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Evidence for an Oscillating Intramolecular Ligand Exchange Mechanism Due to an Alternation between Two Identically Strong Aliphatic Hydrogen to Palladium Interactions

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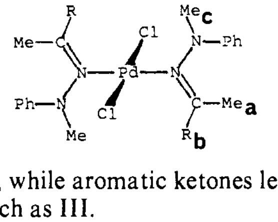
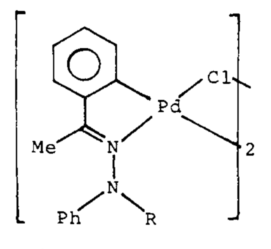
Abstract: The ^{1}H NMR spectra of compound I reveal: (i) the inequivalence of the two hydrazone ligands at low temperature; (ii) the stereodynamic behavior of the compound; (iii) a remarkably large low-field shift for one of the C–Me groups. This latter fact was traced to the effect of the anisotropy of palladium and affords evidence for a strong Pd···HC interaction with one of the methyl groups, resulting in the nonequivalence of the two ligands. The existence of this interaction was further demonstrated by the study of compounds II and IV. The coalescence of all signals in the NMR above 50 °C showed that the two ligands exchange roles rapidly and that there is an alternation in the Pd···Me interaction. This exchange is intramolecular ($\Delta G^{\ddagger} = 69$ kJ mol^{-1}). The analysis of the variations of the chemical shifts with temperature, in terms of the paramagnetic anisotropy of palladium, enabled us to tentatively propose, as the most probable exchange process, a concerted oscillation, rather than a hindered but complete rotation, of the two ligands about the Pd–N bonds.

Dehand and Pfeffer[2,3] recently pointed out that substituted hydrazines, when coordinated to palladium, react with organic ketones to give hydrazones which remain coordinated to the metal through the condensed nitrogen. Depending on the nature of the ketone, the reaction led to two types of compounds: with aliphatic ketones, σ(N)-coordinated bishydrazone compounds were obtained, as for example compounds I and II, while aromatic ketones led to orthometalated compounds such as III.



I R = Me

II R = CH(Me)$_2$



III R = H, Me, Ph

The ^{1}H NMR spectra of compound I (Figure 1) reveal three striking features: (i) the inequivalence of the two hydrazone ligands at low temperatures; (ii) the stereodynamic behavior of the compound; (iii) the remarkably large low-field shift for one of the C–Me groups.

This last feature suggested a favored interaction between the metal and one of the methyl groups. Indeed Vrieze et al. have recently shown that such nonbonded metal-alkyl or -aryl interactions exist in platinum(II) azo,[4] imine,[4] and sulfurdiimine[7] compounds. They also isolated orthometalated compounds by reacting aromatic azo and imine ligands with Ir(I) and Rh(I) chlorides,[5] and showed the importance of the basicity of the metal in these C–H bond-breaking reactions.[6]

Compounds I and II appear to be the first examples in which a molecule contains two identical ligands, each likely to give such a metal-alkyl interaction; the two ligands are thus in a situation where they can compete for this interaction with the result that they will become inequivalent in solution. The investigation of such a situation was expected to provide a better knowledge of such metal-alkyl interactions, and is also thought to be relevant to the question of orthometalation.

This paper also describes the dynamic process which causes the hydrazone ligands to become equivalent in the NMR at higher temperatures, and presents evidence for a new intramolecular exchange mechanism based on the concerted oscillation of the two ligands with respect to the coordination plane. Additional data for this investigation were obtained

