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Intramolecular Rearrangements of Square Planar β-Diketonate Complexes of Palladium(II) and Platinum(II): Evidence for a Dissociative Mechanism

C. J. MAY and J. POWELL

Lash Miller Chemical Laboratories, University of Toronto, Toronto, Canada, M5S 1A1

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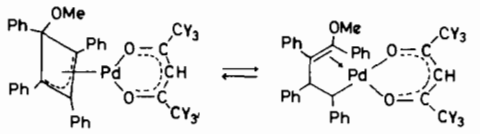
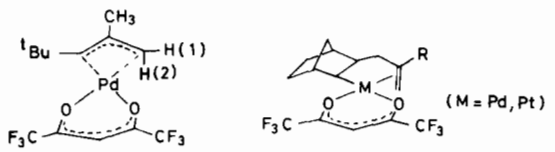
Whilst considerable attention has been given to the mechanism(s) of intramolecular rearrangements of octahedral transition metal–β-diketonate complexes [1, 2] little consideration has been given to comparable rearrangements in square planar β-diketonate complexes. We here report variable temperature nmr studies of series of palladium(II) and platinum(II) hexafluoroacetylacetonate (hfac) complexes which provide definitive and novel information on the nature of these rearrangements. The complexes **2**,



1a **2a** (Y = F)
1b **2b** (Y = H)



3 **4**

3 and **4** contain no plane of molecular symmetry with the result that the low temperature ^{19}F nmr spectra of these complexes (in a variety of solvents) exhibit two singlets of equal intensity assignable to two stereochemically distinct CF_3 groups [3]. On warming, concentration independent CF_3 site exchange (rapid on the nmr time scale) is observed in all cases. In the fast exchange region, complex **4** (M = Pt; R = ^{t}Bu) retains ^{195}Pt coupling to the hfac fluorines (see Figure). For the equilibrium mixture of **1a** ⇌ **2a** no intermolecular exchange of hfac between **1a** and **2a** is observed (both ^1H and ^{19}F nmr) in the region of fast CF_3 site exchange in **2a** (all solvents). The rate of CF_3 site exchange is unaffected by the addition of free hexafluoroacetylacetone. These observations indicate that the process of CF_3 site exchange is either a true intramolecular rearrangement or a solvent assisted process. For a solvent assisted process two mechanistic extremes may be

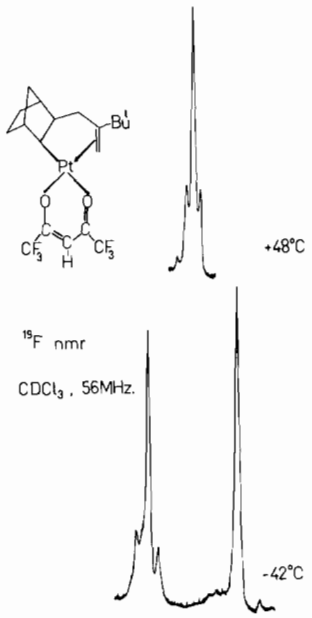
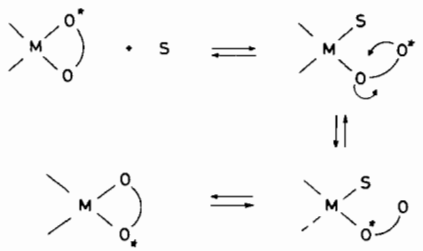


Figure. ^{19}F nmr spectrum of **4** (M = Pt, R = ^{t}Bu) in the no exchange and fast CF_3 site exchange regions.

envisaged: (i) formation of a five coordinate species of the type "[complex]s" (s = solvent molecule) followed by a pseudo rotation and loss of solvent; and (ii) an associative solvent displacement of one of the chelating hfac oxygens, *e.g.*:



Most of the complexes **1–4** are soluble in a wide range of solvents. In particular we have found that CF_3 site exchange occurs rapidly in dry pentane and dry heptane (see Table) where no suitable coordinating solvent molecule is available to initiate processes such as (i) and (ii). Thus the mechanism of CF_3 site exchange does not occur by an associative solvolysis. There are three remaining mechanistic possibilities. (iii) A square planar ⇄ tetrahedral rearrangement; (iv) a partial dissociation of the hfac to give a three coordinate intermediate; and/or (v) partial dissociation of the hydrocarbon ligand to give a three coordinate intermediate. Since process (v) would result in the formation of a σ-allylic species for complex **3** and therefore result in simultaneous exchange of the

TABLE. Exchange Parameters for CF_3 Site Exchange in a Selection of Complexes of Type 2–4. Spectra were recorded at 56 MHz (^{19}F), 60 MHz (^1H).

