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PALLADIUM(0) AND PLATINUM(0) COMPLEXES OF *p,p'*-DIISOPROPYLDIBENZYLIDENEACETONE AND THEIR NMR SPECTRA

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Summary

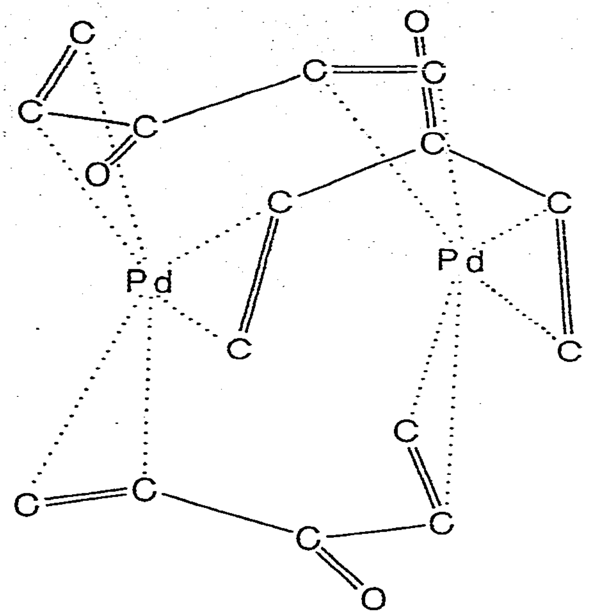
The zerovalent diisopropyldibenzylideneacetone (dipdba, *p*-*i*-$PrC_6H_4CH=CHCOCH=CH$-*p*-*i*-PrC_6H_4) complexes $M_2(dipdba)_3$ (III, M = Pd; IV, M = Pt) have been prepared and their NMR spectra studied in solution. The ^1H and ^{13}C NMR spectra of III and IV show complex patterns which are consistent with the complexes having very asymmetric structures in solution. The metal atoms are π-bonded to the olefins and the frameworks are stereochemically rigid over the temperature range —90°C to +60°C on the NMR time scale. The ^1H spectra show the aryl groups to be rotating at +25°C but to be frozen out on the NMR time scale at low temperatures.

Since the first zerovalent complex of palladium containing the dibenzylideneacetone [dba, PhCH=CHCOCH=CHPh] ligand was prepared by Ishii and coworkers [1] there has been controversy concerning the structures of these species and of their platinum(0) analogues [2]. This arose in part because the intense colours and low solubilities of the "$M(dba)_2$" complexes made spectroscopic studies difficult in solution.

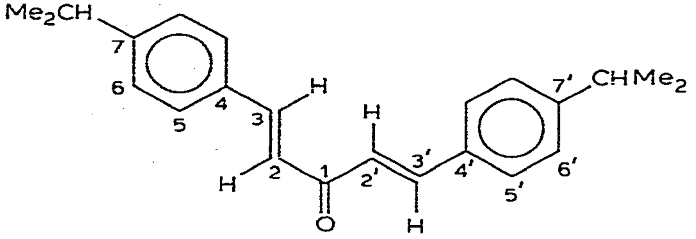
The structures of the palladium complexes in the solid state have been elucidated by X-ray diffraction studies of $[Pd_2(dba)_3(CHCl_3)]$ [3], $[Pd_2(dba)_3(CH_2Cl_2)]$ [4], $[Pd(dba)_3]$ [5], and [Pd(dba)(bipyridyl)] [6]. In all of these complexes the Pd(0) was trigonally coordinated to olefinic bonds of the dba molecules which were, with one exception [4], always in the *s-cis*, *s-trans* conformer. It was also suggested that "$Pd(dba)_2$" was probably $[Pd_2(dba)_3]$ with an extra dba of crystallisation [3,4].

In order to establish the nature of these complexes in solution a more soluble derivative was needed and we have therefore synthesised the palladium and platinum complexes of *p,p'*-diisopropyldibenzylideneacetone (dipdba, I) and have studied their ^1H and ^{13}C NMR spectra.

