NMR Studies on Zerovalent Metal π-Complexes of Dibenzylideneacetone. I. Ligand Conformation and Bonding in the Binuclear Palladium Complex

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To elucidate the ligand conformation and the metal–olefin bonding nature in the binuclear palladium complex of dibenzylideneacetone, $Pd_2[(C_6H_5CH{=}CH)_2CO]_3$, ^1H NMR studies have been performed on the deuteriated complexes $Pd_2[(C_6D_5CH{=}CH)_2CO]_3$, $Pd_2[(C_6D_5CD{=}CH)_2CO]_3$, and $Pd_2[(C_6D_5CH{=}CD)_2CO]_3$. Examination of the spectra has revealed that the three dibenzylideneacetone ligands which triply bridge the two Pd atoms are all in the *s-cis,trans* conformation. The most probable bonding scheme of the three ligands to the two Pd atoms is as follows: one Pd atom is ligated by one *s-trans* and two *s-cis* olefinic moieties and hence the other by one *s-cis* and two *s-trans* to yield a metal–olefin bonding stronger in the former combination than in the latter. A linear correlation between the couplings and the mean chemical shifts of the *trans* olefinic protons suggests a dominant role of metal to olefin π-back donation in differentiating the olefinic moieties in their bonding strength to the metal atoms and in retaining the characteristic rigid structure of the complex.

Concurrently reported X-ray structural analyses[1–3] of the binuclear Pd complexes of dibenzylideneacetone (dba), $(C_6H_5CH{=}CH)_2CO$, of the formula $Pd_2(dba)_3$-(solvent) showed an interesting disparity in the conformations of the dba ligands. Pierpont and Mazza[1,2] conducted a structural analysis on a crystal of $Pd_2(dba)_3$-(CH_2Cl_2) and found two dba molecules in the *s-cis,trans* conformation and one in the more symmetric *s-trans,trans* conformation, whereas the analysis[3] of a crystal of $Pd_2(dba)_3(CHCl_3)$ indicated all three to be in the *s-cis,trans* conformation. The $Pd_2(dba)_3$ molecule in both crystals possesses essentialy the same configurational arrangement, *i.e.*, the two olefinic double bonds of a given dba ligand coordinate separately to Pd atoms (Pd–Pd distance 3.24 Å) to form a binuclear complex in which each of the Pd atoms exhibits trigonal coordination. The fact that the solvent molecules of crystallization in the $Pd_2(dba)_3$ molecule play a decisive role in changing the conformation of the dba ligand in the crystals prompted us to elucidate the ligand conformation of $Pd_2(dba)_3$ in solutions.

Another motive of this study emerged from a desire to elucidate the metal to olefin bonding nature. The $Pd_2(dba)_3$ molecule can provide genuine information on the π-olefin–metal bonding since the molecule contains a ligand in which only the olefinic portions are involved in bonding to the metal atoms.

With the above interests, we have performed a ^1H NMR study on the $Pd_2(dba)_3$ molecule. Examination of the NMR parameters for the olefinic moieties of the ligands has led to a clarification of the ligand conformation and suggested the bonding nature of the ligands to the Pd atoms.

Results and Discussion

Analysis of the ^1H NMR Spectrum of $Pd_2(dba)_3$.
As earlier reported,[3] the signals of the olefinic protons in $Pd_2[(C_6H_5CH{=}CH)_2CO]_3(CHCl_3)$ are partially obscured by those of the phenyl protons, although they are spread considerably to high field as a direct consequence of coordination. The whole pattern of olefinic protons was observed in the spectrum of $Pd_2[(C_6D_5CH{=}CH)_2CO]_3(CHCl_3)$ in $CDCl_3$ (Fig. 1A). The interpretation of this intricate spectrum was assisted by the availability of the spectra of $Pd_2[(C_6D_5CD{=}CH)_2CO]_3$-$(CHCl_3)$ and $Pd_2[(C_6D_5CH{=}CD)_2CO]_3(CHCl_3)$ in $CDCl_3$ (Fig. 1C and D). These well resolved spectra were obtained through a number of pattern accumulations carried out by a pulsed 100 MHz NMR system in the Fourier transform mode. The fast pulsed scans greatly reduced the measurement time, so that liberation of the coordinated dba was minimized. The resonances