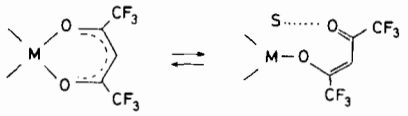
Complex	Solvent	T_c (°K)	$\Delta\nu(H_z)$	$\Delta G^{\neq}_{T_C}$ (kj mol^{-1})
2a	n-pentane	290	49	60
	n-heptane	291	51	60
	$CDCl_3$	271	35	56
	acetone	209	37	43
	methanol	186	>35	<38
2b[a]	$CDCl_3$	306	7.0	68
3	n-heptane	253	18	54
4 (M = Pt, R = ^{t}Bu)	n-pentane	282	64	57
	$CDCl_3$	272	60	55
4 (M = Pd, R = ^{t}Bu)	$CDCl_3$	<200		<42
4 (M = Pt, R = H)	$CDCl_3$	325	52	66
4 (M = Pd, R = H)	$CDCl_3$	212	33	43

[a] ^1H nmr data for methyl site exchange.

syn and *anti* protons $H_{(1)}$ and $H_{(2)}$ [4] (*not observed*) one is left with process (iii) and/or (iv) as the remaining mechanistic possibilities.

Whilst square planar ⇄ tetrahedral rearrangements are well known for nickel(II) complexes [5] the only previous proposals of tetrahedral intermediates in palladium(II) and platinum(II) chemistry involve the photochemically initiated isomerizations of [Pt(glycinato)$_2$] [6] and [$PtCl_2(PR_3)_2$] [7]. The only dissociative three coordinate intermediate postulated to date involves the spontaneous *cis* to *trans* isomerization of *cis*-[PtCl(*o*-tolyl)(PEt_3)$_2$] in methanol [8]. The evidence for a rate determining dissociative step for this isomerization is based on the observed chloride ion concentration dependence and steric factors are thought to be a controlling factor in the observation of this reaction pathway.

To definitively distinguish between mechanisms (iii) and (iv) is difficult. However, several observations point to the dissociative mechanism (iv) as being the more likely pathway for the observed CF_3 site exchange. A comparison of several hfac derivatives with their acetylacetonato analogs {*e.g.* **2b** (Y = H) studied in $CDCl_3$ – see Table} shows that CF_3 site exchange in hfac complexes occurs more rapidly than acac CH_3 site exchange. This is consistent with the more ionic character of transition metal–hfac bonds relative to transition metal–acac bonds [9]. The rate of CF_3 site exchange is enhanced by polar solvents with pentane ≈ heptane < $CDCl_3$ < acetone < MeOH. The effect of solvent may be associated with solvation of a unidentate hfac intermediate *viz.*:



However the rate of CF_3 site exchange in acetone or MeOH may be enhanced by an additional associative solvolysis pathway. A comparison of palladium and platinum analogs shows $\Delta G^{\neq}$ for CF_3 site exchange to be *ca.* 20 kj mol^{-1} greater for the platinum(II) complexes. A study of a series of complexes of type **4** (M = Pd) shows the rate of CF_3 site exchange to be quite sensitive to the nature of R, increasing in the order R = Me < $CH_2{}^t$Bu < H ≈ Ph < ^{t}Bu ≈ Cl.

In contrast to **4** (M = Pt) the complex [PtCl(Me_2PhP)hfac] in $CHBr_3$ shows no evidence of CF_3 site exchange up to 390 °K. This suggests that the observed β-diketonate site exchange is favoured when the two ligands *trans* to the β-diketonate are both strong *trans* labilisers and when the β-diketonate is a good leaving ligand (hfac > acac). Thus the data are consistent with a dissociative pathway the energetics of which are probably governed by electronic factors (*trans*-labilising effects) rather than steric ones {as suggested for the *cis* to *trans* isomerization of [PtCl(*o*-tolyl)(PEt_3)$_2$] [8]}. Consequently, the k_1-term for the kinetics of ligand substitutions in square planar complexes may, under suitable circumstances, be reflective of a dissociative pathway rather than associative solvolysis as is currently accepted.

Acknowledgment

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