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Preliminary communication

Synthesis of Pt(II)-η^3-benzyl complexes: crystal structure of $[Pt(Bu^t_2P(CH_2)_3PBu^t_2)(\eta^3$-*anti*-1-$MeCHC_6H_4Br$-4)][$BF_4$] *

L.E. Crascall, S.A. Litster, A.D. Redhouse and J.L. Spencer

Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT (U.K.)

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Abstract

Treatment of bis(1,5-cyclooctadiene)platinum with 1,3-bis(di-t-butylphosphino)propane and various styrenes and subsequent protonation of the resultant platinum(0) alkene complexes affords a series of cationic complexes $[Pt(Bu^t_2P(CH_2)_3PBu^t_2)(\eta^3$-*anti*-1-$MeCHC_6H_4X)][BF_4]$ (X = Br-3, Br-4 (**2b**), H, Me-4, MeO-4). These have been characterized by NMR spectroscopy and, in the case of **2b**, by a single-crystal X-ray diffraction study.

Although a large number of η^3-allyl complexes of Pt(II) have now been prepared [1], compounds containing η^3-benzyl ligands are less well known. Our investigations into 3-centre, 2-electron bonding have led to the discovery of a facile rearrangement process following protonation of platinum styrene complexes, affording compounds containing an η^3-benzyl ligand in the ground state.

The treatment of $[Pt(cod)_2]$ [2] (cod = 1,5-cyclooctadiene) with $Bu^t_2P(CH_2)_3PBu^t_2$ (dbpp) and styrenes yields the off-white solids $[Pt(dbpp)(\eta^2\text{-}CH_2{=}CHC_6H_4X)]$ [X = Br-3, (**1a**) **, Br-4 (**1b**), H (**1c**), Me-4 (**1d**)]. Alternatively, for X = H, Me-4, and MeO-4, the Na/Hg amalgam reduction of $[PtCl_2(dbpp)]$ in the presence of an excess of the styrene yields the platinum styrene diphosphine complexes **1c**–**1e**, respectively. Protonation of **1** with $HBF_4 \cdot OMe_2$ affords pale orange-green dichroic crystals of the compounds $[Pt(dbpp)(\eta^3$-*anti*-1-$MeCHC_6H_4X)][BF_4]$ (**2a**–**2e**, see Scheme 1), which, in solution in the absence of excess styrene, decompose to form known hydride-bridged dinuclear platinum complexes [3].

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* Dedicated to Professor F.G.A. Stone, F.R.S., on the occasion of his 65th birthday.

** ^{31}P NMR data for **1a**–**1e** in C_6D_6: **1a** δ 44.3, $^1J(PtP)$ 3369, δ 42.1 ppm, $^1J(PtP)$ 3322, $J(PP)$ 37.7 Hz; **1b** δ 44.5, $^1J(PtP)$ 3346, δ 43.2, $^1J(PtP)$ 3335, $J(PP)$ 39.6 Hz; **1c** δ 44.6, $^1J(PtP)$ 3326, δ 42.9, $^1J(PtP)$ 3356, $J(PP)$ 41.4 Hz; **1d** δ 44.4, $^1J(PtP)$ 3302, δ 43.1, $^1J(PtP)$ 3363, $J(PP)$ 42.5 Hz; **1e** δ 44.7, $^1J(PtP)$ 3275, δ 43.5, $^1J(PtP)$ 3374, $J(PP)$ 43.2 Hz.

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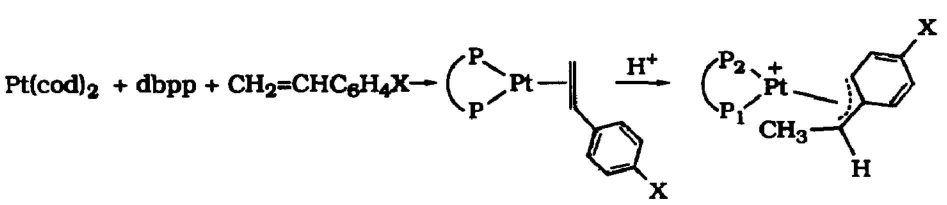

(1) (2)