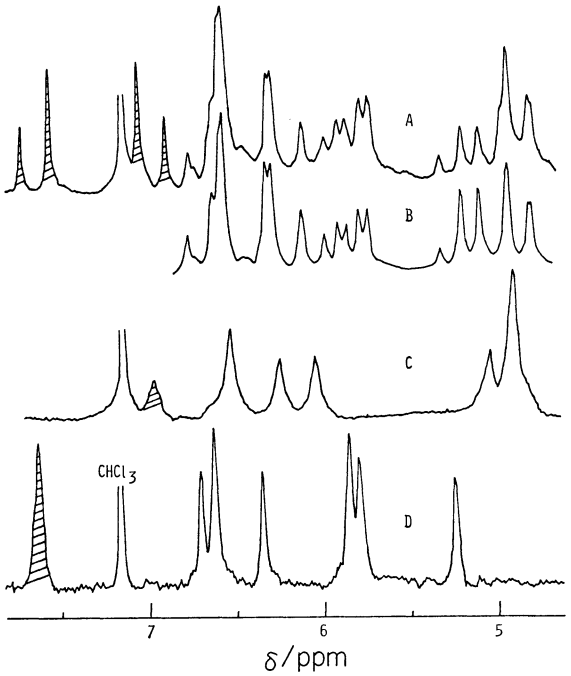


Fig. 1. ^1H NMR spectra measured in $CDCl_3$ at 25 °C. A: $Pd_2[(C_6D_5CH{=}CH)_2CO]_3$, C: $Pd_2[(C_6D_5CD{=}CH)_2$-$CO]_3$, and D: $Pd_2[(C_6D_5CH{=}CD)_2CO]_3$ and B: the computer-simulated spectrum of $Pd_2[(C_6D_5CH{=}CH)_2$-$CO]_3$.

originating from the free dba are shown with striped lines in Fig. 1. The spectra of Fig. 1C and D explicitly gave the resonance positions of the olefinic protons on the carbonyl side (H_A) and those of the olefinic protons on the phenyl side (H_B), respectively, in the coordinated dba. The chemical shifts of H_A and H_B (δ_A and δ_B) were used to assign the olefinic AB quartet families by spin decoupling in the spectrum of Fig. 1A, and then to simulate the spectrum by providing the coupling constants (J_{AB}) as small variables. An optimal simulation spectrum (Fig. 1B) was obtained to give the ^1H NMR parameters of the six olefinic moieties in the dba ligands (Table 1).

Table 1. ^1H NMR parameters of the olefinic protons of dba in $Pd_2(dba)_3$ in $CDCl_3$ at 25 °C

Olefin	J_{AB}/Hz	δ_A/ppm	δ_B/ppm	δ_{AB}/ppm	$\bar{\delta}_H$/ppm
a	14.2	6.619	6.688	0.069	6.654
b	13.7	6.134	6.765	0.631	6.450
c	13.8	6.322	6.422	0.100	6.372
d	12.7	4.935	5.900	0.965	5.418
e	12.7	4.916	5.853	0.937	5.385
f	12.3	5.057	5.243	0.186	5.150

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.

From the Table, it can be seen that the six olefinic moieties which manifest various AB quartet patterns divide into two distinct and separate groups of three with respect to either the coupling J_{AB} or mean chemical shift $\bar{\delta}_H[=(\delta_A+\delta_B)/2]$ of the olefinic protons in the *trans* configuration; the three olefinic moieties **a**, **b**, and **c** with J_{AB} of *ca.* 14.0 Hz are located on the low field side ($\bar{\delta}_H$; *ca.* 6.5 ppm) and the other three **d**, **e**, and **f** with J_{AB} of *ca.* 12.5 Hz on the high field side ($\bar{\delta}_H$; *ca.* 5.3 ppm). The high field shift of the olefinic proton signals upon coordination has been observed for many metal–olefin π-complexes, especially for low valency transition metal complexes[4] and has been directly related to the amount of metal to olefin π-back donation.[5,6] It follows that the olefinic moieties **d**, **e**, and **f** are stronger in the π-bonding with the Pd atom than the other olefinic moieties **a**, **b**, and **c**.[10]