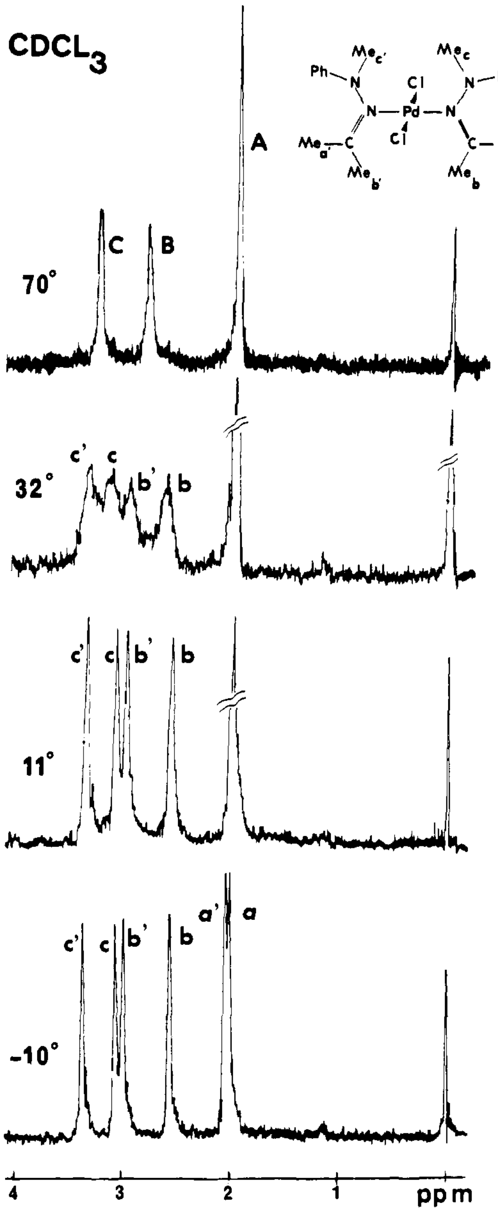
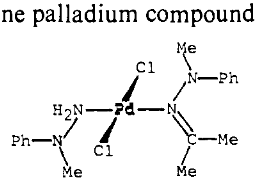


Figure 1. Temperature dependence of the proton spectra for a 0.07 M solution of compound I in $CDCl_3$.

from the synthesis and study of the first mixed hydrazine-hydrazone palladium compound IV.



IV

Experimental Section

General. Compound I was prepared according to the literature.[2] The ^1H NMR spectra were recorded on a JEOL C-60 HL spectrometer, and the ^1H NMR spectrum for compound II in toluene was recorded on a JEOL PFT-100 spectrometer.

***trans*-Dichlorobis(isopropyl methyl ketone *N*-phenyl-*N*-methylhydrazone)palladium(II). $PdCl_2(PhMeNN{=}CMe\text{-}i\text{-}Pr)_2$ (II).** *trans*-Dichlorobis(*N*-phenyl-*N*-methylhydrazine)palladium(II) (100 mg, 0.24 mmol) was added to 5 mL of boiling isopropyl methyl ketone; a red solution was obtained within 2 min; 100 mL of ether was added to the cooled solution, which was then filtered. The product crystallized after 24 h. The yellow crystals were collected on a filter, washed with acetone (5mL), and dried under vacuum (yield 20%). Anal. Calcd for $C_{24}H_{36}Cl_2N_4Pd$: C, 51.67; H, 6.46; N, 10.05. Found: C; 50.65; H, 7.25; N, 10.35. Main infrared vibrations (KBr and polyethylene, cm^{-1}): $\nu(C{=}N)$ 1600 (s); $\nu_{As}(Pd\text{-}Cl)$ 338 (s).

***trans*-Dichloro(*N*-phenyl-*N*-methylhydrazine) (acetone *N*-phenyl-*N*-methylhydrazone)palladium(II). $PdCl_2(PhMeNNH_2)(PhMeNN{=}CMe_2)$ (IV).** *trans*-Dichlorobis(*N*-phenyl-*N*-methylhydrazine)palladium(II) (100 mg, 0.24 mmol) was dissolved in boiling acetone. An orange-red solution formed after 5 min. The solution was evaporated and the residue extracted with 10 mL of CH_2Cl_2. The solution was filtered and 50 mL of pentane was added; after one night the product separated as thin orange-red needles (yield 40%). Anal. Calcd for $C_{17}H_{24}Cl_2N_4Pd$: C, 44.21; H, 5.20; N, 12.14. Found: C, 44.35; H, 5.05; N, 12.25. Main infrared vibrations (KBr and polyethylene, cm^{-1}): $\nu_{As}(NH_2)$ 3195 (s); $\nu_s(NH_2)$ 3098 (s); $\nu(C{=}N)$ 1632 (s); $\delta(NH_2)$ 1600 (vs); $\nu_{As}(PdCl)$ 340 (vs).

