NMR Studies on Zerovalent Metal π-Complexes of Dibenzylideneacetone. II. Structure and Pt-H Coupling in the Binuclear Platinum Complex

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(Received March 1, 1979)

The NMR analysis on the olefinic protons of the binuclear complex $Pt_2[(C_6H_5CH{=}CH)_2CO]_3$ was conducted on the deuteriated compounds $Pt_2[(C_6D_5CH{=}CH)_2CO]_3$, $Pt_2[(C_6D_5CD{=}CH)_2CO]_3$, and $Pt_2[(C_6D_5CH{=}CD)_2CO]_3$. Examination of the various ^1H NMR parameters revealed the individual characteristics of the six coordinated olefins of three dibenzylideneacetone ligands with respect to the metal-olefin bonding and coordination geometry. The three ligands which triply bridge the two Pt atoms are composed of one *s-cis,cis* ligand which is distant from the Pt atoms and of two *s-cis,trans* ligands which are close to the Pt atoms. Asymmetry in the coordination, which is caused by the gliding of the olefinic double bond to the metal atom, becomes greater as the olefinic moiety approaches the metal atom more closely. The major transmission route of the Pt–olefinic proton coupling is attributable to metal to olefin π-back bonding.

The first introduction of the zerovalent Pd complex of dibenzylideneacetone(dba), $Pd_2(dba)_3$(solvent) (solvent: dba, $CHCl_3$, CH_2Cl_2, and so on) was made by Ishii's group.[1] Maitlis' group[2] prepared its Pt analog $Pt_2(dba)_3$(dba). A novel type of these Pd and Pt complexes, which contains a ligand where only the olefinic portions are involved in the bonding to the metals, has attracted much interest and has been extensively investigated, especially in connection with the reactivity with various compounds.[3-6] For the Pd complex, the X-ray analyses on $Pd_2(dba)_3(CHCl_3)$[6] and $Pd_2(dba)_3(CH_2Cl_2)$[7,8] have been also performed. However, the bonding and structural studies on $Pt_2(dba)_3$ have not been done until now.

In the preceding paper,[9] the ligand conformations of $Pd_2(dba)_3$ in solution have been clarified by the ^1H NMR method and have been compared with those in crystalline state.[6,8] In this study, the treatment established with $Pd_2(dba)_3$ is applied to evaluate the structure of $Pt_2(dba)_3$. Our continuing interest in the relation between NMR parameters and metal-olefin bonding is intensified by a new insight into the coordination geometry of the olefins in the present complex; we now have a suitable model for olefin coordination.

Results and Discussion

The ^1H NMR spectra of the olefinic protons in the deuteriated $Pt_2(dba)_3$ compounds, $Pt_2[(C_6D_5CH{=}CH)_2CO]_3$, $Pt_2[(C_6D_5CD{=}CH)_2CO]_3$, and $Pt_2[(C_6D_5CH{=}CD)_2CO]_3$, are shown in Figs. 1-A, B, and C, respectively. These spectra exhibit some additional absorptions due to the couplings of the olefinic protons with the ^{195}Pt isotope (natural abundance 34%). The chemical shift δ_A of the olefinic proton on the carbonyl side (H_A) and the chemical shift δ_B of the olefinic proton on the phenyl side (H_B) were exactly determined from each main peak in the spectra of Figs. 1-B and C, respectively. Further analysis was conducted by spin decoupling in the spectrum of Fig. 1-A, to find the pairs of H_A and H_B in *trans* position of the olefinic moieties and hence to determine the olefinic coupling constant J_{AB}. Thus the spectrum was found to consist of six AB quartet patterns with attendant ^{195}Pt satellites. The J_{AB}, δ_A, and δ_B values together with the internal shift $\delta_{AB}(=\delta_B-\delta_A)$ and the mean shift $\bar{\delta}_H[=(\delta_A+\delta_B)/2]$ are summarized in Table 1, where the six olefins **a** to **f** are arranged in the decreased order of $\bar{\delta}_H$ (in the