The six olefinic moieties can also be divided into another two distinct groups of three with respect to the internal chemical shift $\delta_{AB}(=\delta_B-\delta_A)$; the three olefinic moieties **a**, **c**, and **f** with δ_{AB} smaller than 0.2 ppm and the other three **b**, **d**, and **e** with δ_{AB} larger than 0.6 ppm. It should be noted that the former group contains two of the olefinic moieties with $\bar{\delta}_H$ of *ca.* 6.5 ppm and so the latter contains only one of them. Therefore the separation of the olefinic moieties with respect to δ_{AB} must differ in its origin from the separation with respect to $\bar{\delta}_H$.

Conformation of the dba Ligands. In the preceding paper[12] it has been shown that the parameter δ_{AB} is a good measure of the conformation of the olefinic moiety of dba. Thus it has been fully proven that the *s-cis* form of the olefinic moiety must have a minimum value of δ_{AB} (0.5 ppm) which increases slightly by a deformation towards the *s-skew* form, while the *s-trans* form must have a maximum value of δ_{AB} (1.5 ppm) which decreases rapidly even by a small deformation towards the *s-skew* form. From the above relation between the δ_{AB} value and the form of the olefin, it can be said that the six olefinic moieties of the coordinated dba molecules consist of three in the *s-cis* form (olefins **a**, **c**, and **f**) and three in the *s-trans* form (olefins **b**, **d**, and **e**).[13]

The existence of an equal number of both forms in the olefinic moieties necessarily demands at least one of the dba ligands with *s-cis,trans* conformation. In mutual allocation between H_A of one of the two olefinic portions of dba and H_B of the other, only the allocation between H_A of the *s-cis* olefin and H_B of the *s-trans* olefin in the *s-cis,trans* conformation brings about the closest proximity between H_A and H_B (Fig. 2); hence an intramolecular NOE will be a maximum for one of

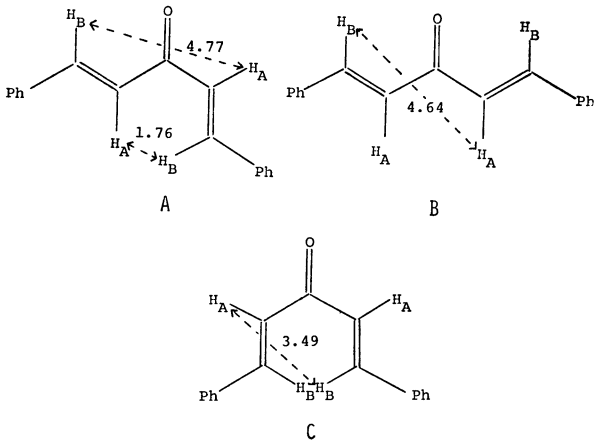


Fig. 2. Three basic conformations of dba. A: *s-cis, trans* B: *s-cis, cis*, and C: *s-trans, trans* and distances (in Å), between H_A and H_B in the different olefinic moiety in a given dba, estimated from the bond lengths and angles assumed in the preceding paper.[12]

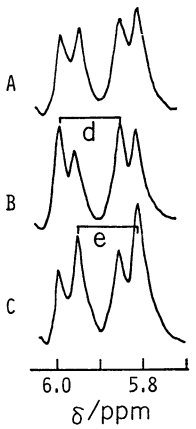
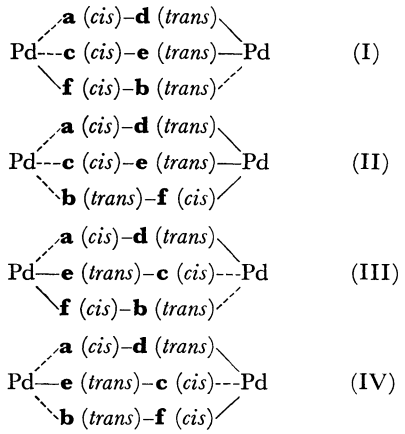


