Fluxional Behavior of η^1,η^2-Cyclooctenylpalladium Acetylacetonate and Related Complexes

Robert A. Stockland, Jr. and Gordon K. Anderson*

Department of Chemistry, University of Missouri−St. Louis, 8001 Natural Bridge Road, St. Louis, Missouri 63121

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The cyclooctenylpalladium complexes [Pd(η^1,η^2-C_8H_{12}·R)(acac)] exhibit fluxional behavior in solution that equilibrates the acac methyl environments. Free energies of activation for the process have been determined by variable-temperature NMR spectroscopy. These appear to show no dependence on the nature of *exo* substituents, and they are higher for bulky *endo* groups. Lower $\Delta G^{\ddagger}$ values are obtained in more polar solvents or with added phosphines, suggesting the operation of an associative mechanism. In contrast, the platinum complex [Pt(η^1,η^2-C_8H_{12}·OMe)(acac)] is static up to 380 K, as is the *C,N*-bonded palladium species [Pd($C_6H_4N{=}NC_6H_5$-2)(acac)]. These are fluxional, however, in the presence of a tertiary phosphine. The hexafluoroacetylacetonate (hfac) complex [Pd(η^1,η^2-C_8H_{12}·OMe)-(hfac)] exhibits a lower value of $\Delta G^{\ddagger}$ than its acac analogue, with or without added PEt_3. When a phosphine is added to one of the metal complexes, low-temperature ^{31}P NMR studies reveal equilibria involving a phosphine-ligated species, the starting acac complex, and free phosphine. The position of equilibrium depends on the nature of the R group and on the phosphine. The rearrangement is proposed to take place from a five-coordinate species, either by a series of pseudorotations or by way of a turnstile mechanism. Although it is not possible to distinguish between these two, the simplicity of the latter in this case is particularly attractive.

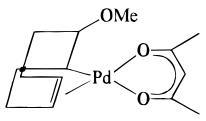
Introduction

Substitution reactions of square planar metal complexes have been studied in considerable detail and are generally believed to take place by associative pathways.[1] Isomerization reactions have also been the subject of some investigations,[2] and although associative mechanisms are widely accepted, dissociative processes involving T-shaped intermediates have also been proposed.[3] Among the associative mechanisms are the traditional consecutive displacement mechanism, as well as intramolecular rearrangements of five-coordinate intermediates. The latter include the well-known Berry pseudorotation, and further evidence has been presented recently[4] for the operation of an alternative "turnstile" mechanism.[5]

During our studies of the stereochemistry of nucleophilic attack on coordinated cyclooctadiene, we prepared a series of cyclooctenylpalladium complexes of the type [Pd(η^1,η^2-C_8H_{12}·R)(acac)].[6] These complexes were characterized by ^1H and ^{13}C NMR spectroscopy and, in some cases, by X-ray crystallography. In the course of the NMR investigations we noticed that the resonances due to the methyl groups of the acetylacetonate (acac) ligands were, in general, broad at ambient temperature, suggesting that the molecules were fluxional. In this paper we report the results of our investigation of the nature of this intramolecular exchange, the effect of solvent on the process, and the effects of added ligands on these and related complexes.

Results

At ambient temperature, the ^1H NMR spectrum of [Pd(η^1,η^2-C_8H_{12}·OMe)(acac)] in $CDCl_3$ solution was found to contain the expected resonances for the cyclooctenyl ring, the methoxy group, and the acac C*H*, but the acac



methyl groups gave rise to two quite broad signals.[6] As the temperature was lowered, these signals sharpened, and at temperatures below 270 K two sharp singlets were observed at 1.87 and 2.00 ppm. As the temperature was raised above ambient, the methyl signals broadened further and coalesced at 318 K, then appeared as one relatively sharp singlet at 1.94 ppm at higher temperatures. The low-temperature spectrum is consistent with the expected static structure, in which one acac methyl group would lie *trans* to the Pd−C σ-bond and the other would be *trans* to the coordinated double bond. As the temperature is raised, the molecule

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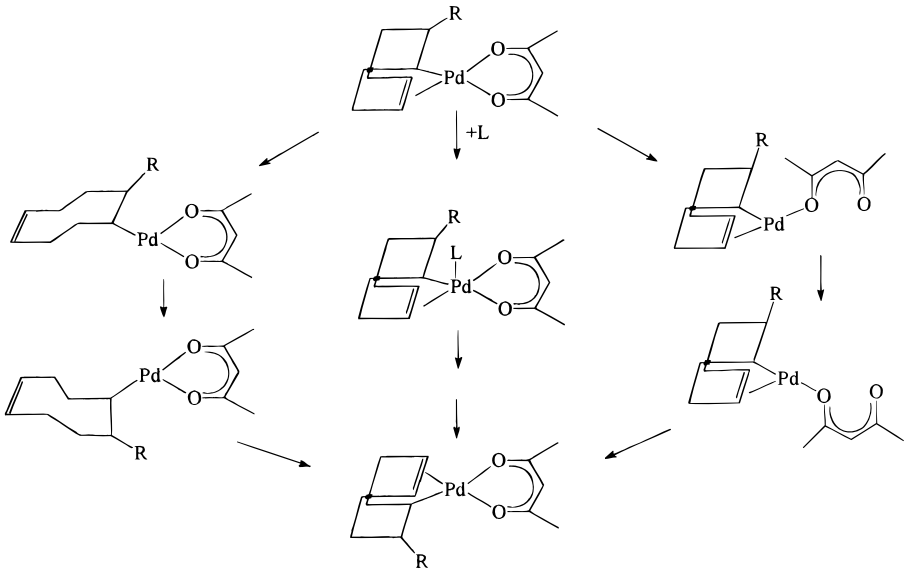
Scheme 1