Scheme 1

Compound **2b** has been characterized by an X-ray diffraction study *. This revealed an η^3-benzylic bonding mode for the $MeCHC_6H_4Br$-4 group (Fig. 1). The platinum atom is bonded to C(8), C(65) and C(64) with progressively longer Pt–η^3-C distances. This asymmetry is not untypical [4], and a number of compounds containing the η^3-benzyl moiety exhibit a similar trend. The pattern of bond distances within the C_6H_4 ring (i.e. two short, C(62)–C(63) [1.373(13) Å], C(61)–C(66) [1.333(16) Å], and three long, C(63)–C(64) [1.429(16) Å], C(61)–C(62) [1.420(15) Å], C(65)–C(66) [1.425(12) Å]) is consistent with the proposal that the aromatic delocalisation within the ring is disrupted upon coordination to the metal atom, leading to a degree of electron localization [5].

In η^3-allyl metal complexes substituted at a terminal carbon, the *syn*-isomer is expected to predominate because of lower steric interaction with the metal atom [6]. However, the crystal structure of **2b** (Fig. 1b) shows that the methyl group adopts an *anti*-conformation.

The cations **2a**–**2e** are asymmetric and hence have two non-equivalent phosphorus atoms. The ^{31}P-$\{^1H\}$ NMR data for (**2a**–**2e**) are shown in Table 1. One of the $^1J(PtP)$ values is large and sensitive to the electron-donating ability of the substituent X, and this is fully consistent with one phosphorus atom lying *trans* to a weakly coordinating C_6H_4X group. As the substituent X becomes more electron donating, the value of $^1J(PtP_{trans})$ increases, suggesting that the Pt–η^3-$MeCHC_6H_4X$ interaction becomes progressively weaker.

The ^1H NMR spectra of **2** are temperature dependent, indicating dynamic behaviour in solution. A fluxional process, such as *syn–anti* methyl site exchange, could account for this observation, although it must occur via a mechanism which does not allow the phosphorus atoms to become equivalent. Fluxional processes occurring in η^3-allyl platinum and palladium systems have been examined [7].

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* Crystallographic data for **2b**: $[Pt(Bu^t_2P(CH_2)_3PBu^t_2)(CH_3CHC_6H_4Br)][BF_4]$, $M = 797.4$, monoclinic, $P2_1/n$, a 17.752(7), b 10.153(2), c 18.643(4) Å, $\beta = 111.04(3)°$, U 3136(1) Å^3, $Z = 4$, D_c 1.689 Mg m^{-3}, λ(Mo-K_a) 0.71073 Å, μ 5.92 mm^{-1}, $F(000) = 1584$. A total of 6109 independent reflections were collected at -70 °C on a Nicolet R3m/V four circle diffractometer. The structure was solved by using Patterson and Fourier synthesis. Absorption was corrected for using the numerical face-indexing technique, 4450 reflections with $F > 4.0\sigma(F)$ were used for full-matrix least-squares refinement. Hydrogen atoms were introduced in idealised positions and constrained to ride on their respective carbon atoms. The final R-values were $R = 4.97\%$ and $R_w = 5.30\%$. The atomic coordinates, bond lengths, angles and thermal parameters are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K. Any request should be accompanied by the full literature communication.