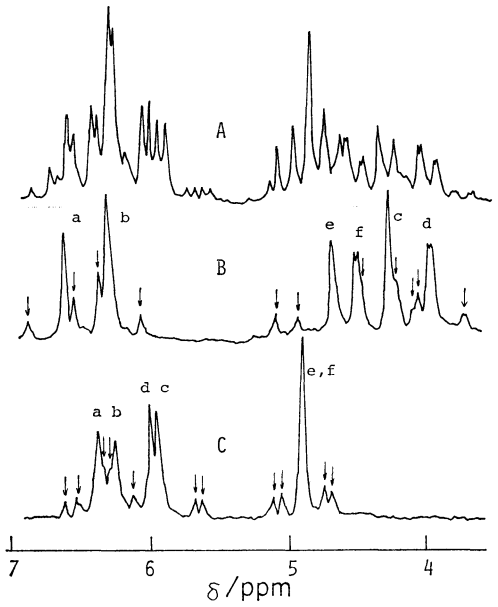


Fig. 1. ^1H NMR spectra of $Pt_2[(C_6D_5CH{=}CH)_2CO]_3$ (A), $Pt_2[(C_6D_5CD{=}CH)_2CO]_3$ (B), and $Pt_2[(C_6D_5CH{=}CD)_2CO]_3$ (C) recorded in $CDCl_3$ at 25 °C. In B and C, **a**—**f** denote the proton signals of the respective olefins and the arrows indicate the satellites due to the ^{195}Pt couplings of the olefinic protons.

Table 1. ^1H NMR parameters of the olefinic protons of dba in $Pt_2(dba)_3$ in $CDCl_3$ at 25 °C

Olefins	J_{AB}/Hz	δ_A/ppm	δ_B/ppm	δ_{AB}/ppm	$\bar{\delta}_H$/ppm
a	12.7	6.666	6.396	−0.270	6.531
b	12.7	6.357	6.278	−0.079	6.318
c	10.9	4.301	5.969	1.668	5.135
d	11.2	4.000	6.023	2.023	5.012
e	10.9	4.704	4.905	0.201	4.805
f	11.1	4.537	4.905	0.368	4.721

δ_A and δ_B: in ppm with tetramethylsilane. $\delta_{AB}=\delta_B-\delta_A$ and $\bar{\delta}_H=(\delta_A+\delta_B)/2$. For free dba (in $CDCl_3$ at 25 °C): J_{AB}, 16.0 Hz; δ_A 7.090; δ_B 7.750; δ_{AB}, 0.660; and $\bar{\delta}_H$, 7.420 ppm.

increased order of the chemical screening).

The ^{195}Pt coupling with H_A (J_{Pt-A}) and that with H_B (J_{Pt-B}) were definitely determined[10] from the separation of the two satellites which are symmetrically disposed on either side of each main signal in the spectra of Figs. 1-B and C, respectively. But for the couplings with H_B's of olefins **e** and **f** a definitive assignment was difficult, because of an identity of the chemical shifts of the respective protons. Table 2 lists the coupling constants J_{Pt-A} and J_{Pt-B}, together with their average $\bar{J}_{Pt-H}[=(J_{Pt-A}+J_{Pt-B})/2]$ and difference $J_{Pt-A,B}(=J_{Pt-A}-J_{Pt-B})$.

TABLE 2. 195 Pt–OLEFINIC PROTON COUPLINGS IN $Pt_2(dba)_3$ IN $CDCl_3$ AT 25 °C

Olefins	J_{Pt-A}/Hz	J_{Pt-B}/Hz	$\bar{J}_{Pt-H}$/Hz	$J_{Pt-A,B}$/Hz
a	53.7	49.3	51.5	4.4
b	48.3	56.6	52.5	−8.3
c	43.9	65.4	54.7	−21.5
d	50.8	63.8	57.3	−13.0
e	84.0	43.0 [a] (32.2)	63.5 (58.1)	41.0 (51.8)
f	87.9	32.2 [a] (43.0)	60.1 (65.5)	55.7 (44.9)

a) The coupling of H_B's of olefins **e** and **f** were not determined (see text).