undergoes a fluxional process, which at the highest temperatures equilibrates the positions of the two acac methyls. Based on the coalescence temperature T_c and the difference between the frequencies of the two methyl signals $\Delta\nu$, a value of 15.5 ± 0.1 kcal/mol may be calculated for $\Delta G^{\ddagger}$ for this process.[7]

One can envision a number of possible mechanisms for this rearrangement. A dissociative process in which either the C=C double bond or one arm of the acac ligand dissociates from the metal, followed by isomerization of the T-shaped species thus formed, could account for the observations. Alternatively, associative mechanisms in which the solvent serves as a weak nucleophile and promotes rearrangement within a five-coordinate intermediate by pseudorotation or some other process are also possible (Scheme 1). Whatever the mechanism, such a rearrangement of a square planar complex containing two bidentate ligands is quite unusual. As mentioned earlier, there has been considerable debate over the years regarding the involvement of associative and dissociative processes in isomerization reactions of square planar metal complexes.[2] Although the present reaction is not an isomerization, since it is a rearrangement between two identical species, the possible mechanisms are likely to be similar.

Changing the solvent to toluene-d_8 resulted in a higher T_c value, and $\Delta G^{\ddagger}$ increased slightly to 16.2 kcal/mol. In contrast, when the more nucleophilic solvent CD_3CN was used, $\Delta G^{\ddagger}$ was reduced to 14.8 kcal/mol. In fact, when CD_3CN was added gradually to a toluene-d_8 solution of [Pd(η^1,η^2-C_8H_{12}·OMe)(acac)], gradual decreases in T_c and $\Delta G^{\ddagger}$ were observed (Table 1). These results appear to be most consistent with a solvent-assisted rearrangement, and even the almost nonpolar toluene molecule may produce a transient η^2-bound species.[8]

We have made a comparison of a series of cyclooctenylpalladium derivatives of the type [Pd(η^1,η^2-C_8H_{12}·R)(acac)] in $CDCl_3$ solution. The results are shown in Table 1, and they reveal the following. The three *exo* isomers (R = OMe, OEt, $CH(CO_2Me)_2$) give identical $\Delta G^{\ddagger}$ values (within experimental error). A smaller $\Delta G^{\ddagger}$ value is found for the *endo* complex [Pd(η^1,η^2-C_8H_{12}·Ph)(acac)] (14.9 kcal/mol), whereas the *endo* derivatives with the bulkier $C_6H_2Me_3$ or $C(CO_2Me)$=$C(CO_2Me)Me$ groups produce slightly larger values (15.9 and 16.1 kcal/mol, respectively).

Table 1. Free Energies of Activation for Complexes of the Type [Pd(η^1,η^2-C_8H_{12}·R)(O⌒O)] (O⌒O = acac, hfac)

R	O⌒O	solvent	T_c (K)[a]	$\Delta G^{\ddagger}$ (±0.1 kcal/mol)
OMe (*exo*)	acac	$CDCl_3$	318	15.5
OMe (*exo*)	acac	toluene-d_8	329	16.2
OMe (*exo*)	acac	CD_3CN	303	14.8
OEt (*exo*)	acac	$CDCl_3$	313	15.3
$CH(CO_2Me)_2$ (*exo*)	acac	$CDCl_3$	314	15.4
Ph (*endo*)	acac	$CDCl_3$	302	14.8
$C_6H_2Me_3$ (*endo*)	acac	$CDCl_3$	318	15.9
$C(CO_2Me)$=$C(CO_2Me)Me$ (*endo*)	acac	$CDCl_3$	328	16.1
OMe (*exo*)	hfac	$CDCl_3$	280	12.6

[a] T_c refers to the coalescence of the acac CH_3 or hfac CF_3 signals.

Although only a limited number of examples have been examined, it appears that the nature of the *exo* substituent is unimportant, whereas some dependence on the nature of the *endo* group is found. We noted previously[6] that in the *exo* isomer [Pd(η^1,η^2-C_8H_{12}·OMe)(acac)] the eight-membered ring adopts a shape very similar to that found in cyclooctadiene complexes such as [$PdCl_2$(cod)]. In contrast, the *endo* isomers showed considerable distortion of the cyclooctenyl ring, and this strain inherent in the starting complex may be responsible for the lower $\Delta G^{\ddagger}$ in the phenyl-substituted complex. The greater size of the $C_6H_2Me_3$ and $C(CO_2Me)$=$C(CO_2Me)Me$ groups, and hence higher energy needed to move them, is likely to increase the barrier to rearrangement in these cases.

