Co-ordinatively Unsaturated Diphosphine Platinum(II) Alkyl Cations: A New Class of β-Agostic Complexes

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Treatment of tris(norbornene)platinum with diphosphines and subsequent protonation affords a series of cationic complexes $[Pt(C_7H_{11})(L_2)]^+$ (L_2 = peralkyldiphosphine) in which the norbornyl ligand binds to platinum *via* σ-alkyl and β-C–H agostic interactions; the strength of the latter bond varies and has been characterised by n.m.r. and *X*-ray structure analysis.

It has become clear in the past decade that agostic complexes in which ligand α- or β-C–H bonds act as two-electron donors to otherwise unsaturated metals, may occur in the centre and left of the transition series (*i.e.*, the scandium to cobalt subgroups).[1] We report here that such complexes also exist in the nickel subgroup, specifically for platinum. Remarkably these compounds are co-ordinatively unsaturated, even allowing for the agostic interaction. Furthermore the species we have prepared provide an ideal opportunity to study the strength of the agostic interaction as a function of the ligand set at platinum. This is valuable since the factors which favour the agostic over the related olefin-hydride and alkyl species remain only partly understood. We have viewed β-agostic complexes as models for the intermediate stages of the β-elimination and olefin insertion reactions,[2] the compounds reported here are particularly informative in this regard.

Treatment of $[Pt(nb)_3]$ (nb = norbornene)[3] with diphosphines readily yields the off-white crystalline solids $[Pt(nb)L_2]$ in yields >95% [L_2 = $Cyh_2P(CH_2)_2PCyh_2$ (**1a**),† (Cyh = cyclohexyl), $Bu^t_2P(CH_2)_2PBu^t_2$ (**1b**), $Cyh_2P(CH_2)_3PCyh_2$ (**1c**), $Bu^t_2P(CH_2)_3PBu^t_2$ (**1d**) and *o*-$(Bu^t_2PCH_2)_2C_6H_4$ (**1e**)]. Protonation of (**1**) with either $HBF_4{\cdot}OEt_2$ or CF_3SO_3H affords the microcrystalline compounds $[Pt(C_7H_{11})(L_2)]Y$ (**2a**—**2e**, Y = BF_4, CF_3SO_3, see Scheme 1) in yields >90%. In the temperature range 300—195 K the ^1H n.m.r. spectrum of (**2b**) shows a resonance at δ −1.05 p.p.m. [*J*(PtH) 136 Hz, *J*(PH) 56.7 and 7.9 Hz) characteristic of a hydride ligand but with a much reduced Pt–H interaction (*cf.* ^1J(PtH) and ^2J(PH) for *cis*-$[PtH_2\{Bu^t_2P(CH_2)_2PBu^t_2\}]$ are 1101, and 184 and 16.4 Hz respectively).[4] Consistent with a relatively weak Pt–H interaction the one-bond Pt–P coupling constant for the phosphorus *trans* to the high-field proton is much larger than normal in Pt^{II} hydride complexes at 4909 Hz. Furthermore the ^{13}C n.m.r. spectrum of (**2b**) at 195 K shows a carbon resonance at δ 30.0 p.p.m. with ^1J(CH) 149 and 64 Hz typical of an agostic alkyl group. These observations are clearly indicative of the norbornyl ligand being bound to platinum in (**2**) in an η^2-mode with a weakened β-C–H bond co-ordinated in an agostic manner (Scheme 1). In order to provide structural characterisation we have conducted a low-temperature *X*-ray diffraction study‡ on (**2b**, Y = BPh_4) the product of anion metathesis of (**2b**, Y = BF_4) with $NaBPh_4$ in CH_2Cl_2.

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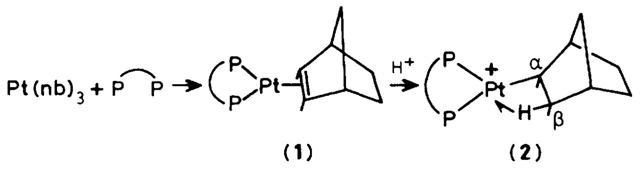
† ^{31}P n.m.r. Data for (**1a**—**1e**): (**1a**) δ 71.8 p.p.m., ^1J(PtP) 2982 Hz; (**1b**) δ 102, ^1J(PtP) 3067; (**1c**) δ 24.3, ^1J(PtP) 3116, (**1d**) δ 46.5, ^1J(PtP) 3195, (**1e**) δ 48.9, ^1J(PtP) 3331.