Results and Discussion

I. The Nonbonded Palladium-Methyl Interaction. A typical ^1H NMR spectrum measured at −10 °C on a 0.07 M solution of *trans*-$PdCl_2(PhNMeN{=}CMe_2)_2$ (I) in $CDCl_3$ is given in Figure 1. It shows the presence of two signals for the N-Me and for each of the two C-Me groups (respectively signals c and c′, a and a′, b and b′). These six signals remain of equal area throughout the accessible concentration range (0.18–0.013 M) and when the polarity of the solvent is varied on going from $CDCl_3$ to toluene and nitromethane, which implies that all six methyl group signals belong to the same molecular species. This in turn means that the two hydrazone ligands are nonequivalent at low temperature in the solution, contrary to what has been found in the solid where the molecule is centrosymmetric.[8]

The NMR assignments (Table I) are based on a comparison with the spectrum of the free ligand. The assignment of signal b′ to a C-Me group and of signal c to a N-Me group is supported by the coalescence of these signals with signals b and c′, respectively, when the temperature is raised.

The differences (Δ) in chemical shifts between the free and coordinated ligands are made explicit in Table I. The major cause of the observed large antishielding effects is assigned to the anisotropy of the magnetic susceptibility of palladium. This anisotropy is known to cause a downfield shift for the protons which are close to the metal and above its coordination plane.[4–7,9–11]

Signals a and a′ are only slightly shifted, indicating that they undergo little influence from the metal. On the other hand, the permanent inequivalence of the methyl groups bound to carbon (signals a and b remaining distinct even at 90 °C) implies that there is no rotation about the N=C bond. Thus the Me (a) and (a′) groups always remain far from the metal.

The most interesting clue is given by the large low-field shift of proton b and to an even greater extent of proton b′ (respectively 0.64 and 0.95 ppm from the free ligands shifts), indicating that they are closer to the metal than protons a and in a more suitable position above its coordination plane to undergo its antishielding effect. The recently published crystal structure data for compound I[8] allowed us to estimate the $Pd\cdots H_b$ distance in the solid to be 2.4 Å, assuming a CCH_b angle of 109.3° and a $C\text{-}H_b$ bond length of 1.06 Å. This distance of contact between the metal and proton H_b is very short: distances of that order (2.45 Å) have been estimated for *cis*-dichlorobis(methylamino(methoxy)carbene)palladium,[12] of which the structural analogies with compound I have been pointed out.[13] Furthermore, a contact distance of 2.6 Å was found between palladium and the ortho hydrogen atom of the phenyl ring in dichlorobis(azobenzene)palladium(II), which is assumed to be an intermediate in the orthopalladation of azobenzene.[14]

Thus both the NMR shift data and the Pd···H distance in the solid point to the existence of a strong "nonbonded" interaction between palladium and protons b′ in compound I.

Since the two coordinated hydrazone ligands are chemically identical, they can compete with one another with respect to

Table I. ^{1}H NMR Data for *trans*-$PdCl_2[PhNMcN{=}CMeR]_2$ (I, R = Me; II, R = $CHMe_2$) and *trans*-$PdCl_2[PhNMeN{=}CMe_2]$ $[PhNMeNH_2]$ (IV)

Compd	Temp, °C	CCH_{3b} or $\mathit{CH}(CH_3)_2$	CCH_{3a}	$CH(\mathit{CH}_3)_2$	NCH_3	NH_2
I δ^a	82	2.85	1.98		3.29	
δ	0	2.70 (b)	2.03 (a)		3.20 (c)	
		3.01 (b')	2.07 (a')		3.33 (c')	
Δ^b	0	0.64 (b)	0.13 (a)		0.25 (c)	
		0.95 (b')	0.17 (a')		0.38 (c')	
$3\Delta^b$	0	1.92 (b)				
		2.85 (b')				
IV δ	82	3.02	2.12		3.22 (hydrazine)	4.90
					3.37 (hydrazone)	
δ	0	3.02	2.20		3.17 (hydrazine)	4.92
					3.35 (hydrazone)	
Δ	0	0.96	0.30			
$3\Delta^b$	0	2.88				
II δ	−13	4.63 (II_1)	1.93 (II_1)	1.13 (II_1)	3.45 (II_1)	
Δ^b	−13	2.09 (II_1)				
δ	−13	4.63 (b) (II_2)	1.93 (II_2)	1.13 (b) (II_2)	3.34 (c) (II_2)	
		5.20 (b')	1.93	1.37 (b')	3.44 (c')	
Δ	−13	2.09 (b) (II_2)				
		2.70 (b')				