In contrast to the palladium complex, the appearance of the ^{1}H NMR spectrum of [Pt(η^1,η^2-C_8H_{12}·OMe)(acac)] in toluene-d_8 solution is indicative of a static structure up to 380 K. If this molecule should be fluxional at even higher temperatures, the free energy of activation must

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Table 2. Free Energies of Activation for [Pd(η^1,η^2-C_8H_{12}·R)(O⌒O)] (O⌒O = acac, hfac) in the Presence of Added Ligands in Toluene-d_8 Solution

R	O⌒O	added ligand	no. of equiv	T_c (K)[a]	$\Delta G^{\ddagger}$ (±0.1 kcal/mol)
OMe	acac	none		329	16.2
OMe	acac	CD_3CN	1	330	16.2
OMe	acac	CD_3CN	10	325	16.0
OMe	acac	CD_3CN	100	317	15.6
OMe	acac	py	1	320	15.7
OMe	acac	PPh_3	1	263	12.2
OMe	acac	$PMePh_2$	1	258	12.2
OMe	acac	PEt_3	1	263	11.4
OMe	hfac	PEt_3	1	218	10.6

[a] T_c refers to the coalescence of the acac CH_3 or hfac CF_3 signals.

be in excess of 20 kcal/mol. The static nature of the platinum derivative is probably due to stronger metal−alkene bonding. The palladium-substituted azobenzene complex [Pd(C_6H_4N=NC_6H_5-2-*C*,*N*)(acac)][9,10] is also static at accessible temperatures, i.e., up to 380 K in toluene-d_8 solution, and this may be due to the presence of a stable, planar five-membered chelate ring.

As noted above, the effect of a polar solvent is to lower the $\Delta G^{\ddagger}$ value for the fluxional process. Thus, we decided to investigate the effects of added ligands on the rearrangement. The results are collected in Table 2. When 1 equiv of pyridine was added to a toluene-d_8 solution of [Pd(η^1,η^2-C_8H_{12}·OMe)(acac)], there was little change in the appearance of the ^{1}H NMR spectrum at ambient temperature (except for additional signals due to pyridine), and $\Delta G^{\ddagger}$ = 15.7 kcal/mol. When 1 equiv of PPh_3 was added, a lower free energy of activation of 12.2 kcal/mol was found. In this case, additional information could be obtained from the variable-temperature $^{31}P\{^1H\}$ NMR spectra. At room temperature the spectrum was extremely broad and no signals were detectable, but on cooling to 240 K two singlets were observed in an approximate 1:1 ratio. The lower frequency resonance (−6.3 ppm) is due to free PPh_3, and the second signal at 37.4 ppm is presumably due to a palladium complex containing a coordinated PPh_3. This suggests the existence of an equilibrium as shown in eq 1. With the more nucleophilic phosphine $PMePh_2$ an identical $\Delta G^{\ddagger}$ value was found (12.2 kcal/mol). In this instance the $^{31}P\{^1H\}$ NMR spectrum was again very broad at ambient temperature, but at 240 K the spectrum indicated that almost quantitative conversion to a species of the form [Pd(C_8H_{12}·OMe)(acac)($PMePh_2$)] (δP 24.9) took place. With the even more basic PEt_3 the equilibrium again lies greatly toward the phosphine-ligated species. A single resonance was observed at 34.9 ppm at 240 K (the spectrum was again broad at ambient temperature), but a lower activation barrier of 11.4 kcal/mol was obtained.

$$[M(\eta^1,\eta^2\text{-}C_8H_{12}\cdot R)(acac)] + L \rightleftharpoons [M(C_8H_{12}\cdot R)(acac)L] \quad (1)$$

With the bulkier [Pd(η^1,η^2-C_8H_{12}·$C_6H_2Me_3$)(acac)] the equilibrium position with different phosphines is more dramatic. With 1 equiv of PPh_3 only a somewhat broad signal due to the free phosphine was observed (δP −5.0) at 298 K in toluene-d_8 solution, and this sharpened as the temperature was lowered. Even at 250 K no resonance was detectable for a ligated PPh_3; at 200 K a signal at 38.9 ppm was observed, but it accounted for less than 10% of the total intensity. At 298 K the ^{1}H NMR spectrum contained one broad resonance at 1.9 ppm for the acac methyls, which decoalesced at 273 K. Below this temperature two singlets were detected, and at 200 K two sharp resonances were observed at 1.89 and 2.01 ppm. The value of $\Delta G^{\ddagger}$ determined for this system is 13.3 kcal/mol. With 1 equiv of PEt_3 the spectrum was very broad at 298 K, but cooling to 200 K resulted in the appearance of sharp resonances for [Pd(C_8H_{12}·$C_6H_2Me_3$)(acac)(PEt_3)] (δP 26.6) and free PEt_3 (δP −22.6), with a complex:free phosphine ratio of about 10:1. Again, a broad resonance for the acac methyls was found at ambient temperature, and at 200 K two sharp singlets are found at 1.90 and 2.00 ppm. As in the PPh_3 case, the value of $\Delta G^{\ddagger}$ for this system is 13.3 kcal/mol.