Bonding Nature. The chemical shifts $\bar{\delta}_H$'s for all the olefinic portions move to the high field side and the coupling constants J_{AB}'s are reduced as a consequence of direct coordination of the olefinic double bond to the Pt atom. However, the degrees of the up field shift ($\Delta\delta_H$) and of the reduction of the coupling (ΔJ_{AB}) from $\bar{\delta}_H$ and J_{AB} of free dba allow us to divide the six olefinic moieties into two groups: the two olefins **a** and **b** have ΔJ_{AB} of 3.3 Hz and $\Delta\bar{\delta}_H$ of about 1.0 ppm, and for the remaining four, **c**—**f**, ΔJ_{AB} and $\Delta\bar{\delta}_H$ lie in the narrow range of 4.8—5.1 Hz and 2.3—2.7 ppm. When we recall[9] that both the parameters directly reflect the strength of metal-olefin π-bonding which is controlled mainly by the distance from each olefin to the metal atom, the above fact leads us to state that olefins **a** and **b** with the smaller ΔJ_{AB} and $\Delta\delta_H$, are weaker in the π-bonding and are more distant from the Pt atom than the other four.

The average values of ΔJ_{AB} and $\Delta\bar{\delta}_H$ in the six olefins are 4.4 Hz and 2.00 ppm, respectively. These are small compared with the corresponding values 6.1 Hz and 3.3 ppm in the zerovalent dba complex $Pt(PPh_3)_2(dba)$.[11] This can be understood in terms of the stabilization effect of the electron donative ligand PPh_3, whose the ionization potential is lower than that of olefin.[12,13] The average values of ΔJ_{AB} and $\Delta\bar{\delta}_H$ in $Pt_2(dba)_3$ are larger than those[9] of 2.7 Hz and 1.51 ppm in $Pd_2(dba)_3$. The larger values in $Pt_2(dba)_3$ can be explained from the view of nd^{10}—$nd^9(n+1)s^1$ promotion energies[14,15] of these d^{10} metals. The above facts indicate that in so far as judging from the average bonding strength in all the coordinated olefins, the binuclear complex is ordinary and to be expected. The characteristics of the binuclear complex appear in the remarkably unbalanced distribution of the bonding strength to the chemically equivalent olefins, as appreciated from the $\Delta\delta_H$ spreading from 0.89 ppm, a popular value of the divalent Pt–olefin complexes, to 2.70 ppm, a typical value of the zerovalent Pt–olefin complexes.[16]

Ligand Conformation. The six olefinic moieties of the three dba ligands can also be classified into two distinct groups with respect to the internal shift δ_{AB}: the two olefins **c** and **d** with δ_{AB} larger than 1.6 ppm and the remaining four with δ_{AB} smaller than 0.4 ppm. Referring to the definitive relation[9,17] between the magnitude of δ_{AB} and the conformation of olefinic moiety ($\delta_{AB}\gtrsim 1.0$ ppm for *s-trans* form and $\delta_{AB}\lesssim 0.4$ ppm for *s-cis* form), we can assign the olefins **c** and **d** with the larger δ_{AB} values to be in the *s-trans* form and the olefins **a**, **b**, **e**, and **f** with the smaller δ_{AB} values to be in the *s-cis* form. Another support for the above assignment was obtained from the temperature dependence of δ_{AB} (Fig. 2). Raising the temperature from −60 to 25 °C the δ_{AB} values of olefins **a** and **b** increased by *ca.* 0.1 ppm, while those of olefins **c** and **d** decreased by *ca.* 0.03 ppm and those of olefins **e** and **f** were unchanged. The temperature change of δ_{AB} implies a conformational distortion of the ligand in which the *s-cis* and *s-trans* olefins acquire some *s-trans* and *s-cis* characters, respectively. Then, since the δ_{AB} is a minimum in the *s-cis* form and a maximum in the *s-trans* form,[17] the δ_{AB} values of *s-cis* and *s-trans* olefins should increase and decrease, respectively, with a rise of temperature. Thus, the preceding assignment for olefins **a**—**d** can be established. The constancy[18] of the δ_{AB} in the *s-cis* olefins **e** and **f** may be due to their diminished thermal flexibilities, which are suggested by their stronger π-bonding with the Pt atom than that of the other *s-cis* olefins.

