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NMR Studies of Zerovalent Metal π-Complexes of Dibenzylideneacetone. III. Conformation and Bonding of the Mononuclear Palladium and Platinum Complexes

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Synopsis. ^{1}H-NMR spectorscopy of the M[(C$_6$H$_5$-CH=CH)$_2$CO]$_3$ (M=Pd,Pt) complexes revealed that the coordinated olefinic moieties are fixed in the *s-trans* form, while the uncoordinated ones are fluxional around the *s-cis* form. The fluxional behavior of the uncoordinated olefins was explained in terms of the π-back donation in the complexes.

The dibenzylideneacetone (dba) ligand provides a unique series[1,2] of zerovalent Pd and Pt complexes in which only the olefinic double bond participates in the bonding to the metal. As has been reported in the preceding papers,[3,4] the binuclear complexes, M(dba)$_3$ (M=Pd, Pt), retain a rigid structure, even in solution, where the two olefinic double bonds of dba are separately joined to the two metal atoms. However, the mononuclear complexes, M(dba)$_3$ (M=Pd, Pt), are expected to be in a more flexible form because of the existence[5] of olefinic portions free from coordination. We wish to report here on the fluxional behavior of the free olefinic portions, seen by ^{1}H-NMR spectroscopy, and on its correlation with the π-back bonding nature in the complexes.

Results and Discussion

Figure 1 shows the ^{1}H-NMR spectra of the compounds, M[(C$_6$D$_5$CH=CH)$_2$CO]$_3$ (M=Pd, Pt). Two kinds of AB quartet patterns are found in both spectra, where the high-field one and the low-field one originate from the protons of the coordinated olefin and from those of the free olefin in a given dba ligand respectively. The NMR parameters are gathered in Table 1, where δ_A and δ_B are the chemical shift of the proton on the carbonyl side (H$_A$) and that on the phenyl side (H$_B$) respectively.

As has previously been discussed,[3,4,6] the conformation of the olefinic moiety of the dba ligand can be discriminated from the magnitude of the internal shift $\delta_{AB}(=\delta_B-\delta_A)$; $\delta_{AB}\leqslant 0.4$ for the *s-cis* form and $\delta_{AB}\geqslant 1.0$ ppm for the *s-trans* form. Therefore, the coordinated olefins with δ_{AB} of 1.22 for the Pd complex and that of 1.08 ppm for the Pt complex are found to be in the *s-trans* form. On the other hand, the uncoordinated olefins have δ_{AB}'s of 0.50 and 0.82 ppm for the respective complex, comparable to that of 0.63 ppm for free dba.

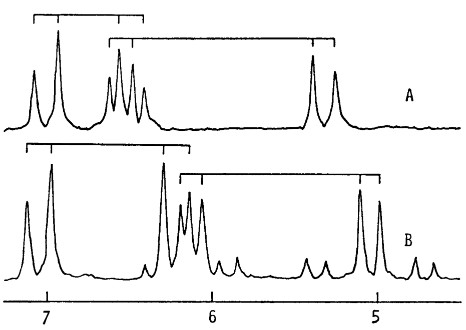


Fig. 1. ^{1}H-NMR spectra of Pd[(C$_6$D$_5$CH=CH)$_2$CO]$_3$ (A) and Pt[(C$_6$D$_5$CH=CH)$_2$CO]$_3$ (B), measured in CDCl$_3$ at −60 °C.

TABLE 1. ^{1}H-NMR PARAMETERS OF Pd(dba)$_3$, Pt(dba)$_3$, AND FREE dba IN CDCl$_3$ AT −60 °C

	Olefins	J_{AB} / Hz	δ_A / ppm	δ_B / ppm	δ_{AB} / ppm	$\bar{\delta}_H$ / ppm
Pd(dba)$_3$	C[a]	13.3	5.343	6.562	1.219	5.953
	U[b]	15.4	6.517	7.017	0.500	6.767
Pt(dba)$_3$	C[c]	11.7	5.075	6.153	1.078	5.614
	U	15.3	6.257	7.076	0.819	6.666
Free dba		16.0	7.188	7.821	0.633	7.504

a) C; coordinated. b) U; uncoordinated. c) J_{Pt-A}; 65.9 and J_{Pt-B}; 44.3 Hz. δ_A and δ_B; in ppm with tetramethylsilane. $\delta_{AB}=\delta_B-\delta_A$ and $\bar{\delta}_H=(\delta_A+\delta_B)/2$.