‡ *Crystal Data* for (**2b**, Y = BPh_4): $C_{49}H_{71}BP_2Pt$, *M* = 928.0, monoclinic, space group $P2_1/n$, a = 13.996(4), b = 18.963(7), c = 18.615(6) Å, β = 114.3(1)°, U = 4503(2) Å^3, Z = 4, D_c = 1.37 g cm^{-3}, $F(000)$ = 1912, $\bar{\lambda}$ = 0.71069 Å, μ(Mo-K_α) = 32.5 cm^{-1}. Data were collected on a Nicolet R3m/V diffractometer at 200 K for a unique quadrant of reciprocal space for $4 < 2\theta < 55°$. The structure was solved by heavy atom methods and refined by least-squares to R = 0.029 for 7985 unique, observed [$I > 1.5\sigma(I)$], absorption corrected data. Hydrogen atoms on C(1) and C(2) were directly located in difference maps and refined freely. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Table 1. Selected $^{1}H^{a}$ and $^{31}P^{b}$ n.m.r. data for the complex cations $[Pt(C_7H_{11})(L_2)]^+$ (**2a**—**2e**) in CD_2Cl_2.

Compound	Diphosphine, L_2	$\delta(H)$	$J(P_{trans}H)$	$J(PtH)$	$\delta(P_{trans})$	$\delta(P_{cis})$	$J(P_{trans}P_{cis})$	$J(PtP_{trans})$	$J(PtP_{cis})$
(**2a**)	$Cyh_2P(CH_2)_2PCyh_2$	−1.84	80.1	324	64.32	74.84	8.5	3866	2695
(**2b**)	$Bu^t_2P(CH_2)_2PBu^t_2$	−1.05	56.7	136	90.16	99.13	17.9	4909	2577
(**2c**)	$Cyh_2P(CH_2)_3PCyh_2$	−1.42	52.7	102	24.68	17.78	9.1	4852	2564
(**2d**)	$Bu^t_2P(CH_2)_3PBu^t_2$	−1.78	51.3	85	47.38	37.54	9.8	5067	2532
(**2e**)	$Bu^t_2PCH_2C_6H_4CH_2PBu^t_2$	−2.14	52.2	79	52.60	37.39	n.r.	5266	2620

[a] Agostic hydrogen only. [b] P_{trans} and P_{cis} refer to the phosphorus atoms *trans* and *cis* respectively to the agostic hydrogen.



Scheme 1

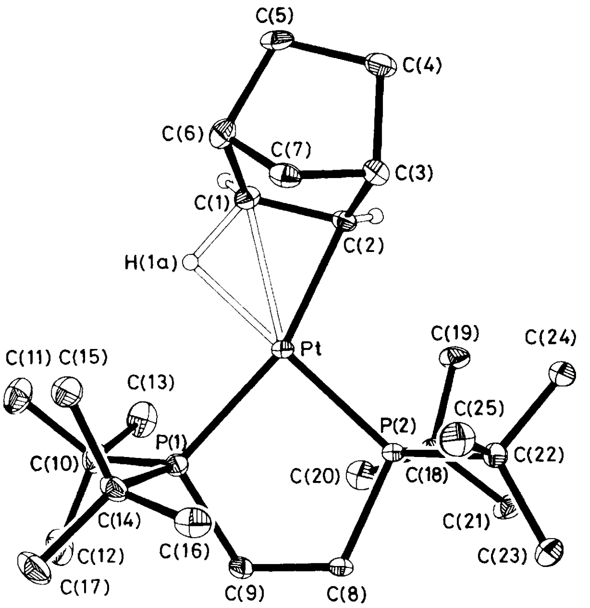


Figure 1. Molecular structure of the cation of (**2b**) with all hydrogens omitted except those on C(1) and C(2), viewed perpendicular to the platinum co-ordination plane. Important molecular dimensions include: bond lengths (Å) Pt–P(1) 2.311(1), Pt–P(2) 2.256(1), Pt–C(1) 2.309(5), Pt–C(2) 2.096(4), C(1)–C(2) 1.480(6), C(1)–H(1a) 1.28(6); bond angles(°) Pt–C(2)–C(1) 78.3(2), P(2)–Pt–P(1) 89.3(1), P(1)–Pt–H(1a) 91.3(17), P(2)–Pt–C(2) 107.4(1), P(2)–Pt–H(1a) 169.9(13); torsion angle (°) Pt–C(2)–C(1)–H(1a) −2.7(22).