Fig. 3. NOE effects. A: Ordinary signals of H_B's of olefins **d** and **e** near 5.9 ppm in the spectrum of $Pd_2[(C_6D_5CH{=}CH)_2CO]_3$, B: enhancement of H_B signal of olefin **d** on an irradiation of H_A of olefin **a**, and C: enhancement of H_B signal of olefin **e** on an irradiation of H_A of olefin **c**. These spectra were successively taken under identical conditions.

these proton signals when the other is saturated. Figure 3 shows the results of irradiation of the H_A protons in the olefinic moieties. As expected, the irradiation of H_A in the *s-cis* olefin **a** caused an appreciable enhancement of the signal intensity of H_B in the *s-trans* olefin **d**. This indicates that the *s-cis* olefin **a** and *s-trans* olefin **d** are linked to constitute one *s-cis,trans* dba ligand. The signal enhancement of H_B in olefin **e** was also observed on irradiation of H_A in olefin **c** to show the existence of another dba ligand of *s-cis,trans* conformation. Thus the remainder, the *s-trans* olefin **b** and *s-cis* olefin **f** should combine to give the third *s-cis,trans* ligand. Thus it may be concluded that the $Pd_2(dba)_3$ molecule in solution retain the three dba ligands in a *s-cis,trans* conformation as in the crystalline state.

If the conformations of the dba ligands in the crystal could be conserved in solution as in $Pd_2(dba)_3(CHCl_3)$, for $Pd_2(dba)_3(CH_2Cl_2)$ an ^1H NMR spectrum differing from that of $Pd_2(dba)_3(CHCl_3)$ would be expected. The ^1H NMR spectrum of $Pd_2[(C_6D_5CH{=}CH)_2CO]_3$-$(CH_2Cl_2)$ prepared by the recrystallization of Pd_2-$[(C_6D_5CH{=}CH)_2CO]_3(CHCl_3)$ in CH_2Cl_2 was measured in CD_2Cl_2. The spectrum showed that the resonance pattern of the olefinic protons was completely identical with that of $Pd_2[(C_6D_5CH{=}CH)_2CO]_3(CHCl_3)$ in $CDCl_3$, implying that in solution, the sterically repulsive *s-trans,trans* dba ligand[12] in the crystalline $Pd_2[(C_6D_5$-$CH{=}CH)_2CO]_3(CH_2Cl_2)$ changes to the less repulsive *s-cis,trans* form. The appearance of the *s-trans,trans* form in the crystal may be due to a packing requirement on the crystallization involving the solvent molecule.

In consideration of the bonding scheme of the three dba ligands to the two Pd atoms, the three ligands may be denoted as **a**(*cis*)–**d**(*trans*), **c**(*cis*)–**e**(*trans*), and **f**(*cis*)–**b**(*trans*) according to the binding manner of the olefinic moieties as already determined. The following four bonding schemes will be considered:



Here, the π-bonding strengths, as estimated already, between the olefinic moieties and the Pd metal are indicated by the solid line for the stronger bonds and by the broken line for the weaker ones. Although there is no direct method for determining the ligand allocation because of an absence of spin interaction between the ligands, schemes III or IV would be prefered from circumstantial evidence: the first scheme in which each Pd atom is attached by three *s-cis* or three *s-trans* olefins is improbable since the allocation differs from that[3] in the crystalline $Pd_2(dba)_3(CHCl_3)$. Indeed in scheme I the three olefinic moieties around each Pd atom must be equivalent in all the NMR parameters contrary to the experimental results. The remaining three all satisfy the allocation of the ligands in the crystalline complex. Some differences in the δ_{AB} values of ligand **b–f** from those of the other two ligands may be considered to come from a difference in the spatial location of the olefinic protons towards the carbonyl group[17] of the neighbouring ligand. In this respect scheme II is not compatible, since a molecular model indicates that the two ligands in inverse conformational allocation, *e.g.* **b–f** and **a–d** or **b–f** and **c–e** in II, must be similar to each other in spatial location.[18] The results of the decomposition process of the complex are against scheme II. Figure 4 shows the spectra of $Pd_2[(C_6D_5CD{=}$