A material of composition corresponding to $Pd(dipdba)_2$ (II) was obtained by



The framework of [$Pd_2(dba)_3$]CH_2Cl_2 in the solid state (phenyls omitted; after Ref.[4]).



s-cis, s-trans-p,p'- diisopropyldibenzylideneacetone
(dipdba, I)

reaction of dipdba with Na_2PdCl_4 in methanol in the presence of sodium acetate. When this was crystallised from THF/MeOH dark purple crystalline unsolvated [Pd_2(dipdba)$_3$] (III) was obtained. This complex was stable in the solid and moderately stable in solution (even in chloroform); osmometric studies showed it to be monomeric in solution.

The ^{13}C spectrum showed three resonances in the $>C=O$ region while the olefinic resonances (which appeared at δ 125.0 and 143.0 in the free ligand (I)) were observed as ten lines in the region δ 83.6—110.8, two of which (δ 84.8 and 107.4) were of approximately twice the intensity of the remaining eight. The shift to lower frequency of these resonances is quite characteristic of π-bonded carbons [7], and the multiplicity shown by these lines as well as those of the ketone carbons (which are shifted by much smaller amounts) indicates that each of the three dipdba ligands in [Pd_2(dipdba)$_3$] is asymmetric and in a different environment. The conclusion is also supported by our observation of six aromatic resonances arising from C(4) and C(4′) and of six due to C(7) and C(7′).

The 220 MHz ^{1}H NMR spectra supported the ^{13}C spectrum and showed one additional feature at low temperatures (Fig. 1). At +25°C in $CDCl_3$ four pairs of doublets [each with J(H—H) = 12 Hz] were clearly resolved which were assigned to four of the coordinated *trans*- —CH=CH— bonds by decoupling experiments as follows: δ (a) 4.90, 5.86; (b) 4.94, 5.29; (c) 5.07, 5.91; and (d) 6.09 and 6.73. The remaining olefinic resonances were hidden in two multiplets which also contained the aromatic protons and which were centred at δ 6.45 and 6.92. On lowering the temperature to —30°C the olefinic resonances remained in approximately the same places but the aromatic resonances broadened. At —60°C the olefinic resonances were still unchanged (apart from small changes in shift) but the aromatic resonances were now observed as two relatively sharp multiplets at δ 7.35 and 7.8 and as broad signals centred at δ 5.0 and 6.7 under the olefinic multiplets. The most interesting feature of this spectrum was, however, the emergence of two singlets (δ 6.26, 6.56 of approximate intensity 2H each) which we identify as arising from four further olefinic protons. On further cooling (to —90°C in CD_2Cl_2) these singlets split further into AB doublets (J(H—H) = ca. 12 Hz); this effect we attribute to small changes in chemical shift with temperature and not to a fluxional process. The isopropyl groups were observed as unresolved multiplets throughout the temperature range.

We interpret these spectra to imply that the [Pd_2(dipdba)$_3$] has a very asymmetric structure in which all the olefinic bonds are different but that they are rigidly attached to the metals and do not take part in any fluxional process.