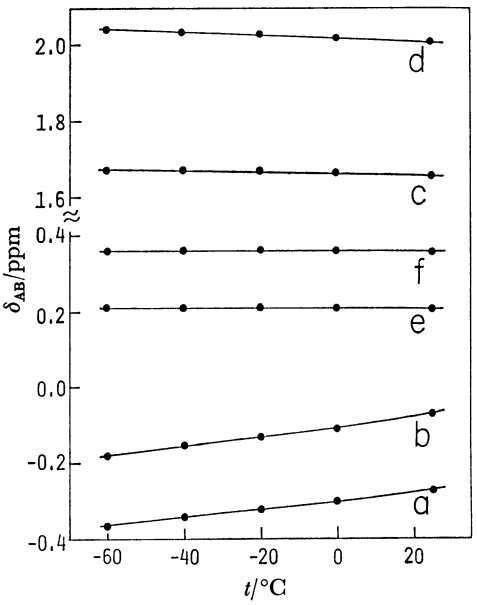


Fig. 2. Temperature dependence of the internal shift δ_{AB} for each olefinic moiety **a** to **f** in $Pt_2(dba)_3$, measured in $CDCl_3$.

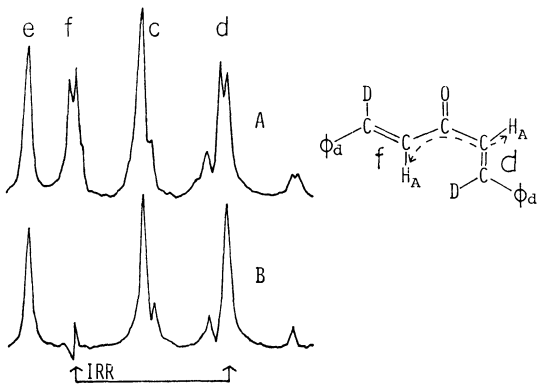
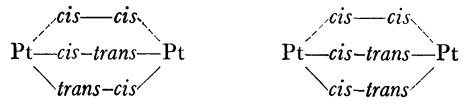


Fig. 3. The high field spectrum of $Pt_2[(C_6D_5CD{=}CH)_2\text{-}CO]_3$ showing the splitting of 1.5 Hz of H_A's in olefins **d** and **f** (A) and the spectrum decoupled by the irradiation of H_A of olefin **f** (B).

A clue to find the pair of the olefinic moieties which constitute one dba ligand was provided by the observation of the fine splitting (1.5 Hz) of the H_A signals in olefins **d** and **f** (Fig. 3-A); decoupling of the H_A signal showed that these splittings came from the long range coupling between the H_A's (Fig. 3-B). This indicates that *s-cis* olefin **f** and *s-trans* olefin **d** are linked to constitute the *s-cis,trans* dba ligand. The remaining three *s-cis* and one *s-trans* olefins inevitably give one *s-cis,trans* and one *s-cis,cis* dba. The most probable pair yielding another *s-cis,trans* conformation would be olefins **c** and **e**, because not only *s-trans* olefins **c** and **d** but also *s-cis* olefins **e** and **f** are closely similar to each other in all the NMR data gathered in Tables 1, 2, and Fig. 2. Thus, third dba ligand with *s-cis,cis* conformation should be composed[19] of olefins **a** and **b**, which also have analogous NMR parameters to justify the combination. This is the first finding of the *s-cis,cis* form fixed as a ligand, though it is a prevailing conformation[17] in the free dba.