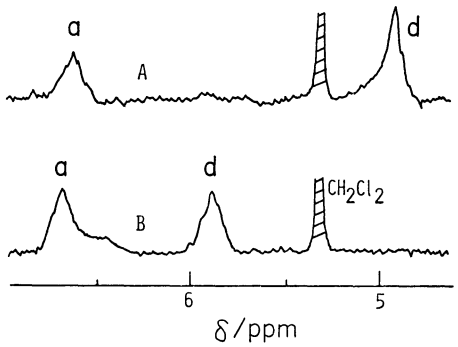
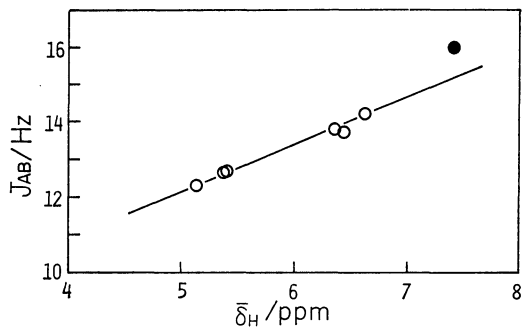


Fig. 4. ^1H NMR spectra of $Pd_2[(C_6D_5CD{=}CH)_2CO]_3$ (A) and $Pd_2[(C_6D_5CH{=}CD)_2CO]_3$ (B) measured in CD_2Cl_2 at 40 °C.

$CH)_2CO]_3$ and $Pd_2[(C_6D_5CH{=}CD)_2CO]_3$ in CD_2Cl_2 at 40 °C, where the broadened signals resulting from only the ligand **a–d** can be observed. This may indicate a slower elimination of the one specific ligand in the complex in accordance with the results of the thermogravimetric analysis.[3] The above behaviour of ligand **a–d** is difficult to understand in scheme II where ligands **a–d** and **c–e** are similar in both bonding and conformational allocation to the two Pd atoms. In the scheme III or IV the ligand **a–d** is different from the other two in either bonding or conformational allocation. Thus it may be justifiably said that the allocation of the three ligands in the complex is that in III or IV. Both schemes lead to the conclusion that the Pd atom coordinated by one *s-trans* and two *s-cis* olefins binds the olefins more strongly than does the one coordinated by one *s-cis* and two *s-trans* olefins. It should be reasonable to expect a difference in the Pd–olefin bonding between the conformation of *cis-trans-trans* and that of *cis-cis-trans*.

Pd–Olefin Bonding Nature. It has been already shown that either the chemical shift $\bar{\delta}_H$ or coupling J_{AB} classifies the six olefinic moieties into two groups of three with respect to their π-bonding strengths to the metal atoms. The parallel correlation between J_{AB} and $\bar{\delta}_H$ can be seen in Fig. 5 where the correlation is embodied in a line passing near the point for the free dba molecule (J_{AB}; 16.0 Hz and $\bar{\delta}_H$; 7.42 ppm in $CDCl_3$ at 25 °C) showing that the reduction of J_{AB} causes



Fgi. 5. A correlation between J_{AB} and δ_H of olefinic protons of dba. ○: $Pd_2(dba)_3$ and ●: free dba.

the high field shift of $\bar{\delta}_H$. This suggests[19] that the coupling is mainly influenced by the same source as that for the chemical shift $\bar{\delta}_H$, *i.e.* the amount of π-back donation. A similar result has also been discussed with the divalent Pt–olefin complexes.[20]

