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X-Ray Structure and Solution Behavior of the Five-coordinate Bis(hexafluoroacetylacetonato)-(tertiary phosphine)-Palladium(II) and -Platinum(II) Complexes

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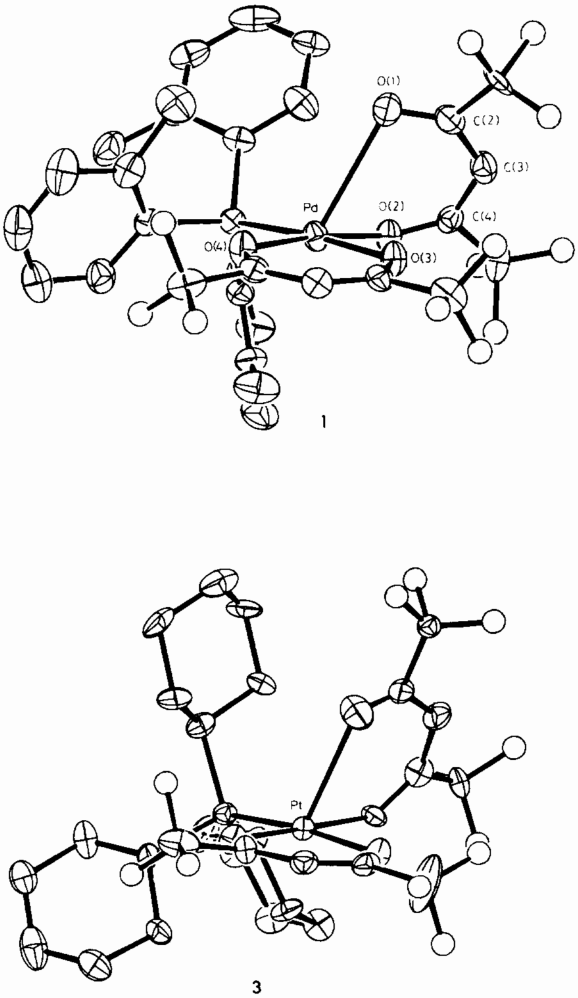
Five-coordinate complexes of d^8 metals are believed to be involved, as intermediates, in ligand substitution [1] and some *cis–trans* isomerization [2] reactions of square planar complexes. Some stable five-coordinate complexes of palladium(II) [3] and platinum(II) [4] have in fact been reported although they are not so popular as those of nickel(II) and cobalt(II) [5]. The present communication reports the X-ray structure and stereochemically non-rigid behavior in solution, of five-coordinate palladium(II) and platinum(II) complexes of the $M(hfac)_2(PR_3)$ type.

Bis(hexafluoroacetylacetonato)palladium(II), $[Pd(hfac)_2]$ [6], reacted with an equimolar amount of tri-*o*-tolylphosphine in n-hexane at room temperature to afford red crystals of $[Pd(hfac)_2P(o\text{-tolyl})_3]$ (*1*) in an 85% yield. The corresponding platinum(II) complexes $[Pt(hfac)_2P(o\text{-tolyl})_3]$ (*2*) and $[Pt(hfac)_2PCy_3]$ (*3*) were obtained as orange crystals in 89 and 93% yields respectively, by the similar reactions of $[Pt(hfac)_2]$ [7] with tri-*o*-tolylphosphine and tricyclohexylphosphine. These complexes are stable in air and exist as mononuclear molecules in dichloromethane solution [8] exhibiting absorption maxima (molar absorptivity) at 302 (18200) and *ca.* 410 nm (2500) in the case of *1* and at 275 (11600), 280 (11500), and 308nm (9600) in the case of *2*.