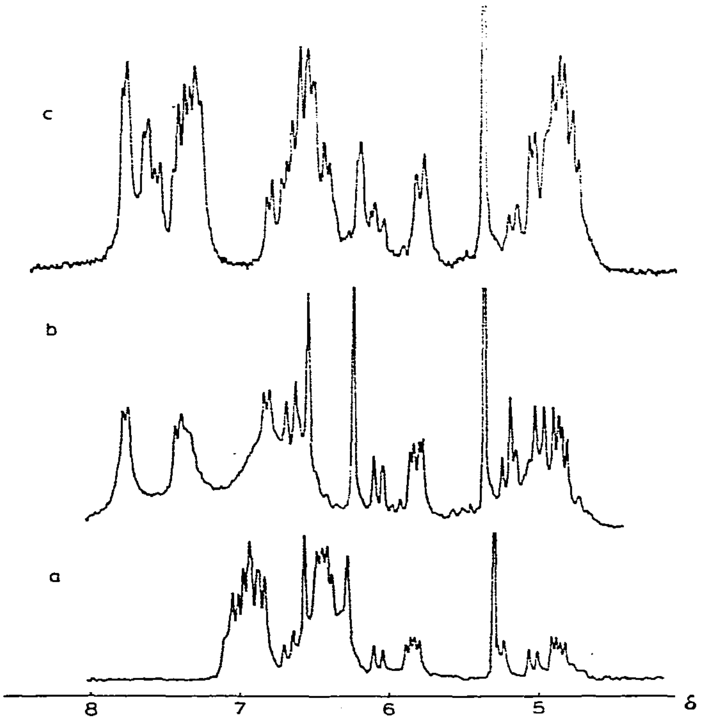


Fig. 1. 220 MHz ^{1}H NMR spectra of [Pd_2(dipdba)$_3$] (III) (δ 4—8, in CD_2Cl_2) at (a) +25°C, (b) —50°C and (c) —90°C.

Since the spectra remain the same up to +60°C the framework is clearly very rigid. The change in the peak positions of the aromatic protons indicates that the rings are rotating at +25°C but are frozen out at low temperature. At least two different rates of freezing out the rotation are evident from a qualitative analysis of the spectra. For example, the —50°C spectrum of III in CD_2Cl_2 shows sharp resonances centred at δ 7.35 and 7.77 (Fig. 1) which we interpret as arising from a freezing of rotation of some of the aryl groups; on lowering the temperature to —90°C further fine structure becomes apparent (at δ 7.20, 7.45) and further signals appear at δ 6.5 which we ascribe to the freezing out of the remaining aryl groups. Corresponding changes occur in the higher field region (δ, 4.9) too.

The spectra are completely consistent with those expected if the molecule has the structure in solution that is adopted by $[Pd_2(dba)_3(solvent)]$ in the solid [3,4] where each olefinic group and each phenyl has a different position.

We are, however, unable to say whether the structure $[Pd_2(dipdba)_3]$ in solution is that adopted in the solid $[Pd_2(dba)_3(solvent)]$ or whether different conformers of dipdba leading to a similar asymmetry are present. Models of $Pd_2(dba)_3$ or III show that the solid state arrangement leads to a very rigid and hindered cage and it is therefore not too surprising that only the aryl groups can move with any ease.

The ^{13}C NMR spectrum of the "$Pd(dipdba)_2$" compound (II) in $CDCl_3$ also showed very clearly the presence of only resonances due to free dipdba and to $Pd_2(dipdba)_3$. This material is therefore simply a mixture of I and III, and we conclude that $Pd(dipdba)_2$, like $Pd(dba)_2$, has no independent existence.

No exchange could be detected between free and coordinated dipdba in complex II either in the ^{13}C spectrum (at +25°C) or in the ^{1}H spectrum below 50°C. Above that temperature small changes in the intensity of the free dipdba ligand were observed which suggest that slow (on the NMR time scale) exchange may be occurring. In view of the high reactivities of $[Pd_2(dba)_3]$ and $[Pd_2(dipdba)_3]$ a high lability may be expected; however, the rigid framework of the molecule means that equilibria are probably established quite slowly.

The platinum complex $[Pt_2(dipdba)_3]$ (IV) was obtained by an analogous route to that used to prepare III but the yield was significantly lower and the complex was somewhat less stable in solution. This, together with the rather poorer solubility of IV made the accumulation of a good ^{13}C F.T. NMR spectrum difficult. Owing to the rather poor signal to noise ratio it was not possible to distinguish the platinum satellites (due to coupling to ^{195}Pt, 34%) of most of the resonances with any certainty. The general form of the spectrum was however similar to that of III except that the olefinic resonances were shifted to even lower frequency (δ 68.6 to 97.4) while two of the $\geq\underline{C}O$ resonances were close that of free dipdba and one was at higher frequency.