The reason for differing degrees of π-back donation in the olefinic moieties requires discussion. In $Pd_2(dba)_3$, the factors affecting the strength of π-bonding may be limited to the geometries around the metal–olefin bond. Two geometrical factors emerge from the structural data[2] on a crystal of $Pd_2(dba)_3(CH_2Cl_2)$.[21] The first one is the tilt angle of the olefinic double bond to the trigonal plane which the metal atom makes with the centers of the three olefinic double bonds. These angles are 9, 17, 21, and 37° for the *s-trans* olefins as compared to 67 and 80° for the *s-cis* olefins. The molecular models of the binuclear systems generally suggest that the double bonds of the *s-trans* and those of the *s-cis* olefin are forced parallel and perpendicular to the trigonal plane, respectively, due to conformational constraints. The recent molecular orbital treatment[22] of tris-(ethylene)nickel $Ni(C_2H_4)_3$ has shown that the "in plane" configuration is more effective in the π-back donation than the "up right" configuration. If this rule could be immediately applied to the present case the *s-trans* olefin would form the stronger π-bonding with the Pd atom than the *s-cis* olefin. However, as already seen it was not always so. Therefore the double bond tilting may not be the main factor in determining the strength of each metal–olefin π-bonding in $Pd_2(dba)_3$. The second factor, the distance between the olefinic double bond and the Pd atom, may be responsible for the π-bonding strength. The distances measured with the average of the metal–olefinic carbon distances fall into two ranges of 2.19—2.22 Å for the three *s-trans* and 2.28—2.30 Å for the one *s-trans* and two *s-cis* olefins. It is to be expected that the shorter ones cause better π-back donation through the improved overlapping of the metal hybridized orbital with the olefin π^*-orbital. For example, in the complexes such as $[PtCl_3(olefin)]^+$,[23] $PtCl_2$(4-methylpyridine *N*-oxide)(olefin),[24] and PtX-(acac)(olefin)(X=Cl, Br)[25] stronger shielding of the olefinic proton has been observed in ethylene as compared with the substituted ethylenes. This may be explained in terms of an easing of approach of the small ethylene molecule to the metal atom.[4] Thus it may be infered that the same mechanism operates for the present binuclear complex in solution, where the olefinic moieties **d**, **e**, and **f** with the stronger π-back bonding are closer and the olefinic moieties **a**, **b**, and **c** are more distant from the Pd atom.

The asymmetric allocation, probably forced by the minimal potential requirement, in the conformations of the dba molecules to the Pd atoms results in a slight distortion of the trigonal symmetry, and makes the olefinic moieties maintain their individual characteristics even in solution. The characteristics in the π-bonding occur from the geometry around each metal–olefin bond, especially the metal–olefin distance settled by the total configuration of the complex rather than the direction of the olefinic double bond to the trigonal plane.

Experimental

Materials. 1,5-Di(phenyl-d_5)-1,4-pentadien-3-one $(C_6D_5CH{=}CH)_2CO$, 1,5-di(phenyl-d_5)-1,4-pentadien-3-one-1,5-d_2 $(C_6D_5CD{=}CH)_2CO$, and 1,5-di(phenyl-d_5)-1,4-pentadien-3-one-2,4-d_2 $(C_6D_5CH{=}CD)_2CO$ were prepared by the same method as described elsewhere.[12] Tris[1,5-di(phenyl-d_5)-1,4-pentadien-3-one]dipalladium(chloroform) $[(C_6D_5CH{=}CH)_2CO]_3Pd_2(CHCl_3)$ was prepared according to the procedure in the preceding paper.[3] Tris[1,5-di(phenyl-d_5)-1,4-pentadien-3-one]dipalladium(dichloromethane) $[(C_6D_5CH{=}CH)_2CO]_3Pd_2(CH_2Cl_2)$ was prepared by allowing a dichloromethane solution of $[(C_6D_5CH{=}CH)_2CO]_3Pd_2(CHCl_3)$ to deposit deep violet needle-like crystals; mp 137—138 °C. Tris[1,5-di(phenyl-d_5)-1,4-pentadien-3-one-1,5-d_2]dipalladium(chloroform) $[(C_6D_5CD{=}CH)_2CO]_3(CHCl_3)$ and tris[1,5-di(phenyl-d_5)-1,4-pentadien-3-one-2,4-d_2]dipalladium(chloroform) $[(C_6D_5CH{=}CD)_2CO]_3Pd_2(CHCl_3)$ were also prepared by a method similar to that used to prepare $[(C_6D_5CH{=}CH)_2CO]_3Pd_2(CHCl_3)$. These gave deep violet needle-like crystals; mp 126—128 °C and 125—127 °C in 85 and 95% yield, respectively.