[a] In parts per million relative to Me_4Si in $CDCl_3$. [b] Δ refers to the chemical shift difference between the resonances of the complex and the free hydrazone.

that interaction. As a result the Pd-Me interaction is at any given moment stronger with one of the two ligands, as shown by the larger value of Δ found for b′ as compared to b at −10 °C. The ^{1}H NMR is thus able to detect such a preferential interaction of one of the two ligands with the metal at low temperature. This difference in interaction is obliterated above 50 °C when the resonances of the two ligands have coalesced, indicating that they exchange roles rapidly on the NMR time scale: only an average value is then found (Δ = 0.78 ppm).

Additional support for these views was provided by the study of the mixed *trans*-palladium hydrazine (hydrazone) compound IV for which the methyl group b resonance was expected to exhibit a comparably important downfield shift. Moreover in this case there is no possible competition between the two ligands, and this important low-field shift was thus expected to be retained unchanged while the temperature was increased. It was indeed found (Table I) that Pd-Me_b interaction is the strongest (Δ = 0.96 ppm). This figure is the same as that measured for the most shifted signal b′ in compound I in its "frozen" low-temperature structure. No splitting of the ligand signals was observed in the NMR of IV down to −60 °C, which rules out an isomerization arising either from restricted rotation about the N-N bond,[15] from inversion of nitrogen, or from a change in donor atom in the ligand.

Further evidence for an intramolecular Pd···H_b interaction in the hydrazone complexes was obtained from the study of *trans*-$PdCl_2(PhMeNN{=}CMe\text{-}i\text{-}Pr)_2$ (II), in which two of the C-Me groups have been substituted by isopropyl groups. The low-temperature ^{1}H NMR spectrum (Figure 2) indicates the presence of two isomers. The three signals arising from each Me group, two of which have the same area, are better separated when the spectra are measured in toluene rather than in $CDCl_3$. However, the poor solubility of compound II in toluene prevented us from using this solvent in a routine manner. The two isomers, the structures of which will be discussed below, are in ca. 55/45 ratio. In the more abundant one, II_1, the two ligands are equivalent at low temperature and give the set of signals labeled 1 in Figure 2, while they are nonequivalent in the other one II_2, as shown by the two sets of signals of equal areas labeled 2 in Figure 2.

Inspection of the chemical shift differences Δ between the free and coordinated hydrazone resonances for the two isomers shows that coordination has little effect on the chemical shifts of all C-Me groups, including those of the isopropyl groups. The N-Me resonances exhibit about the same low-field shifts as in compounds I and IV. On the other hand, a drastic downfield shift is found for the isopropylic protons upon coordination (Δ = 2.70 and 2.09 ppm for isomer II_2; 2.09 ppm for isomer II_1), indicating that these protons stand very close to the metal.