The 220 MHz ^{1}H NMR spectrum of IV in $CDCl_3$ showed very similar features to that of III (Fig. 2), in particular four pairs of olefinic doublets (all $J(H—H) = 11$ Hz) were observed which were assigned by decoupling experiments as follows: δ (a) 3.95, 5.98; (b) 4.26, 5.94; (c) 4.46, 4.84 and (d) 4.64, 4.86. The two highest field resonances (δ 3.94, 4.26) were well-separated and showed coupling to ^{195}Pt ($J(H—Pt) = 49$ and 44 Hz respectively), confirming that the double bonds were indeed coordinated.

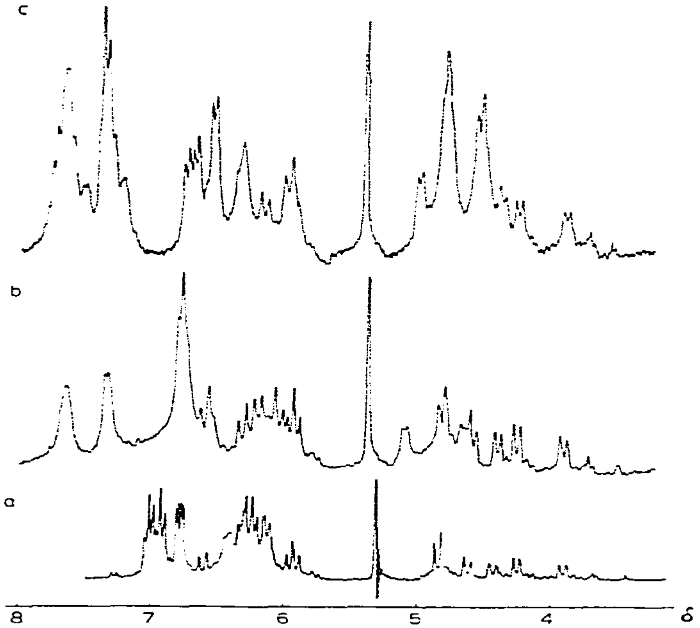


Fig. 2. 220 MHz ^{1}H NMR spectra of [Pt_2(dipdba)$_3$] (IV) (δ 4—8 in CD_2Cl_2) at (a) +25°C, (b) —50°C and (c) —90°C.

Again the remaining four olefinic resonances were hidden underneath aromatic multiplets. On lowering the temperature a similar series of changes to that seen for [Pd_2(dipdba)$_3$] occurred; while the eight olefinic doublets described above did not change significantly in position (as indicated by decoupling experiments at —50°C) the aromatic resonances first broadened and then separated and sharpened. At —90°C in CD_2Cl_2 the spectrum showed the same olefinic pattern as at higher temperatures but some of the olefinic resonances were now overlaid by aromatic ones which were observed as broad multiplets at δ 4.54, 4.8, 4.97, 6.32, 7.3 and 7.65. The shifts in the aromatic resonances also uncovered (at —50°C) two further pairs of doublets [δ (e) 6.03, 6.32 and (f) 6.21, 6.50] which are assigned to the remaining four olefinic resonances. Thus all twelve olefinic protons can be seen and all are different.

The behaviour of the aromatic resonances on cooling the solution was closely similar to that observed for the palladium complex III and we suggest that here too there are at least two different rates of freezing out of the aryl rotations.

The ^{1}H NMR spectrum of a 1 : 1 mixture of dipdba and [Pd_2(dipdba)$_3$] in $CDCl_3$ was unchanged up to the highest temperature attainable (+60°C). This indicates that the complex IV is still rigid and does not exchange with the free ligand at a measurable rate on the NMR time scale up to this temperature.