Two types of the bonding scheme will be considered from the manner where the two *s-cis,trans* ligands, together with the symmetric *s-cis,cis* ligand, are bridged to the two Pt atoms:

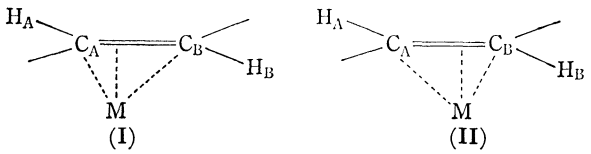


(I) (II)

The solid and broken lines denote the strong and weak bonds, respectively in the π-bonding strength as already determined. Scheme I is reasonable if we consider the fact that in a crystal[8] of $Pd_2(dba)_3(CH_2Cl_2)$ the two *s-cis,trans* ligands together with the symmetric *s-trans,trans* ligand are allocated in such a manner as in I. Scheme I with *the same* conformational combination (*cis-cis-trans*) around each metal atom is also rationalized by the fact that *the same* bonding strength is given for each metal atom; it binds the two of the three olefins strongly and the one weakly: this situation is completely complementary with the situation[9] in $Pd_2(dba)_3$, which is obtained by substituting the word *different* instead of *the same* in the above description. It may be reasonable to say that the olefin conformations around the metal can control the geometry about the metal-olefin bonds and hence the bonding strength to the metal. Scheme II is in conflict with the above consideration.

Pt–H Coupling. As shown in Table 2, the Pt couplings with the individual protons (J_{Pt-A} and J_{Pt-B}) distribute in so much large a range, from 32 to 88 Hz, as to cover the values[16] for various Pt–olefin complexes, but the average value of the twelve couplings falls in 56.6 Hz, a popular value of the Pt–olefinic proton coupling. Interestingly, the mean coupling $\bar{J}_{Pt-H}$ keeps an approximate correlation with the mean shift $\bar{\delta}_H$; as $\bar{\delta}_H$ decreases with going from olefin **a** to **f**, $\bar{J}_{Pt-H}$ tends to increase. This means that the Pt–olefinic proton coupling is influenced mainly by the same origin as that in the up field shift, *i.e.* metal to olefin π-back donation. This deduction is easily accepted if one considers[20] that in zerovalent Pt–olefin complexes the π-back bonding plays a major role[25] in the total Pt–olefin bonding. The coupling may be transmitted by a Fermi contact mechanism *via* the σ-π mixing[26] on the olefinic carbon with the strong π-back bonding. Thus, the Pt–H coupling increases with an increase of the π-back donation, closely related to an approach of the olefin to the metal atom.

Another interesting feature appears in the coupling difference $J_{Pt-A,B}$. The absolute value of $J_{Pt-A,B}$ also correlates roughly with J_{Pt-H} and with $\bar{\delta}_H$. The origin of the appearance of $J_{Pt-A,B}$ must be ascribed to an asymmetric coordination owing to the gliding[27] of the olefinic double bond to the metal atom:



Through the gliding, one of the carbons C_A and C_B approaches the metal while the other departs from the metal. In the first approximation, it could be said that the carbon close to the metal takes the larger π-back donation and so the proton attached to this carbon spin-couples with the metal atom more strongly. Thus, the positive sign of $J_{Pt-A,B}$ in olefins **a**, **e**, and **f** can be interpreted on the basis of gliding model I, where the metal atom glides toward C_A, whereas the negative sign in olefins **b**, **c**, and **d** can be interpreted on the basis of gliding model II where the metal atom glides toward C_B. The magnitude of $J_{Pt-A,B}$ can be explained in terms of the extent of coordination asymmetry coming from the gliding such as exemplified by the ratio of the C_A–M and C_B–M distances. The X-ray analysis[8] on the analogous compound $Pd_2(dba)_3$ has clarified the existence of the glidings shown in I and II. Eventually, the correlation between $\bar{J}_{Pt-H}$ and $J_{Pt-A,B}$ in $Pt_2(dba)_3$ indicates that the closer the olefinic moiety approaches the metal, the greater becomes the asymmetry in coordination, as expected from the structure where the two olefinic moieties of dba ligand bridge the two metal atoms.

