# Bis- and Tris-(dibenzylideneacetone)platinum and the Stabilization of Zerovalent Complexes by an Unsaturated Ketone

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*Summary* The new complexes $(dba)_2Pt$ and $(dba)_3Pt$ (dba = dibenzylideneacetone) are reported; the metal in $(dba)_2Pt$ and $(dba)_2Pd$ is bonded by the ketonic, and not by the olefinic groups.

WE report the first complexes of platinum(0) involving the ligand dibenzylideneacetone (dba, PhCH=CH·CO·CH=CHPh) and on the novel type of bonding which stabilizes such complexes. The first complex of this type, $(dba)_2Pd$, was recently described by Takahashi *et al.*, and our interest in low-valent olefin complexes has led us to extend this to the synthesis of $(dba)_2Pt$ and $(dba)_3Pt$.

The deep purple, air-stable $(dba)_2Pt$ was prepared (41%) by reaction of $KPtCl_4$ with 3 mol. equiv. of dba in refluxing aqueous ethanol under nitrogen in the presence of sodium acetate.

The tris-complex, $(dba)_3Pt$, a yellow microcrystalline solid, was obtained (40%) by a similar route in refluxing aqueous methanol *in the presence of air or oxygen.* However, analysis showed that no extra oxygen was incorporated into the complex. This complex was also stable in the solid but dissolved in a variety of solvents to give green solutions that rapidly turned purple and from which $(dba)_2Pt$ and dba in 1 : 1 ratio were isolated. This, together with the observed molecular weight, shows that complete dissociation (1) has occurred. Addition of a large excess of dba to

$$(dba)_3Pt \rightarrow (dba)_2Pt + dba \qquad (1)$$

$(dba)_2Pt$ did not give the tris-complex. Both the bis- and tris-complexes gave dba and platinum when heated (decomp. >170°), on treatment with carbon monoxide, or when set aside for longer periods of time in solution.

TABLE

*Spectra of* dba, $(dba)_2Pd$, *and* $(dba)_2Pt$

*I.r.* (1700—1500 $cm^{-1}$) *in* $CHCl_3$

| dba (in $cm^{-1}$) | $(dba)_2Pd$ (in $cm^{-1}$) | $(dba)_2Pt$ (in $cm^{-1}$) | |
|---|---|---|---|
| 1652[a] m–s | 1656[a] w | 1652[a] w | ν(CO) |
| 1621[a] vs | 1613 vs, br | 1624 vs | ν(C=C) |
| 1604 sh | | | ν(C=C) aromatic |
| 1591 m | | 1593 s, br | |
| 1578 m–s | 1579 m | 1579 m | |
| | 1544 m,br | 1527 mbr | ν(CO) |

*U.v.–visible in* $CH_2Cl_2$

| $\lambda_{max}$ nm | log $\epsilon$ | $\lambda_{max}$ nm | log $\epsilon$ | $\lambda_{max}$ nm | log $\epsilon$ |
|---|---|---|---|---|---|
| 233 | 3·90 | 235 | 4·48 | 235 | 4·27 |
| 325 | 4·38 | 336 | 4·54 | 336 | 4·48 |
| | | 378 (shoulder) | 4·27 | | |
| | | 538 | 3·92 | 568 | 3·51 |

[a] These bands appear as closely spaced (⩽ 4 $cm^{-1}$) doublets or as asymmetric peaks; this effect may arise from Fermi resonance, see ref. 5.

The n.m.r. spectrum (100 MHz; $CDCl_3$) of $(dba)_2Pt$ was, surprisingly, identical to that of dba itself. In particular the coupling constant (16·5 Hz) and chemical shifts of both types of olefinic protons remained unaltered on complex formation; this renders unlikely the possibility that the molecule is fluxional or taking part in an exchange process. There was also no evidence for coupling to $^{195}Pt$ ($I = \frac{1}{2}$; 34% abundance) of either the olefinic or aromatic protons. A similar result was obtained in $CH_2Cl_2$ solution where the spectrum was unchanged down to −66°. The palladium complex, $(dba)_2Pd$, was only somewhat soluble but the n.m.r. spectrum was again identical to that of dba and $(dba)_2Pt$.

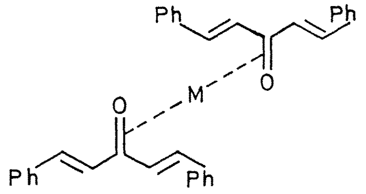
By contrast, Müller and Göser[2] found that the olefinic protons in cyclo-octa-1,5-diene were moved by 1·3 p.p.m. to higher field on complexing to platinum in bis(cyclo-octa-1,5-diene)platinum(0) and were coupled to $^{195}Pt$ (55 Hz).

The i.r. spectra of the bis-complexes in solution (Table) show that, by comparison with dba, ν(C=O) has almost disappeared while ν(C=C) remains intense and relatively unchanged. The only new bands detected in the spectra are of medium intensity and rather broad, at 1544 (Pd) and 1527 (Pt) $cm^{-1}$. We suggest that these are modified ν(CO) bands. The i.r. spectra both of dba and of the complexes are considerably changed in the solid (Nujol mull) but it is apparent that a similar effect occurs there.†

These results suggest that in solution the metal atoms are bound by the carbonyl groups rather than by the double bonds as was originally proposed.[1]

This conclusion is also supported by the electronic spectra of the complexes in $CH_2Cl_2$ solution, which are strikingly similar to those of dba itself except for the very intense long-wavelength charge-transfer bands that give the complexes their colours and which are most reasonably ascribed to metal → ligand ($d \rightarrow \pi^*$) transitions.

This unusual and unexpected result may be contrasted with the more conventional bonding situation which occurs in the quinone complexes of nickel(0),[3] where the metal is π-bonded to both olefinic double bonds. This is probably due to the preferred *s-cis* geometry of dba,[4,5] which does not allow good overlap between both double bonds and the metal orbitals.



(I)

Models indicate that, of the two possibilities for complex formation, by "end-on" or "sideways" co-ordination, the latter is more reasonable and we suggest the structure (I) for the bis-complexes. The bonding implied has some analogy to that in $CS_2$ complexes of $Pd^0$ and $Pt^0$, the crystal structures of which have been determined.[6,7]

$(dba)_2Pt$ and $(dba)_3Pt$, as well as $(dba)_2Pd$[1] are synthetically very useful starting materials, for example, for the oligomerization of acetylenes. Details of these and other reactions will be reported shortly.

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† The spectrum of $(dba)_3Pt$ as a Nujol mull is identical to that of $(dba)_2Pt$.

[1] Y. Takahashi, T. Ito, S. Sakai, and Y. Ishii, *Chem. Comm.*, 1970, 1065.
[2] J. Müller and P. Göser, *Angew. Chem. Internat. Edn.*, 1967, **6**, 364.
[3] G. N Schrauzer, *Adv Organometallic Chem.*, 1964, **2**, 17.
[4] S. V. Tsukerman, V. D. Orlov, Yu. N. Surov, and V. F. Lavrushin, *Zhur. Strukt. Khim.*, 1968, 67.
[5] K. Noack and R. N. Jones, *Canad. J. Chem.*, 1961, **39**, 2201.
[6] R. Mason and A. I. M. Rae, *J. Chem. Soc.* (*A*), 1970, 1767.
[7] T. Kashiwagi, N. Yasuoka, T. Ueki, N. Kasai, M. Kakudo, S. Takahashi, and N. Hagihara, *Bull. Chem. Soc. Japan*, 1968, **41**, 296.