As mentioned previously, [Pd(C_6H_4N=NC_6H_5-2-*C*,*N*)(acac)] itself is static up to 380 K. Addition of PEt_3, however, quantitatively produced a phosphine-coordinated complex, which exhibited a ^{31}P resonance at 26.1 ppm at 260 K (similar to that found for [PdCl(C_6H_4N=NC_6H_5-2-*C*,*N*)(PEt_3)] but quite different from the bis(phosphine) complex [PdCl(C_6H_4N=NC_6H_5-2-*C*)(PEt_3)$_2$][11]), which was fluxional down to a coalescence temperature of 200 K. Although spectra could be obtained over only a narrow temperature range below the coalescence, a $\Delta G^{\ddagger}$ value of only 9.5 kcal/mol was obtained. To determine whether the presence of the pendant N atom is critical to the rearrangement process in [Pd(C_6H_4N=NC_6H_5-2-*C*)(acac)(PEt_3)], we prepared the related phenylpalladium complex containing one PPh_3 ligand [PdPh(acac-*O*,*O*)(PPh_3)].[12] This showed no fluxional behavior at 298 K in toluene-d_8 solution, exhibiting a single resonance in its ^{31}P NMR spectrum at 33.4 ppm, and two sharp methyl signals at 1.66 and 1.83 ppm. Addition of 1 mol equiv of PPh_3 resulted in a single, sharp ^{1}H resonance for the acac methyls at 1.79 ppm at 298 K, however, which broadened as the temperature was lowered. Decoalescence occurred around 230 K, but even at 180 K the two methyl signals at 1.7 and 1.9 ppm remained quite broad. The NMR spectra indicated some conversion to the *C*-bonded acac complex [PdPh(acac-*C*)(PPh_3)$_2$] (δH 1.57 (CH_3), 4.76 (C*H*); δP 25.9 at 200 K), but broad signals due to [PdPh(acac-*O*,*O*)(PPh_3)] and free PPh_3 were also observed in the $^{31}P\{^1H\}$ NMR spectrum. These results suggest that free PPh_3 does indeed catalyze the rearrangement of [PdPh(acac)(PPh_3)].

An obvious question concerns the nature of these phosphine-coordinated complexes. Are they five-coordinate, or does the tertiary phosphine displace either the alkene moiety or one arm of the acac ligand? In the case of [Pd(C_8H_{12}·OMe)(acac)(PEt_3)], no coupling is detected between the hydrogens of the alkene group and the coordinated phosphorus in the low-temperature ^{1}H or ^{31}P−^{1}H correlated NMR spectrum. This may suggest that the alkene is not coordinated, but such a long-range coupling might be very small (although other four-bond P−H couplings were detected in the two-dimensional

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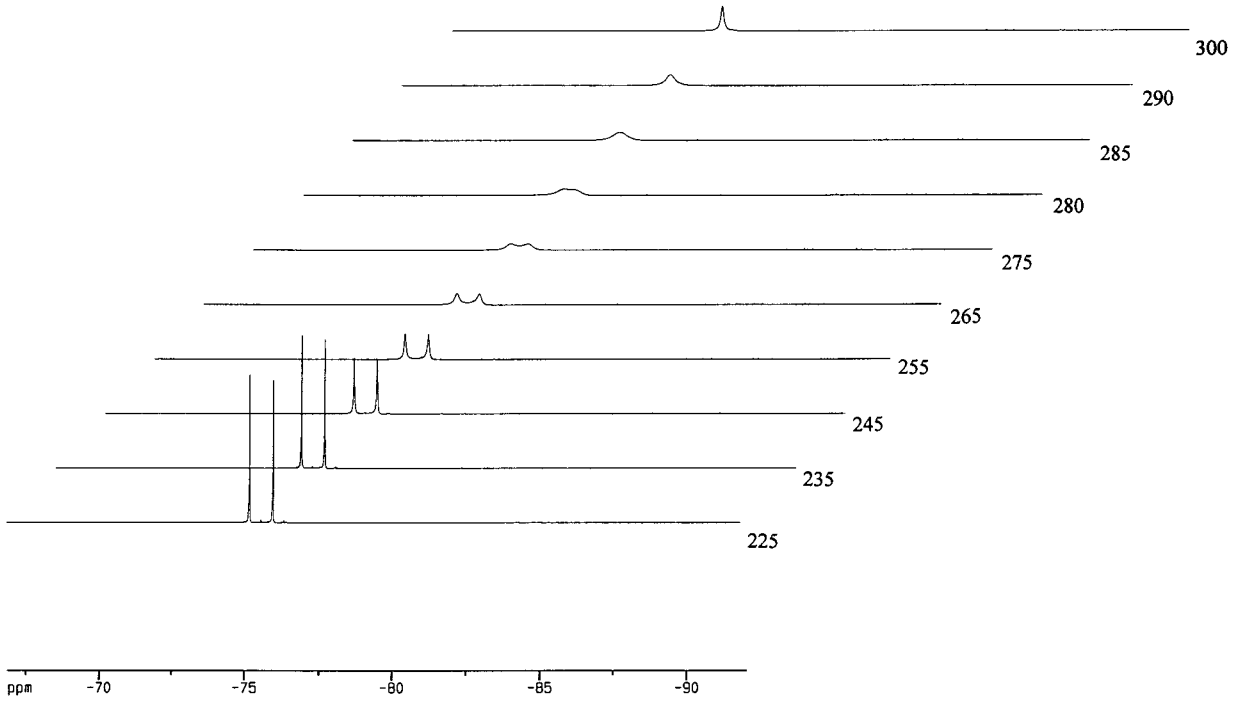