These results suggest that the [Pt_2(dipdba)$_3$] has a basically analogous structure to that of [Pd_2(dipdba)$_3$], though it is not possible to say which conformers of dipdba are present. It also appears that Pt bonds more strongly to the olefinic carbons of dipdba by accepting more electron density from the olefinic bonds than the Pd does. In the palladium complex the excess negative charge may be considered to be transferred to the carbonyl oxygen (effectively reducing the C=O bond order), whereas in the platinum complex the metal accepts this charge and the C=O bond order is little changed. This is also apparent from the ν(CO) in the infrared spectra, where the high intensity peak at 1653 cm^{-1} in dipdba is absent in [Pd_2(dipdba)$_3$] but is seen in [Pt_2(dipdba)$_3$] at 1636 cm^{-1} *.

Experimental

NMR data were obtained using Perkin—Elmer (220 MHz, ^{1}H), R-12B (60 MHz, ^{1}H) and JEOL PFT-100 (25.15 MHz, ^{13}C) spectrometers and are collected at the end of this section or shown in Figs. 1 and 2.

Pd_2(dipdba)$_3$ (III)

A mixture of dipdba [8] (3.3 g, 10.3 mmol) and a methanolic solution of Na_2PdCl_4 (0.8 g, 2.76 mmol, in 20 ml MeOH) was stirred in an open beaker at +55°C. Anhydrous sodium acetate (2.6 g, 31.7 mmol) was added and the mixture stirred at +55°C for 5 mins. The mixture was allowed to cool to +20°C and a brown solid was filtered off which was washed successively with water (4 × 25 ml), methanol (2 × 25 ml) and light petroleum (25 ml) before being dried under vacuum (yield = 2.61 g). This material analysed for "Pd(dipdba)$_2$". (Found: C, 73.9; H, 7.2. $C_{46}H_{52}O_2Pd$ calcd.: C, 74.3; H, 7.0%).

This brown solid was dissolved in tetrahydrofuran (100 ml) at +20°C to give a dark maroon solution. The solution was filtered to remove traces of metal and the volume of the filtrate reduced to 20 ml in vacuo. Methanol (20 ml) was slowly added and the solution set aside for 18 h at 0°C. A dark purple crystalline solid formed which was filtered off, washed with methanol (3 × 25 ml) and dried under vacuum. The complex was recrystallised from tetrahydrofuran and methanol to give an analytically pure sample of [Pd_2(dipdba)$_3$] (yield = 1.22 g, 75%). (Found: C, 70.96; H, 6.98%; M, 1116. $C_{69}H_{78}O_3Pd_2$ calcd.: C, 70.98, H, 6.68%; M, 1168).

Pt_2(dipdba)$_3$ (IV)

Sodium acetate (6.0 g, 73.0 mmol) and dipdba (5.0 g, 15.7 mmol) were stirred in refluxing ethanol (100 ml) under a nitrogen atmosphere and a solution of K_2PtCl_4 (3.0 g, 7.2 mmol) in water (25 ml) at +20°C was added slowly to give a black suspension in a dark solution. The mixture was refluxed for 1 h and then allowed to cool when the black precipitate was filtered off and washed successively with water (4 × 50 ml), methanol (2 × 50 ml) and light petroleum (25 ml) before being dried under vacuum (yield = 3.4 g).

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[*] *Note added in proof:* Professor Kawazura has recently given us details of an NMR study of Pd_2(dba)$_3$ and Pt_2(dba)$_3$ containing partially deuterated dba ligands. (H. Kawazura, personal communication, and abstracts of VIII International Conference on Organometallic Chemistry, Kyoto, September 1977; H. Tanaka, K.-I. Yamada and H. Kawazura, J. Chem. Soc. Perkin, in press; H. Kawazura, H. Tanaka, K.I. Yamada, T. Takahashi and Y. Ishii; H. Tanaka and H. Kawazura, J. Chem. Soc. Dalton, in press.) The chemical shifts of the olefinic protons in Pd_2(dba)$_3$ and in Pt_2(dba)$_3$ in $CHCl_3$ are very similar to those we observe for Pd_2(dipba)$_3$ and Pt_2(dipdba)$_3$ respectively, and it is therefore very probable that the same conformers are present in the dipdba as in the dba complexes. According to Kawazura's analysis, therefore, Pd_2(dipdba)$_3$ contains three *s-cis,s-trans* ligands and Pt_2(dipdba)$_3$ contains one *s-cis,s-cis* and two *s-cis,s-trans* ligands in solution.