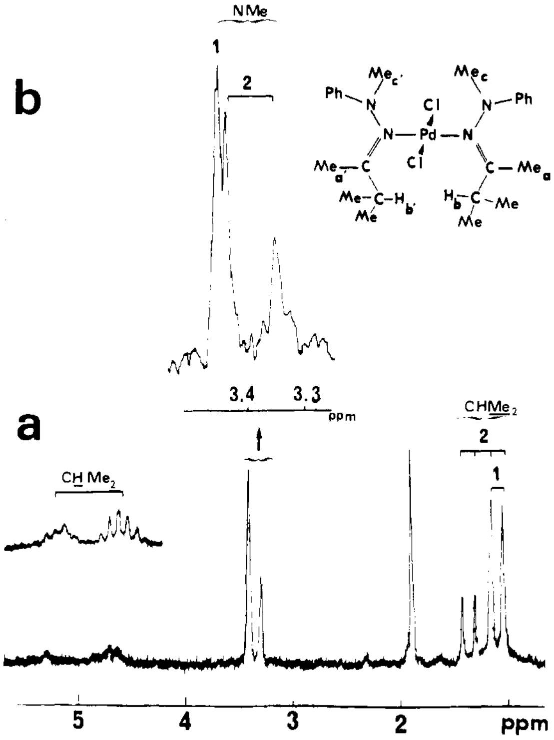


Figure 2. Proton NMR spectrum of compound II: (a) at 60 MHz on a 0.013 M solution in $CDCl_3$ at −10 °C; (b) at 100 MHz on a saturated solution in toluene at 0 °C (5000 scans).

It is also very significant that the same values are obtained for the palladium-induced low-field shifts if one multiplies the observed Δ by the number of protons which undergo the effect, i.e., if one assumes that the influence of the metal is equally shared by the three protons of the fast rotating methyl groups in compounds I and IV. In this way one finds 2.85, 2.70, and

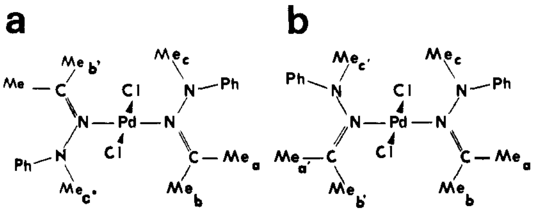


Figure 3. Conformations for compounds I and II in solution: (a) anti; (b) syn.

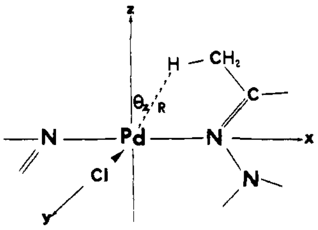


Figure 4. Molecular axis for compound I.

2.88 ppm for the strongest interacting H_b protons in compounds I, II_2, and IV, respectively, and 1.92, 2.09, and 2.09 for the less-influenced protons in compounds I, II_1, and II_2, respectively.

This is consistent with a conformational preference in both isomers of compound II, in which the hydrogen atom of the isopropylic group remains near the z axis. Rotation about the N-C bond is here again hindered and the isopropylic proton remains close to palladium. The two hydrazone planes in II_1 form the same angle with the coordination plane of the metal, while they do not in II_2 where the two ligands are inequivalent. Finally the two isomers interconvert rapidly on the NMR time scale. Unfortunately, the poor solubility of compound II precluded any quantitative analysis of the temperature dependence of the spectra in this case.

It is important to note that precise knowledge of the relative structural disposition of the two ligands is not necessary in order to establish the existence of an interaction between the palladium atom and the protons of a methyl or isopropylic group in compounds I and II. Any further discussion of the structure is at present neither possible nor essential. The nonequivalence of the two ligands in compounds I and II_2 only supposes that they form two different angles with the coordination plane of the metal. The question which remains is whether the structure, although it can no longer be centrosymmetric, will still be pseudo-anti, i.e., close to what it is in the solid, or if it is rather pseudo-syn with the identical parts of the ligands turned on the same side of the coordination plane (Figure 3).

A syn orientation of the ligands was found in the structurally analogous *cis*-dichlorobis(methylamino(methoxy)carbene)-palladium in the solid state; furthermore, in this latter compound, a preferential metal-hydrogen interaction with one of the ligands was clearly evidenced by difference in Pd···H contacts: 2.45 Å for one ligand against 3.00 Å for the other one.[12] Such a marked dissymmetry is to be excluded for compound I in the solid state where it has the anti structure, even though the accuracy of the structure determination is relatively low.[8]

The NMR data for the only detected isomer of compound I are compatible with both structures in solution. The presence of two isomers for compound II while only one is detected for I may be due to steric factors: space-filling molecular models show that for compound II the syn isomer is more crowded than the anti isomer, while there is no obvious difference for compound I. In both isomers of compound II, the Me groups remain far from palladium, which leaves two possible isomers, pseudo-syn and pseudo-anti, but again no obvious assignment arises from the NMR. However, since the Δ data indicate the same preferential metal-hydrogen interaction in compounds I and II_2 ($m\Delta$ = 2.70 ppm), these are expected to have the same structure. The reason why the two equivalent ligands in II_1 ($m\Delta$ = 2.09 ppm) remain away from the interacting position on top of the metal is not yet understood.