Figure 1. Variable-temperature ^{19}F NMR spectra of [Pd(η^1,η^2-C_8H_{12}·OMe)(hfac)] recorded at 475 MHz in $CDCl_3$ solution.

spectrum). More convincing results have been obtained for the platinum system, however. In [Pt(η^1,η^2-C_8H_{12}·OMe)(acac)][13] the two alkene hydrogen resonances appear at 4.52 and 4.57 ppm, and they exhibit broad ^{195}Pt satellites (as expected when recording the spectrum at high field[14]). When PEt_3 was added, however, a species of the form [Pt(C_8H_{12}·OMe)(acac)(PEt_3)] was produced (δP 5.5, ^1J(Pt,P) = 4945 Hz), which exhibited no observable coupling of the alkene hydrogens (δH 5.71 and 5.96 m) with platinum in its ^{1}H NMR spectrum even at low temperatures. The large Pt−P coupling is consistent with PEt_3 lying *trans* to a ligand of low *trans*-influence,[15] such as an O-bound acac, in a square planar complex. This suggests that the complex is four-coordinate, the phosphine having displaced the alkene moiety. Better evidence for a species of the form [Pt(η^1-C_8H_{12}·OMe)(acac-*O*,*O*)(PEt_3)] was obtained from ^{13}C NMR spectroscopy. In [Pt(η^1,η^2-C_8H_{12}·OMe)(acac)] itself, the ^{13}C{^{1}H} NMR spectrum in toluene-d_8 solution at 298 K exhibited two alkene carbon resonances at 74.5 and 77.5 ppm (each with ^1J(Pt,C) = 254 Hz). Addition of 1 equiv of PEt_3 resulted in the loss of these signals and the appearance of two new resonances at 126.1 and 132.3 ppm, neither of which showed coupling to ^{195}Pt (each became a doublet in the ^{1}H-coupled spectrum). This dramatic change in chemical shift and loss of ^{195}Pt coupling indicate that the alkene moiety is no longer coordinated to the metal. Thus, addition of a tertiary phosphine results is formation of a four-coordinate species in which the alkene has been displaced.

[Pt(η^1-C_8H_{12}.OMe)(acac-*O*,*O*)(PEt_3)] is fluxional, exhibiting a single resonance for the acac methyls at 1.69 ppm at higher temperatures and splitting into two signals below the coalescence temperature of 298 K. A $\Delta G^‡$ value of 14.3 kcal/mol was determined for this complex. The platinum system is complicated by formation of small amounts of a carbon-bound acac complex *cis*-[Pt(C_8H_{12}·OMe)(acac-*C*)(PEt_3)$_2$] (δP 10.2 d, ^2J(P,P) 6 Hz, ^1J(Pt,P) 1677 Hz, δP 11.5 d, ^1J(Pt,P) 1826 Hz), and an unidentified, minor species at δP 16.9 s, ^1J(Pt,P) 4195 Hz. Addition of a second equiv of PEt_3 results in complete conversion to *cis*-[Pt(C_8H_{12}·OMe)(acac-*C*)(PEt_3)$_2$] (δH 1.99 (C*H*$_3$), 4.20 (C*H*)).