The crystal structures of *1* and *3* have been determined from the intensity data measured on an automated diffractometer using graphite-monochromated MoK_α radiation. Crystal data: *1*, monoclinic, $a = 13.998(3)$, $b = 11.430(2)$, $c = 10.897(3)$ Å, $\beta = 108.48(2)°$, $Z = 2$, $\mu(MoK_\alpha) = 7.1\ cm^{-1}$, space group $P2_1$; *3*, orthorhombic, $a = 25.652(3)$, $b = 20.398(3)$, $c = 12.781(2)$ Å, $Z = 8$, $\mu(MoK_\alpha) = 45.7\ cm^{-1}$, space group *Pcab*. The intensity data of *3* were corrected for absorption. The number of unique reflections with $I > 3\sigma(I)$ was 3148 ($2\theta_{max} = 55.0°$) for *1* and

TABLE I. Bond Lengths (A) with the Esd's in Parentheses.

	1	*3*
M–P	2.253(2)	2.230(4)
M–O(1)	2.797(6)	2.794(13)
M–O(2)	2.017(5)	1.988(9)
M–O(3)	2.084(6)	2.098(10)
M–O(4)	2.001(6)	1.984(10)
C(2)–O(1)	1.205(11)	1.17(2)
C(4)–O(2)	1.266(9)	1.27(2)
C(2)–C(3)	1.437(11)	1.46(3)
C(3)–C(4)	1.382(12)	1.40(2)



1

3

Fig. 1. The molecular structures of the Pd (*1*) and Pt (*3*) complexes with 30% probability ellipsoids except for all fluorine atoms and the CF_3-carbon atom linked to C(2) in *3* which are shown by circles of arbitrary radii.

TABLE II. ^1H NMR Chemical Shifts in ppm from Internal Me_4Si in CD_2Cl_2.

	1		*2*		*3*
	−50 °C	27 °C	−50 °C	27 °C	27 °C
CH(hfac)	6.15	5.85	6.34	5.89[a]	6.04[a,b]
	5.47		5.41		
CH_3(tolyl)	2.94	2.31	2.74	2.27	
	2.10		2.13		
	1.72		1.69		

[a]Flanked by ^{195}Pt satellites with $^4J(Pt–H)$ = 5 Hz. [b]In $CDCl_3$.

TABLE III. ^{13}C NMR Chemical Shifts (δ) in ppm from Internal Me_4Si in $CDCl_3$ at 30 °C and Coupling Constants (J) in Hz.

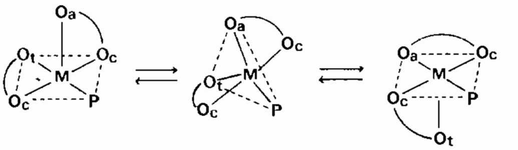
		δ	J(F–C)	J(P–C)	J(Pt–C)
1	CF_3	116.6	286	4	
	CO	174.0	34		
	CH	89.5			
2	CF_3	116.3	283		90
		116.8	288	5	
	CO	169.4	34		*ca.* 14
		174.3	34		
	CH	91.7			44
3	CF_3	117.1	284		89
		117.1	288	4	
	CO	169.4	34		16
		174.5	34		
	CH	91.5	2		44

3270 ($2\theta_{max}$ = 50.0°) for *3*. The structures were solved by the heavy atom technique and refined by the least-squares method to R = 0.040 and 0.064 for *1* and *3*, respectively.

The molecular structures are shown in Fig. 1 and some bond lengths in Table I. Both complexes have a distorted square pyramidal coordination by 4O and P atoms. The P atom lies on a basal plane from which the metal atom deviates by 0.11 Å in *1* and 0.06 Å in *3*. In both structures the basal chelate ring is planar and the M–O(3) bond is significantly longer than the M–O(4) bond owing to the *trans* influence of the phosphines. The remarkably long M–O(1) distance reflects weakness of the apical bond. The chelate ring comprising the apical atom is almost planar in *3* but is folded in *1* from the [Pd, O(1), O(2)] plane by 37.7° so as to alleviate the repulsion by one of the *o*-tolyl groups, and has a significant contribution from the structure $O=C(CF_3)–CH=(CF_3)–O–M$ in either case as shown by the bond-length data in Table I.