This crude sample of (IV) contained some uncoordinated dipdba and was stirred in tetrahydrofuran (100 ml) to give a dark purple solution. After 1 h the solution was filtered to remove some metal and the volume of the filtrate reduced (to 20 ml) in vacuo. Methanol (20 ml) was slowly added and the solution was set aside for 18 h at 0°C. Fine violet-black crystals were deposited which were filtered off, washed with methanol (2 × 25 ml) and dried under vacuum. The complex was recrystallised from tetrahydrofuran and methanol to give an analytically pure sample of [Pt_2(dipdba)$_3$] (yield = 1.4 g, 30%). (Found: C, 61.44; H, 5.85%, M, 1163. $C_{69}H_{78}O_3Pt_2$ calcd.: C, 61.60, H, 5.83%, M, 1345).

^{13}C NMR spectra (at +25°C)

dipdba (I), in CD_2Cl_2: δ 23.8 (Me, 34.5 ($\underline{C}HMe_2$); 125.0 (C(2)); 127.3, 128.7 (C(5), C(6)), 132.8 (C(4)); 143.1 (C(3)); 152.2 (C(7)); 188.8 (C(1)). Pd_2(dipdba)$_3$ (III), in $CDCl_3$: δ 23.8, 24.0 (Me); 33.9, 34.2 ($\underline{C}HMe_2$); 83.6, 84.3, 84.8, 88.3, 88.8, 91.1, 93.5, 96.7, 107.4, 110.8 (C(2) + C(2')); 126.8, 127.6, 128.1, 128.4, (C(5) + C(5') + C(6) + C(6')); 131.9, 132.3, 133.4, 135.2, 135.3, 136.9, (C(4) + C(4')); 148.0, 148.6, 148.8, 150.4, 150.9, 151.1 (C(7) + C(7')); 180.6, 181.7, 184.4 (C(1)). Pt_2(dipdba)$_3$ (IV) in $CDCl_3$: δ 23.9, 24.3 (Me); 34.1, 34.5 ($\underline{C}HMe_2$); 68.6, 69.3, 70.9, 71.2, 76.5, 81.0, 97.4 (C(2) + C(2') + C(3) + C(3')); 125.0, 126.7, 127.3, 127.7, 128.3, 128.7 (C(5) + C(5') + C(6) + C(6')); 132.9, 137.1, 137.7 (C(4) + C(4')); 147.9, 148.3, 148.9, 151.6 C((7) + C(7')), 188.0{37}, 188.7{31}, 195.7{29} (C(1)). (*J*(C—Pt) in parentheses { } in Hz).

^{1}H NMR spectrum

dipdba (I) in $CDCl_3$; δ 1.25 (Me, d, *J*(H—H) = 7 Hz), 2.95 ($C\underline{H}Me_2$, q), 7.02, 7.72 (olefinic CH, 2 × d, *J*(H—H) = 6 Hz), 7.23, 7.52 (aromatic CH, 2 × d, *J*(H—H) = 9 Hz).

Infra-red spectra

ν(CO), Nujol mull. dipdba (I): 1565m (sh), 1570m, 1598vs, 1611s (sh) 1627m, 1653vs, 1659vs (sh) cm^{-1}. Pd_2(dipdba)$_3$ (III): 1569w—m, 1593w—m, 1607m—s, 1617m—s, 1646w cm^{-1}. Pt_2(dipdba)$_3$ (IV): 1570w, 1595w, 1608m—w, 1626w(sh), 1636m, cm^{-1}.

Acknowledgements

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