We have also prepared the hexafluoroacetylacetonate (hfac) complexes [Pd(η^1,η^2-C_8H_{12}·OMe)(hfac)] and [Pd($C_6H_4N{=}NC_6H_5$-2)(hfac)].[16] As with their acac counterparts, the former is fluxional at ambient temperature, but the latter is not. The ^{19}F signals due to [Pd(η^1,η^2-C_8H_{12}·OMe)(hfac)] over a range of temperatures are shown in Figure 1. This temperature-dependent behavior leads to a $\Delta G^‡$ value of 12.6 kcal/mol, lower than that found for the corresponding acac derivative. Addition of PEt_3 to [Pd(η^1,η^2-C_8H_{12}·OMe)(hfac)] resulted in a lower coalescence temperature of 280 K and a $\Delta G^‡$ value of 10.6 kcal/mol. Thus, addition of PEt_3 results in a lowering of $\Delta G^‡$ by about 2 kcal/mol, whereas phosphine addition to the acac derivative caused a decrease of more than 4 kcal/mol. [Pd($C_6H_4N{=}NC_6H_5$-2-*C*,*N*)(hfac)] is also fluxional in the presence of PEt_3, as evidenced by a single resonance in the ^{19}F NMR spectrum. In this case, however, the signal remains sharp down to 200 K so a value for $\Delta G^‡$ could not be determined. The lower $\Delta G^‡$ values obtained for the hfac complexes compared with their acac counterparts may reflect the electron-withdrawing ability of the CF_3 groups, which would stabilize the five-coordinate intermediates in the rearrangement processes.

The temperature-dependent ^{1}H or ^{19}F NMR spectra were simulated in four cases. Line shape analysis of the acac methyl signals for [Pd(η^1,η^2-C_8H_{12}·OMe)(acac)]

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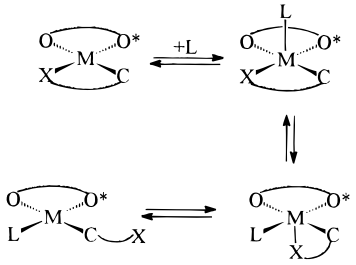
Scheme 2



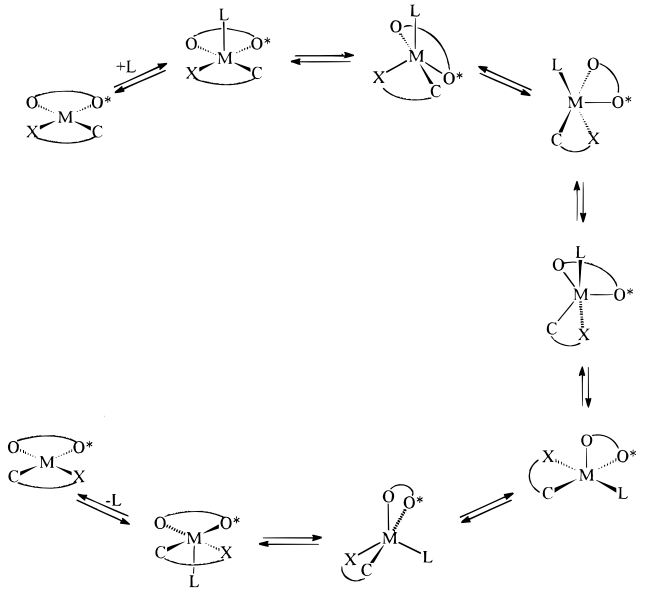
in $CDCl_3$ solution leads to $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values of 6.6 kcal/mol and −29.5 cal/(mol·K), respectively, and the corresponding values in toluene-d_8 are 8.5 kcal/mol and −24.5 cal/(mol·K). Similar analysis of the ^{19}F signals for the corresponding hfac complex gave similar results ($\Delta H^{\ddagger}$ = 8.3 kcal/mol and $\Delta S^{\ddagger}$ = −16.1 cal/(mol·K)). Finally, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values of 8.0 kcal/mol and −20.0 cal/(mol·K), respectively, are obtained for [Pd(η^1,η^2-C_8H_{12}·OMe)(acac)] in the presence of 1 equiv of PPh_3 in toluene-d_8 solution. In every case the activation parameters are consistent with an intramolecular rearrangement process.[17] The negative $\Delta S^{\ddagger}$ values, in particular, are inconsistent with a dissociative mechanism. In the last case, an intramolecular rearrangement of the phosphine-ligated species [Pd(η^1,η^2-C_8H_{12}·OMe)(acac)(PPh_3)] appears most likely.

Discussion

Although a dissociative exchange process in a relatively nonpolar solvent, such as toluene, is plausible, the lowering of $\Delta G^{\ddagger}$ in more polar solvents or, more significantly, in the presence of added ligands suggests strongly that the mechanism of exchange is associative in nature. It appears that an equilibrium is set up, as shown in eq 1. When the most nucleophilic ligands, PEt_3 and $PMePh_2$, are employed, this equilibrium lies well to the right, whereas with PPh_3 or py, or when the ligand is the solvent, it lies further to the left. Even with nonpolar, aromatic solvents, such as toluene, a solvated complex is possible, and η^2-bonded complexes are known.[8]

In principle, the complexes of the form [M(C_8H_{12}·R)(acac)L] could be five-coordinate or four-coordinate with either acac or the cyclooctenyl group acting as a monodentate ligand. Palladium and platinum compounds containing η^1 O-bonded acac and related ligands have been reported,[18] but it appears most likely from our NMR evidence that the phosphine-ligated complexes, at least, are four-coordinate, 16-electron species in which the alkene moiety of the cyclooctenyl group is uncoordinated. Replacement of the coordinated alkene by the neutral ligand is reversible and should proceed by a stereospecific substitution reaction (Scheme 2), which does not result in scrambling of the acac methyls.[19] Thus, we can consider either complex in eq 1 as the one that undergoes intramolecular exchange.