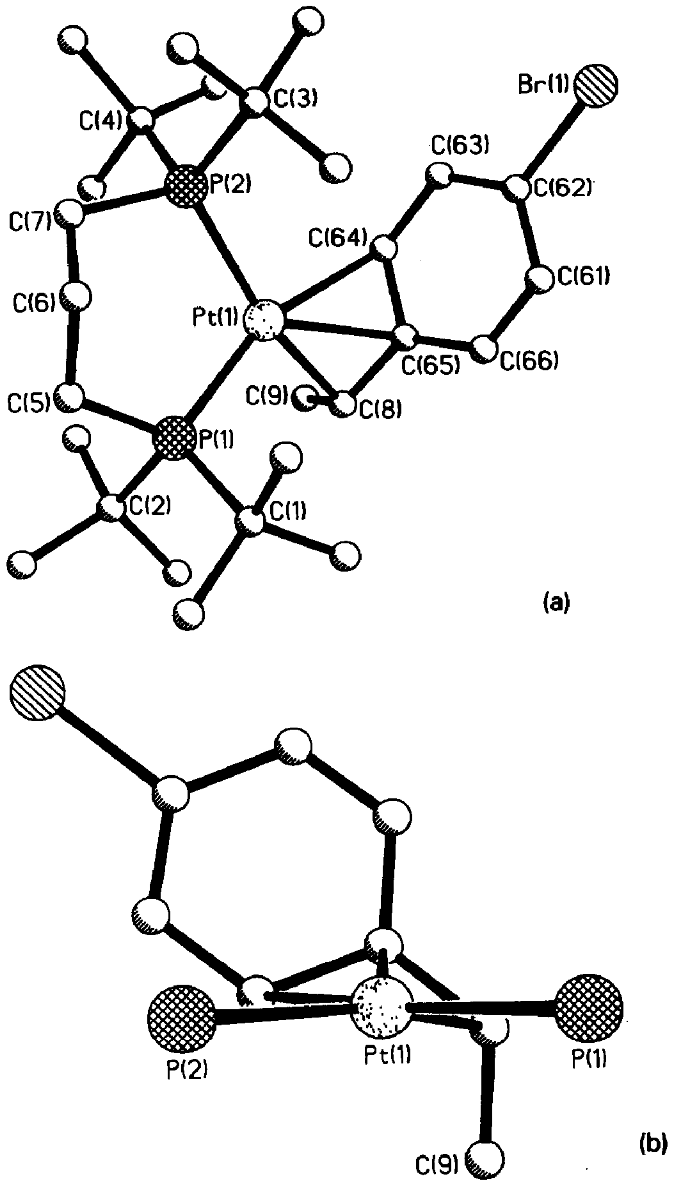


Fig. 1. (a) Structure of cation [Pt(dbpp)(η^3-*anti*-1-MeCHC$_6$H$_4$Br-4)][BF$_4$] (**2b**) with hydrogen atoms excluded for clarity, viewed perpendicular to the platinum coordination plane. Important molecular dimensions include: bond lengths (Å) Pt–P(1) 2.295(3), Pt–P(2) 2.349(3), Pt–C(8) 2.163(11), Pt–C(65) 2.242(10), Pt–C(64) 2.446(9), C(64)–C(65) 1.436(13), C(8)–C(65) 1.423(16); bond angles (°) P(1)–Pt–P(2) 99.6(1), P(1)–Pt–C(8) 97.6(3), P(2)–Pt–C(8) 160.7(3), P(1)–Pt–C(64) 160.9(3), P(2)–Pt–C(64) 99.5(3), C(64)–C(65)–C(8) 118.0(7), C(64)–Pt–C(8) 63.9(4). (b) Cation **2b** with Bu^t groups and hydrogen atoms omitted, viewed parallel to the platinum–phosphorus coordination plane.

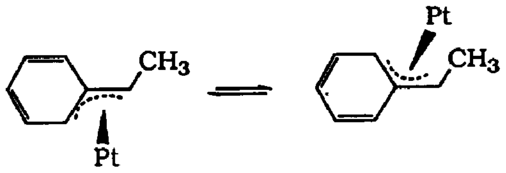
Maitlis and co-workers [8] reported three types of fluxional processes for the η^3-triphenylmethyl complexes [M(CPh$_3$)(acac)] (M = Pt, Pd; acac = MeCOCHCOMe), one of which involved the metal undergoing a [1,5]-suprafacial shift from one η^3-benzylic position to the other equivalent one. In complexes **2a**–**2e**

Table 1

Selected ^{31}P NMR data for the cations $[Pt(Bu^t_2P(CH_2)_3PBu^t_2)(\eta^3\text{-}anti\text{-}1\text{-}MeCHC_6H_4X)][BF_4]$ (**2a**–**2e**) in CD_2Cl_2 [a]

Compound	X	δ_{P_1}	$^1J(PtP_1)$	δ_{P_2}	$^1J(PtP_2)$
2a	Br-3	51.4	5285	41.7	2959
2b	Br-4	49.3	5256	36.0	2998
2c	H	48.3	5294	38.0	2995
2d	Me-4	49.9	5362	36.6	2972
2e	MeO-4	53.8	5492	40.7	2909

[a] Chemical shifts δ in ppm and coupling constants in hertz.



Scheme 2

this would exchange the methyl site whilst the phosphorus atoms would remain non-equivalent (Scheme 2). However, unlike that for **2a**–**2e**, for $[M(CPh_3)(acac)]$ this process was fast on the NMR timescale and could not be frozen out.

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