II. Stereodynamic Behavior of *trans*-$PdCl_2(PhMeN\text{-}N{=}CMe_2)_2$: Evidence for an Oscillating Exchange Mechanism. The collapse of the NMR signals for compound I (Figure 1) occurs at 8 ± 1 °C for a and a′, at 39 ± 1 °C for c and c′, and at 45.5 ± 1 °C for b and b′, showing that the two hydrazone ligands exchange roles rapidly on the NMR time scale. Neither the low-temperature spectrum nor the coalescence temperatures were affected by the addition of an excess of free ligand (up to 10 mol/mol). The spectra also remained unchanged on varying the concentration of compound I, but the concentration range accessible (0.12-0.013 M) was limited. Since small amounts of compound IV were detected in aged solution of I, we also checked that the addition of compound IV has no influence on the spectra of compound I. From these experiments it can be assumed that the exchange process is likely to be intramolecular.

The following activation free enthalpies were then calculated from the line shapes for a two-site model for each of the three coalescence temperatures separately: $\Delta G^{\ddagger}{}_a = 67 \pm 2$, $\Delta G^{\ddagger}{}_b = 69 \pm 1.5$, and $\Delta G^{\ddagger}{}_c = 69 \pm 1.5$ kJ mol^{-1}, from the collapse of signals a and a′, b and b′, and c and c′, respectively. The first value is probably the least reliable, since signals a and a′ lie very close together, and the error may be underestimated.[16] Since all three activation free enthalpies are equal within experimental error, it is likely that the same mechanism is responsible for the three observed coalescences. On the other hand, we have seen that there is no NMR detectable rotation about the N=C bond up to 90 °C, when the product starts decomposing, while on the contrary the rotation about the N-N bond remains unrestricted down to at least −60 °C.

The intramolecular exchange process of the two hydrazone ligands tends to keep the metal pseudo five-coordinated at any given moment, each Me_b group alternatively being right in the cone of anisotropy of palladium and undergoing a strong Pd···H interaction, thus displaying the larger low-field shift. The motion of the two ligands must be concerted, so that at any given moment the angle between them is different from 0 or 180°. From the standpoint of energy, the molecule possesses two symmetrical potential wells, each associated with the existence of one palladium-hydrogen interaction with one of the two ligands.

The alternating character of the Pd···Me interaction thus being established, it became interesting to get some insight into the mechanism by which this alternation occurs. It could result either from a strongly hindered, but complete rotation of the two ligands around the Pd-N bonds, or from an oscillation of the ligands about these bonds.

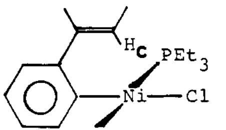
A key observation, which we think should permit the distinction between these two mechanisms, is that there is no significant variation in Me_b chemical shift with temperature, while on the contrary the Me_a resonance moves slightly (by 0.07 ppm) toward higher fields.

Let us indeed consider the average paramagnetic contribution to the shielding constants given in the equation

$$\Delta\sigma = \frac{1}{3R^3} \sum_i \chi_i (1 - 3\cos^2\theta_i) \qquad (1)$$

where R is the Pd···H distance, χ_i the susceptibility along the ith molecular axis, and θ_i the angle between the Pd···H axis and the ith direction[17] (see Figure 4). In a d^8 planar compound such as compound I, the main contribution originates from χ_z, which results in the observed downfield shift. If the rotation around the x axis were free, then the coefficients of χ_y and χ_z would average to zero and there would be a net upfield shift of the methyl groups; but an entirely free rotation is obviously excluded here because of the strong Pd···H interaction.