Scheme 3



It is unlikely that the intramolecular exchange occurs at a four-coordinate species without further involvement of external ligands. In the absence of a fifth ligand, this would require a twist mechanism involving a high-energy tetrahedral transition state, and although such a process has been advanced recently for a four-coordinate palladium(II) system,[20] in that case the molecule exhibited a significant twist even in the ground state. It is more likely that interaction of the starting complex with the free ligand or solvent, or reattachment of the displaced double bond in [M(η^1-C_8H_{12}·R)(acac)L], leading to a five-coordinate derivative occurs, and it is this species that undergoes geometrical exchange. The lower $\Delta G^{\ddagger}$ values found for the phosphine-ligated complexes may reflect the ready availability of a fifth ligand in the form of the displaced alkene moiety, or the existence of a significant concentration of a five-coordinate species in solution. In the absence of an added ligand the solvent would serve as the fifth ligand, and this interaction would be considerably weaker and less able to promote intramolecular rearrangement.

The static nature of [Pd($C_6H_4N{=}NC_6H_5$-2-*C*,*N*)(acac) and its hfac analogue at all temperatures is likely to result, at least in part, from the presence of the planar, five-membered chelate ring. When PEt_3 is added, displacement of nitrogen occurs and the stability provided by this feature is lost. The molecule then becomes fluxional. In contrast, the cyclooctenylpalladium complexes do not possess such a favorable ring system in the first place, and they are fluxional even in the presence of only a weakly coordinating ligand such as a solvent molecule. The static structure of the cyclooctenylplatinum derivative is probably due to the stronger metal−alkene bonding in this case; in general, palladium systems are 10^3−10^4 times more labile than their platinum analogues.

In principle, the rearrangement could take place by pseudorotation of trigonal bipyramidal species, but examination of the potential rearrangements indicates

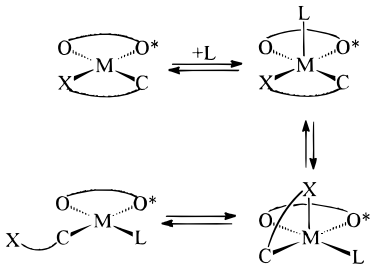
(17) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; Brooks/Cole: Monterey, CA, 1985; p 16.

(18) Okeya, S.; Nakamura, Y.; Kawaguchi, S. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3396. Tanaka, H.; Isobe, K.; Kawaguchi, S.; Okeya, S. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1850.

(19) In each scheme one oxygen of the acac ligand is labeled with an asterisk, to allow differentiation of the reactant and product. Of course, the oxygens are, in fact, indistinguishable.

(20) Tsuji, Y.; Nishiyama, K.; Hori, S.; Ebihara, M.; Kawamura, T. *Organometallics* **1998**, *17*, 507.

Scheme 4



that a number of steps would be necessary to effect isomerization (Scheme 3). This certainly does not preclude such a mechanism, but if a simpler process was available, it might be preferred.

In contrast to the pseudorotation mechanism, if one was to consider the turnstile mechanism, where three adjacent ligands undergo interchange by rotation through 120°, exchange between the two species in eq 1 can be accomplished by a single rotation step (Scheme 4). Subsequent stereospecific substitution of L by X, or vice versa, would complete the rearrangement. Although the available evidence does not prove or disprove the operation of either mechanism, the relative simplicity of the turnstile mechanism is attractive in the present case.

Summary

We have shown that the cyclooctenylpalladium complexes [Pd(η^1,η^2-C_8H_{12}·R)(acac)] and the hfac analogue (R = OMe) are fluxional in solution, the hfac derivative exhibiting a lower $\Delta G^{\ddagger}$ value for the exchange process. Decreased $\Delta G^{\ddagger}$ values are also found in the presence of nucleophiles such as tertiary phosphines. This behavior is interpreted in terms of an intramolecular rearrangement from a five-coordinate species. Although the mechanism of exchange could not be determined unambiguously, the operation of the turnstile mechanism would most readily account for the observations.

Experimental Section

Complexes of the type [Pd(η^1,η^2-C_8H_{12}·R)(acac)] were prepared as described previously.[6] [Pt(η^1,η^2-C_8H_{12}·OMe)(acac)] was prepared according to a reported method by cleavage of [$Pt_2(\mu$-Cl)$_2(\eta^1,\eta^2$-C_8H_{12}·OMe)$_2$],[13] but using Ag(acac) instead of Tl(acac). Ag(acac) and Tl(hfac) were obtained from Aldrich and Alfa/Aesar, respectively. NMR spectra were recorded on a Bruker ARX-500 spectrometer. ^{1}H chemical shifts were measured relative to the residual solvent signal, ^{19}F shifts relative to external $CFCl_3$, and ^{31}P shifts relative to external H_3PO_4, positive shifts representing deshielding; coupling constants are in Hertz. Microanalyses were performed by Atlantic Microlab Inc., Norcross, GA.