The solid state structure of (**2b**) is shown in Figure 1 and is fully consistent with the 195 K n.m.r. spectra. The norbornyl ligand bonds through a σ-bond [Pt–C(2) 2.096(4) Å] and a β-agostic interaction [Pt–C(1) 2.309(5), Pt–H(1a) 1.90(7) Å]. The Pt–P bonds show evidence of the weak *trans* influence of the β-C–H ligand [Pt–P(1) 2.311(1), Pt–P(2) 2.256(1) Å]. The norbornyl geometry is substantially distorted towards that of a norbornene ligand, with Pt–C_α–C_β reduced to 78.3(2)° and the C_α–C_β bond length shortened to 1.480(6) Å [*cf.* C(4)–C(5) 1.524(7) Å], *i.e.*, approaching the values expected for an η^2-olefin (*ca.* 70° and 1.4 Å respectively).[3]

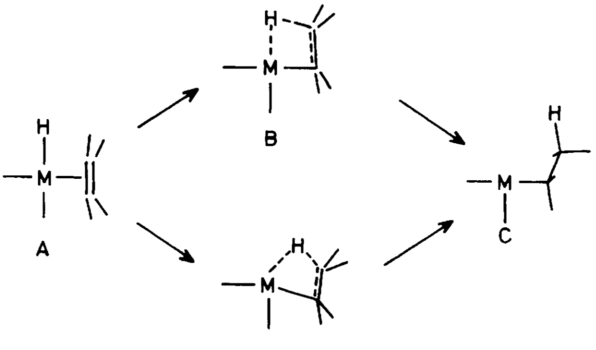


Figure 2

The cation (**2b**) is asymmetric and the four Bu^t groups are not equivalent. However at 300 K the ^1H, ^{13}C and ^{31}P n.m.r. spectra of (**2b**) are consistent with a rapid intramolecular rearrangement process which makes equivalent the two Bu^t groups on each phosphorus and affords the bicyclic norbornyl C_7 framework a time-averaged plane of symmetry, but does not exchange the two phosphorus environments. This suggests a mechanism involving an intermediate hydrido olefin complex in which rotation about the metal–olefin bond is facile (denoted as process B by Brookhart *et al.*),[1b] but in which the integrity of the square planar co-ordination geometry is retained. At 195 K the dynamic process is frozen and the asymmetry of the complex is reflected in the ^1H and ^{13}C n.m.r. spectra. The other norbornyl cations behave similarly. Consistent with this mechanism is the observation that reaction of (**1e**) with CF_3SO_3D leads exclusively to deuteriation at the agostic position: there is no facile H/D scrambling in the norbornyl ligand on either chemical or n.m.r. timescales.

Viewing (**2b**) as a model for the insertion of an alkene into a metal–hydride bond is illuminating. The geometry observed for (**2b**) (Figure 1) suggests that in the course of the insertion reaction the olefin 'fetches' the hydride rather than the hydride migrating to the olefin. These two alternatives are illustrated as A → B → C and A → D → C respectively in Figure 2. In (**2b**) the diphosphine provides a useful, quasi-cartesian framework by which to judge the motion of the other ligands. Given the assumption that (**2b**) lies on the pathway for β-elimination/olefin insertion then alternative A → B → C is clearly indicated by the P–Pt–ligand bond angles. Thus the *trans*-P–Pt–cent (cent being the midpoint of the C–C bond) and the *trans*-P–Pt–H angles are *ca.* 180° in A, but are *ca.* 144 and 170° in (**2b**) (see Figure 1). Whilst various groups have attempted to characterise olefin insertion by m.o. theory calculation of reaction pathways,[5—7] this study provides the first tractable experimental evidence addressing this problem (in other β-agostic species the co-ordination geometry is typically less helpful in defining the ligand motion). The *ab initio* calculated geometry for the analogous agostic alkyl species $[HPd(Et)PH_3]$ shows a weaker β-agostic interaction than found for (**2b**) (Pd ··· H 2.127, Pd ··· C_β 2.538 Å, Pd–C_α–C_β 87.8°).

Variation of the diphosphine [as in (**2a**—**2e**)] provides a means of probing the factors responsible for the strength of the agostic interaction in (**2**). The n.m.r. chemical shifts and particularly the Pt–P, Pt–H, and P–H coupling constants are most helpful in monitoring this interaction (see Table 1). These and other n.m.r. parameters show that the other norbornyl complexes have the same gross structure as (**2b**). However, $^1J(\text{PtH})$ is substantially reduced by increased chelated ring size and also by the increased bulk of the substituents at phosphorus (Bu^t or Cyh), other parameters behaving in a complementary fashion. The implication is that the norbornyl ligand is most alkyl-like in (**2e**) and most norbornene-hydride-like in (**2a**) and that apparently small changes in the distant ligands may cause significant perturbation of the ground-state of (**2**). To verify this suggestion and shed further light on these important problems the solid-state structures of the other complexes (**2**) and the properties of their palladium analogues are currently under investigation.

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