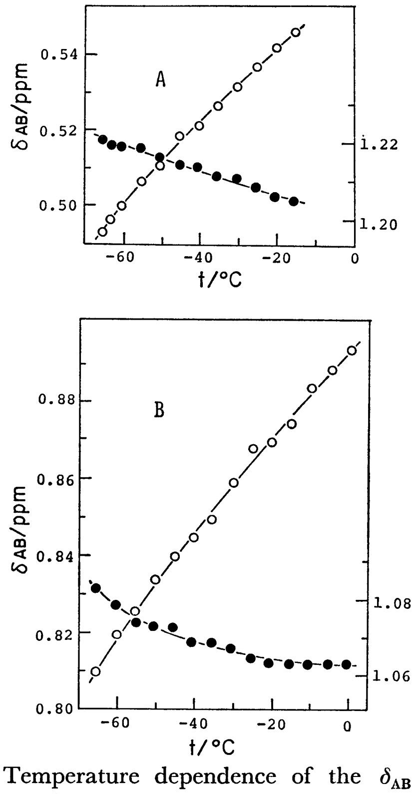
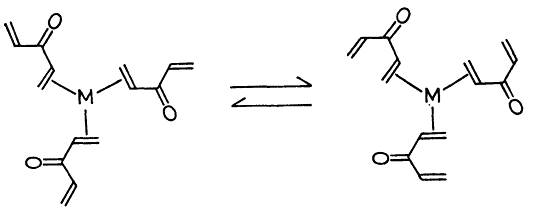


Fig. 2. Temperature dependence of the δ_{AB} for the coordinated (●; right ordinate) and uncoordinated olefins (○; left ordinate): A; Pd(dba)$_3$ and B; Pt(dba)$_3$ in CDCl$_3$.

In order to ascertain the detail of the ligand conformation, we have examined the temperature dependence of δ_{AB} (Fig. 2). With an increase in the temperature, the δ_{AB}'s for the coordinated olefins decrease slightly, indicating a characteristic aspect of the behavior[4] of the fixed *s-trans* form,[7] while the δ_{AB}'s for the uncoordinated olefins increase markedly, as in free dba, in which the olefins are in an equilibrium[6] between the major *s-cis* and minor *s-trans* forms. Thus, the temperature dependence of δ_{AB} for the uncoordinated olefins was analyzed assuming the following equilibrium and thermodynamic relation:



$$\ln\frac{\delta_{AB}^{obsd}-\delta_{AB}^{t}}{\delta_{AB}^{c}-\delta_{AB}^{obsd}} = -\frac{\Delta H}{RT}+\frac{\Delta S}{R},$$

$$\delta_{AB}^{obsd} = c^{c}\delta_{AB}^{c} + c^{t}\delta_{AB}^{t} \quad (c^{c}+c^{t}=1).$$

Here, δ_{AB}^{c} and δ_{AB}^{t} are the intrinsic values of δ_{AB} for the *s-cis* and *s-trans* forms. When the optimal values[8] of ΔH and ΔS are adopted, δ_{AB}^{c} and δ_{AB}^{t} are 0.44 and 1.48 ppm for the Pd complex and 0.50 and 1.47 ppm for the Pt complex; the values are close to the corresponding values[6] of 0.44 and 1.59 ppm for free dba. The conformer populations of the *s-cis* form (c^{c}) are 0.90(−15°) and 0.94(−60°) in the Pd complex and 0.62(−15°) and 0.67(−60°C) in the Pt complex.

Thus, the dba ligands of the Pd complex might exist almost entirely in the *s-cis*, *s-trans* form, as in the crystalline state,[5] while those of the Pt complex could contain an appreciable amount of the *s-trans*, *s-trans* form. The conformational difference between the two complexes can be understood in terms of the metal-olefin π-back donation. As has already been clarified by an INDO calculation of the dba molecule,[6] the *s-trans*, *s-trans* form has a highly repulsive interaction arising mainly from the proximity of the two H_B protons, and so becomes destabilized in the free state. The coordination to the metal, however, causes a little change in the geometry of the dba molecule, such as an out-of-plane bending[9] of the olefinic hydrogens, which diminishes the core repulsion within the ligand and makes feasible the existence of the *s-trans*, *s-trans* form. Such a stabilization effect of *s-trans*, *s-trans* form would be more effective in the Pt complex than in the Pd complex, since the π-back donation is stronger in the Pt complex, as is confirmed[4] by the values of the *trans*-olefinic coupling, J_{AB}, and the mean shift, $\bar{\delta}_H[=(\delta_A+\delta_B)/2]$. We conclude that the π-back donation not only plays a major role in determining the bonding strength of the coordinated olefin in the zerovalent metal complex, but also determines the conformational attitude of the uncoordinated counterpart.

Experimental

The complexes, $M[(C_6D_5CH{=}CH)_2CO]_3$ (M=Pd,Pt), were prepared by the method of Moseley and Maitles,[10] using the dba-d_{10}.[6] To assign δ_A and δ_B, the $M[(C_6D_5CD{=}CH)_2CO]_3$ and $M[(C_6D_5CH{=}CD)_2CO]_3$ compounds were synthesized by a similar method. The samples were prepared at *ca.* −60 °C and were measured on a JEOL PFT/EC 100 spectrometer. Least-squares calculations for the analysis of δ_{AB} were performed on an IBM 1130 machine at Josai University.

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7) The framework molecular model shows the rotation about C–C(O) bond in the coordinated olefinic portion to be restricted because of a sterical hindrance among the neighbouring ligands.

8) ΔH=6.1 in $Pd(dba)_3$, 2.5 kJ mol^{-1} in $Pt(dba)_3$, and $\Delta S=R\ln 2=5.76$ J K^{-1} mol^{-1} in both complexes. For the procedure used to evaluate the thermodynamic relation, see Ref. 6.

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