^1H NMR Measurements. A NMR sample was prepared as a solution containing a saturated amount of a deuteriated complex (smaller than 1%) and a trace of tetramethylsilane in the respective deuteriated solvent. The ^1H NMR spectrum was recorded on a JEOL PS-PFT 100/EC 100 pulsed Fourier transform system operating at 100 MHz with an internal deuterium lock. Typically, 8192 data points were taken over a 1 kHz spectral width at a tilt angle 45°, repeated at 4.2 s intervals. An EC 100 computer was also used, in addition to its ordinary use for the Fourier transformation, pattern accumulation, and data reduction, to simulate an observed spectrum by following a program written by JEOL. The sample used for the NOE experiment was degassed by repeated freezing and thawing under vacuum and measured at low temperature (−50 °C) set by a variable temperature unit VT-3C attached to the spectrometer.

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6) A high field shift of olefinic proton signals on coordination may be attributed to π-back bonding[7] rather than σ-dative bonding in the Dewar-Chatt-Duncanson model:[8,9] the high field shift is remarkable (2—3 ppm) in Pd^0 and Pt^0 complexes where the π-bonding plays a major role in the overall metal–olefin bond, while the shift is relatively small (0.5—1.5 ppm) in Pd^{II} and Pt^{II} complexes showing nearly equal contribution of the π and σ-bonding. There is almost no shift or a slightly low field shift in Ag^I and Au^I adducts of olefin where the σ-bonding is operative.

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10) Although the amount of up field shift of the $\bar{\delta}_H$ values thus varies significantly, the average up field shift is 1.51 ppm, being small in comparison with the shifts (*loc. cit.*) in the other zerovalent Pd-olefin complexes.[11] This implies that the Pd–olefin bonding, as a whole, in $Pd_2(dba)_3$ is comparatively weak. It explain well the comparatively long Pd–olefin distance averaged as 2.25 Å.[2]

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13) This criterion may be a generality for other dba complexes. For example, in (pentamethylcyclopentadienyl) (dibenzylideneacetone) rhodium (C_5Me_5) (dba) Rh the δ_{AB} value has been found to be 1.30 ppm,[14] indicating an *s-trans* form for the olefinic moiety of the dba ligand. Indeed X-ray analysis[15] of the complex has shown the dba ligand to be in the *s-trans, trans* conformation. As indicated by the above example and observed for the other dba complexes,[16] both the δ_{AB} values of the coordinated *s-cis* and *s-trans* olefin, in most cases, tend to become somewhat small compared with the corresponding values for the free dba (0.5 for *s-cis* and 1.5 ppm for *s-trans*). Probably this is because the intrinsic term[12] of δ_{AB} which is independent of the conformational change is reduced as a consequence of the decrease of the π-bond nature in the olefinic double bond upon coordination.

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16) The complexes are $Pt_2(dba)_3$, $Pt(dba)_3$, and $Pd(dba)_3$ (to be published).

17) The carbonyl group contributes to the long range shielding of the olefinic protons.[12]

18) Framework molecular model (Prentice Hall) was successively used to derive the rule, and also showed that the schemes III and IV do not violate the rule.

19) Both J_{AB} and $\bar{\delta}_H$ were found to be independent of the conformational change between *s-cis* and *s-trans* forms.[12]

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21) No discernible geometrical factors on $Pd_2(dba)_3(CHCl_3)$ crystals has been obtained owing to disorder or excessive thermal motion.[3]

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