Experimental

Materials. The binuclear Pt complex $Pt_2(dba)_3(dba)$ was synthesized according to the literature.[4] Recrystallization of the complex in $CHCl_3$ gave deep purple solids with the formula $Pt_2(dba)_3(CHCl_3)$, where an involvement of the solvent molecule was found by mass and elemental analyses. $Pt_2[(C_6D_5CH{=}CH)_2CO]_3(CHCl_3)$, $Pt_2[(C_6D_5CD{=}CH)_2CO]_3(CHCl_3)$, and $Pt_2[(C_6D_5CH{=}CD)_2CO]_3(CHCl_3)$ were prepared by the above procedure using the respective deuteriated dba.[17]

^1H NMR Measurements. The ^1H NMR spectra of the deuteriated complexes in $CDCl_3$ were recorded through a number of pattern accumulations by a JEOL PS-PFT/EC 100 pulsed Fourier transform system. This system overcame the low solubility of the binuclear complex. The measuring conditions were the same as those stated in the preceding paper.[9]

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10) For some cases one of the two satellites was observed. In these cases the coupling was estimated from the observed satellite only.

11) $Pt_2(PPh_3)_2(dba)$ ligated by either of the two olefinic moieties of dba was prepared after the procedure of Ref. 5 to give the J_{AB}, δ_A, and δ_B values of the coordinated olefinic moiety 9.9 Hz, 4.04 and 4.15 ppm with tetramethylsilane (in $CDCl_3$ at 25 °C).

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18) This constancy is to be expected if one considers that the δ_{AB} in the *s-trans* olefins **c** and **d**, with the bonding strength similar to that of the *s-cis* olefins **e** and **f**, changes only slightly. The δ_{AB} does not increase so remarkably with a distortion around the *s-cis* form, while it decreases rapidly around the *s-trans* form.[17]

19) Thus, the *s-cis,cis* ligand (olefins **a** and **b**) with the larger separation between the two olefinic double bonds, together with the two *s-cis,trans* ligands with the smaller separation, bridges the two Pt atoms. Then, the *s-cis,cis* ligand should be distorted so as to reduce the C–C(O)–C angle, in contrast to an increase[8] of the angle of the *s-trans, trans* ligand in a crystal of $Pd_2(dba)_3(CH_2Cl_2)$. This seems to be the reason for the abnormal negative sign of δ_{AB} in the *s-cis* olefins **a** and **b**.

20) In divalent Pt–olefin complexes where the σ and π-bonds contribute nearly equally to the total Pt–olefin bond, the σ-bond as well as the π-bond should be important for the coupling transmission. For example, the up field shift ($\Delta\bar{\delta}_H$) for ethylene in zerovalent $Pt(PPh_3)_2(C_2H_4)$[21] is 3.26 ppm much larger than the value of 1.11 ppm in divalent $[PtCl_3(C_2H_4)]^-$,[22] in contrast to the similar $\bar{J}_{Pt-H}$ values of 62 and 66.8 Hz in the respective complex. The distance[23] between Pt and C in the zerovalent complex (2.11 Å) is similar to that[24] in the divalent complex (2.14 Å), indicating a similar total bonding (σ and π) strength in both the complexes. These facts lead us to consider that the Pt-H coupling is generally affected both by σ and π-bondings, while the up field shift is only affected by π-bonding.

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27) For an asymmetrically substituted ethylene, such a gliding coordination is expected in every case. For example, it is significant for the styrene ligand in $[(PhCH{=}CH_2)PdCl_2]_2$ (J. R. Holden and N. C. Benziger, *J. Am. Chem. Soc.*, **77**, 4987 (1955)).