Preparation of [PdPh(acac)(PPh$_3$)].[12] [$Pd_2(\mu$-Cl)$_2$-Ph_2(PPh$_3$)$_2$] (0.10 g, 0.10 mmol) was dissolved in CH_2Cl_2 (50 mL). Ag(acac) (0.043 g, 0.21 mmol) was added, and the reaction mixture was stirred for 2 h in the absence of light. The solvent was removed, and the residue was extracted with ether and passed through a short Florosil column, eluting with ether (50 mL). The ether was removed, and the solid was dried in vacuo, leaving the product as a colorless powder (0.11 g, 94%).

Preparation of [Pd(η^1,η^2-C_8H_{12}.OMe)(hfac)]. [$Pd_2(\mu$-Cl)$_2$-(η^1,η^2-C_8H_{12}·OMe)$_2$] (0.15 g, 0.27 mmol) was dissolved in CH_2Cl_2 (50 mL), and Tl(hfac) (0.22 g, 0.53 mmol) was added. The reaction mixture was stirred for 2 h, then passed through a Florosil column eluting with CH_2Cl_2 (50 mL). The solvent was removed, and the residue was dissolved in ether and passed through a short neutral alumina column eluting with ether (50 mL). The solvents were removed again, and the remaining oily material was dried in vacuo, yielding the product as an off-white, oily solid (0.12 g, 48%), which was both light- and moisture-sensitive. Anal. Calcd for $C_{14}H_{16}F_6O_3Pd$: C, 37.14; H, 3.54. Found: C, 37.07; H, 3.60. ^{1}H NMR ($CDCl_3$): δH 1.4, 2.0, 2.3, 2.6 m, CH_2; 3.29 s, OCH_3; 3.55 m, C*H*Pd; 3.65 m, C*H*OMe; 6.00 s, C*H* (acac); 5.45, 5.95 m, (C*H*=).

Preparation of [Pd(C_6H_4N=NC_6H_5-2)(acac)].[9] [$Pd_2(\mu$-Cl)$_2$(C_6H_4N=NC_6H_5-2)$_2$] (0.10 g, 0.15 mmol) was dissolved in CH_2Cl_2 (50 mL), and Ag(acac) (0.064 g, 0.31 mmol) was added. The mixture was stirred for 2 h at ambient temperature in the absence of light. The solvents were removed, and the residue was extracted with ether and passed through a Florosil column eluting with ether (50 mL). The solvents were removed again, and the residue was dried in vacuo to leave the product as an orange solid (0.097 g, 81%).

Preparation of [Pd(C_6H_4N=NC_6H_5-2)(hfac)].[16] [$Pd_2(\mu$-Cl)$_2$(C_6H_4N=NC_6H_5-2)$_2$] (0.10 g, 0.15 mmol) was dissolved in CH_2Cl_2 (50 mL), and Tl(hfac) (0.13 g, 0.31 mmol) was added. The reaction mixture was stirred for 2 h in the absence of light. The solvent was removed, and the resulting solid was extracted with ether and passed through a short Florosil column, eluting with ether (50 mL). The solvent was removed, and the solid was dried in vacuo to leave the product as an orange powder (0.13 g, 82%).

Variable-Temperature NMR Experiments. In a typical experiment, approximately 10 mg of the acac complex was dissolved in the appropriate deuterated solvent. When required, the appropriate amount of a ligand was added. The ^{1}H NMR spectrum was recorded over the temperature range 180−300 K (higher temperature ranges were studied when the molecule was not fluxional at ambient temperature), and the CH_3 resonances of the acac ligand were monitored. In the slow exchange regime two signals were observed, and the frequency difference ($\Delta\nu$) for the two methyls at the coalescence temperature (T_c) was obtained by extrapolation from the low-temperature data. Exchange rate constants, k_c, at the coalescence temperature were calculated using the equation $k_c = \pi(\Delta\nu)/2^{1/2}$. The exchange constants were used to determine $\Delta G^{\ddagger}$ at the coalescence temperature from the Eyring equation $k_c = (k'/h)T_c \exp(-\Delta G^{\ddagger}/RT_c)$, where k' is Boltzmann's constant, h is Planck's constant, and R is the ideal gas constant.[7] The hfac complexes were studied similarly, using ^{19}F NMR spectroscopy to monitor the CF_3 signals. In four cases the ^{1}H or ^{19}F NMR spectra below coalescence were simulated using the program DNMR4.[21]

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(21) DNMR4: Bushweller, C. H.; Letenore, L. J.; Brunelle, J. A.; Bilofsky, H. S.; Whalon, M. R.; Fleischman, S. H. Quantum Chemistry Program Exchange, Program No. 466, Indiana University, Bloomington, IN.