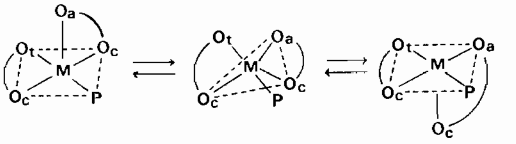
The ^1H and ^{13}C NMR data in Tables II and III, respectively, indicate that these complexes are stereochemically nonrigid in solution. Each of *1* and *2* exhibits two methine-proton signals at −50 °C, indicating that nonequivalence of the two hfac ligands as observed in crystals persists in solution at low temperature. The methyl protons in the phosphine ligands also give three signals due to restriction of free rotation around the M–P bond. With an increase in temperature both of these signals become broad, collapse at around −30 °C, and finally result in sharp singlets at 27 °C. The ^{31}P NMR spectrum of *2* in $CDCl_3$ at room temperature shows a singlet at 7.08 ppm upfield from external H_3PO_4 flanked by ^{195}Pt satellites, while ^{195}Pt resonates as a doublet at 295.7 ppm upfield from external K_2PtCl_4, $^1J(Pt–P)$ being 4483 Hz. These results suggest that the M–P bond is retained intact and the exchange of environment between the two hfac ligands at room temperature is attained not by dissociation–association of the phosphine, but by an intramolecular mechanism.

On the other hand, the ^{13}C NMR spectra at room temperature indicate that four CF_3CO groups in *1* are stereochemically equivalent on the NMR time scale, whereas those in *2* and *3* are divided into two nonequivalent sets, respectively. The ^{19}F NMR spectrum of *2* in $CDCl_3$ also exhibits two signals, one as a singlet at 91.78 ppm downfield from external C_6F_6 flanked by ^{195}Pt satellites with $^2J(Pt–F)$ = 16 Hz and the other as a broad signal at 89.26 ppm. The spectral feature of the platinum(II) complexes may be rationalized by a site exchange between the apical O and the O *trans* to P according to a twist mechanism such as depicted in eqn. (1).



(1)

In order to explain the palladium(II) case, another mode of twist is necessary such as exemplified by eqn. (2) which causes the optical inversion.



(2)

Similar ^{13}C NMR pattern was also observed for the reaction mixtures of $[Pd(hfac)_2]$ and $[Pt(hfac)_2]$ with triphenylphosphine, triphenylarsine, and phenyldi(*o*-tolyl)phosphine, although the product complexes from the former two ligands were not isolated. On the other hand, the palladium(II) and platinum(II) complexes of other β-dicarbonyl compounds such as acetylacetone, trifluoroacetylacetone, benzoylacetone, and ethyl acetoacetate have shown no sign of the five-coordinate intermediate in the reactions with various phosphorus and nitrogen bases.

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References

1 *E.g.* L. Cattalini, *Progr. Inorg. Chem., 13,* 263 (1970).
2 *E.g.* W. J. Louw, *Inorg. Chem., 16,* 2147 (1977).
3 *E.g.* M. K. Cooper, D. W. Yaniuk, M. M. Partlin and J. G. Shaw, *J. Organometal. Chem., 131,* C33 (1977).
4 *E.g.* A. Konietzny, P. M. Bailey and P. M. Maitlis, *J. Chem. Soc. Chem. Comm.,* 78 (1975).
5 L. Sacconi, *Coord. Chem. Rev., 8,* 351 (1972); R. Morassi, I. Bertini and L. Sacconi, *ibid., 11,* 343 (1973).
6 S. Okeya, Y. Nakamura and S. Kawaguchi, to be published.
7 S. Okeya and S. Kawaguchi, *Inorg. Synth., 20,* (1980).
8 These complexes gave satisfactory analysis and molecular weight. In solution and on standing as solid in air for a long time, compound 1 decomposes gradually to result in $[(\mathrm{hfac})\overline{\mathrm{PdCH_2C_6H_4}\text{-}o\text{-}\mathrm{P}}(o\text{-tolyl})_2]$.