the origin.[8] As shown in Table 1, the magnitudes of ^1J(Pt-C) in Pt(II) σ complexes are generally much larger than that of ethylene π complex, and the more the s character of the carbon in coordination, the larger their magnitudes.

According to the theory of the Pople and Santry,[4] the coupling constant is given by Eq.1:

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

Table 1. One-bond ^{195}Pt-^{13}C coupling constants in various organoplatinum(II) complexes, *trans*-$[PtLClQ_2]$.

carbon-ligand L	hybridization of carbon[a]	*cis*-ligand Q	^1J(Pt-C)/Hz	Ref.
C_2H_4	p	Cl^-	+192	This work
Me^-	sp^3	$AsMe_3$	643	8)
		PMe_2Ph	673	8)
Ph^-	sp^2	$AsMe_3$	858	9)
CO	sp	$AsPh_3$	1724	10)
		Cl^-	1757	This work
		PPh_3	1788	10)

a) formal hybridization of carbon in coordination.

where γ is the gyromagnetic ratio and $[S(0)]^2$ is the s electron density at the nucleus. The s characters of the coupled atoms can be related to the mutual polarizability of the valence s orbitals of the atom A and B (π(AB)) (Eq.2):

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

where ε is the orbital energy and C is the orbital coefficient.

In order to clarify the large difference in magnitude of ^1J(Pt-C) between the ethylene π complex and the carbonyl complex, the constituents of Eq.2, i.e., the s orbital coefficients and their products, (Pt_sxC_s), in both the occupied and unoccupied orbitals in $[Pt(CO)Cl_3]^-$ and $[Pt(C_2H_4)Cl_3]^-$ were calculated by the self-consistent charge extended Hückel method[7] and were depicted together with their orbital energies (Fig.1). An unoccupied mo with large coefficient product (negative), including the antibonding s-s interaction between the Pt and C atoms, is easily pointed out for both complexes. On the other hand, the coefficient patterns of the occupied orbitals in these complexes are in a marked contrast. An occupied mo with dominantly large s-s interaction is noted for $[Pt(CO)Cl_3]^-$, reflecting the σ-type coordination

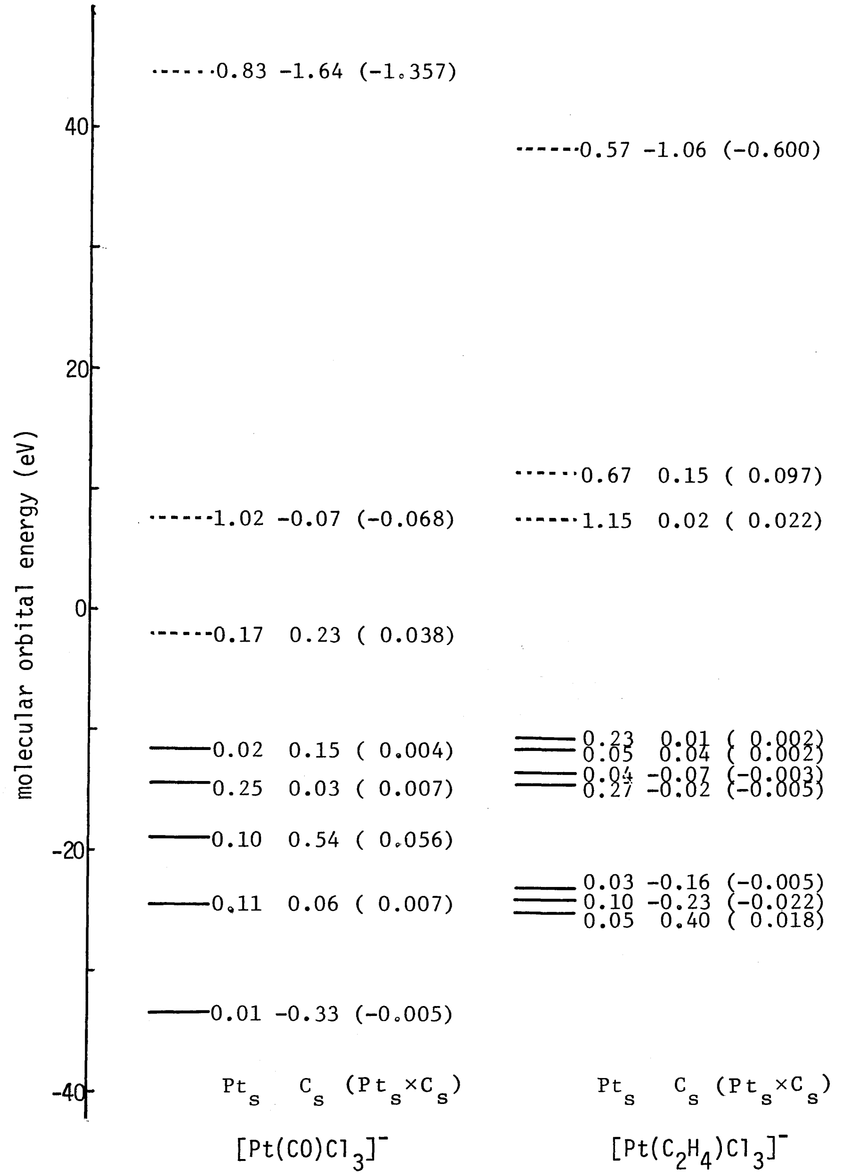

Fig.1. Valence s orbital coefficients of Pt(6s) and C(2s), together with their products, in the a_1 symmetry molecular orbitals of $[Pt(CO)Cl_3]^-$ and $[Pt(C_2H_4)Cl_3]^-$.

via the sp hybridized carbon, whereas no conspicuous orbital is found for $[Pt(C_2H_4)-Cl_3]^-$.

The circumstance that a particular orbital is predominant in both occupied and unoccupied orbitals as found for $[Pt(CO)Cl_3]^-$ has been assumed in the mean excitation energy approximation.[4] The opposite signs of dominant $C_{is_A}C_{is_B}$ and $C_{js_A}C_{js_B}$ in Eq.2, together with the negative value of $(\varepsilon_i - \varepsilon_j) = -\Delta E$, lead to the positive sign of π(AB). The positive sign of $^1\pi$(Pt-C) and hence of ^1J(Pt-C) in $[Pt(CO)Cl_3]^-$ is thus derived. This assignment seems to be reasonable in the analogy of the positive sign of ^1K(Hg-C) in R_2Hg, where the s character of the coordinated carbon and the magnitude of the coupling constant are in an excellent linear relationship.[11]

The small magnitude of ^1J(Pt-C) in $[Pt(C_2H_4)Cl_3]^-$ will be accounted for in terms of the small s-s interaction between the platinum and carbon atoms, since not only the back-donation but also the donation in coordination is composed mainly of the p_π electrons for ethylene. With respect to the value of $(Pt_s x C_s)$ in the occupied orbitals, the pattern of non-dominant orbitals competing with each other is characteristic of the Zeise's anion as shown in Fig.1. It is therefore reasonable that the sign of ^1J(Pt-C) in the Pt(II)-olefin π-complex becomes either positive or negative depending on the kinds of olefins and *trans*-ligands.[3]

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