In the case of hindered rotation about the x axis, the values of θ_z for $\mathrm{H_b}$ protons would also be varied from ca. 0 to 2π; however, the weight of the small values of θ_z, corresponding to $\mathrm{H_b}$ being in the deshielding cone of palladium, would be preponderant in the coefficient of χ_z. This weight would decrease slightly when, the temperature being raised, rotation occurs more frequently, resulting in a decrease in $(1 - 3\cos^2\theta_z)$. The $\mathrm{Me_b}$ resonances would therefore be slightly shifted toward higher fields when the temperature is raised. A parallel but smaller shift would be expected for the $\mathrm{Me_a}$ resonance, since the contribution of χ_z to its chemical shift is less than for $\mathrm{Me_b}$. Such an effect was found in the ^{1}H NMR spectrum of *trans*-chloro(o-α-methylstyrylbis(triethylphosphine))nickel(II) (V), where, as a result of restricted rotation of the propenyl group, $\mathrm{H_c}$ is on top of the metal and its resonance is shifted to high fields when the temperature increases.[18]



V

On the contrary, if the mechanism is an oscillation about the Pd–N bonds, and provided this oscillation is of small amplitude, only little variation of θ_z with temperature would occur: for small oscillations the $\mathrm{Me_b}$ groups stay deep in the cone of anisotropy of the metal during the process, with, as a consequence, $(1 - 3\cos^2\theta_z)$ remaining almost constant. The $\mathrm{Me_b}$ resonance would then be expected to show no significant temperature dependence. On the other hand, the $\mathrm{Me_a}$ groups, which stand further away from the metal, in a region where $(1 - 3\cos^2\theta_z)$ changes more rapidly with θ_z, will experience a stronger upfield shift of their resonance. It is only when the amplitude of the oscillations becomes important, i.e., at higher temperatures, that the upfield shift would become significant for the $\mathrm{Me_b}$ resonances and the two mechanisms (oscillation and hindered rotation) would then no longer be distinguishable.

Thus the fact that there is no significant temperature dependence for the $\mathrm{Me_b}$ resonance, whereas the $\mathrm{Me_a}$ resonance is slightly shifted toward higher fields when temperature increases, is consistent with a concerted intramolecular exchange mechanism occurring through oscillations of small amplitude about the Pd–N bonds. Note that these considerations and conclusions are valid for both an anti and a syn conformation of compound I.

The oscillating process for compound I is further supported by the behavior of compound IV. Indeed no significant temperature dependence of the chemical shifts is found for $\mathrm{Me_b}$, while the slight upfield shift for $\mathrm{Me_a}$ parallels that measured for compound I.

The fact that the process of lowest activation energy is an oscillation does not exclude the possibility of a complete rotation about the Pd–N bonds occurring at higher temperatures. Such a rotation is necessary to account for the interconversion of isomers $\mathrm{II_1}$ and $\mathrm{II_2}$. Unfortunately, due to the low solubility of compound II, we were unable to compare the free activation energies associated with (i) the intramolecular exchange of the two hydrazone ligands in isomer $\mathrm{II_2}$, and (ii) the interconversion of the two isomers $\mathrm{II_1}$ and $\mathrm{II_2}$.

The various likely contributions to $\Delta G^{\ddagger}$ in the oscillating process of compound I are: (i) the breaking of the CH···Pd interaction; (ii) the motion of the two ligands; and (iii) in the case of an anti structure, the oscillation of the palladium atom through its coordination plane, since it would be pseudo-five-coordinated alternatively above and under this plane. Since the transition state implies breaking of the metal–hydrogen interaction, the evaluated activation energy ($\Delta G^{\ddagger} = 69$ kJ mol^{-1}) can be considered as an estimate of the upper limit of Pd···HC interaction. This value is in fairly good agreement with the strength of the CH···Mo interaction previously found in $[\mathrm{Et_2B(pz)_2}]\mathrm{Mo(CO)_2}(\eta^3\text{-allyl})$[19] ($\Delta G^{\ddagger} = 71$ kJ mol^{-1}).

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