

High Stereo- and Regio-selectivity in the Reaction of 1,2-Bis-(dimethylphosphino)ethanehydridomethylplatinum with *p*-Chlorophenyl Isonitrile

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The title compound reacts rapidly with *p*-chlorophenyl isonitrile at $-60\text{ }^{\circ}\text{C}$ giving exclusively the *E*-iminomethyl complex, produced by insertion into the Pt-H bond, and on an intermolecular comparison, reaction is *ca.* 10^8 times faster than the corresponding insertion into Pt-Me; in methanol solution (dmpe)PtMe₂ [dmpe = bis(dimethylphosphino)ethane] reacts with *p*-chlorophenyl isonitrile to give *Z*-(dmpe)PtMe{C(OMe)=NC₆H₄Cl} whose X-ray structure is presented.

Successful development of homogeneous catalytic hydrocarbon activation requires two factors. The first of these involves conversion of the alkane into an alkylmetal hydride, which has been amply demonstrated.¹ Trapping and displacement of this entity to complete the catalytic cycle has proved a more difficult proposition.^{1a,2} Thus reaction with co-ordinated CO to form an acylmetal hydride which eliminates an aldehyde only gives a thermodynamically favourable overall reaction³ at very high pressures of CO. The corresponding isonitrile \rightarrow imine reaction⁴ is thermodynamically favourable and could form the basis of a viable catalytic cycle. We report the trapping of a platinum methyl hydride which has direct bearing on this point.

Bis(dimethylphosphino)ethanehydridomethylplatinum [Pt(dmpe)H(Me)] (**1**) was synthesised from the corresponding methyl benzoate (**2**) [from Pt(dmpe)Me₂; PhCO₂H, Et₂O, -30 to $0\text{ }^{\circ}\text{C}$] by reduction with excess of LiHBEt₃ or LiBH₄ in CH₂Cl₂ or tetrahydrofuran (thf) below $-40\text{ }^{\circ}\text{C}$. Complex (**1**)

is stable in solution at room temperature, in contrast to previously reported platinum methyl hydrides.⁵ Presumably thermal elimination of methane is inhibited by the rigid chelate, since the transition state prefers⁶ to have an enhanced P-Pt-P angle.

Addition of *p*-chlorophenyl isonitrile to complex (**1**) in thf at $-60\text{ }^{\circ}\text{C}$ leads to formation of a single product, the *E*-iminomethyl (**3**).⁷ This suggests that hydride migration is stereoelectronically controlled and places the new C-H bond *trans* to the developing lone-pair on nitrogen. Above $-30\text{ }^{\circ}\text{C}$, the first-formed product equilibrates with its *Z*-isomer (**4**). The stereochemistry was established by difference nuclear Overhauser effect (n.O.e.) experiments which showed a 6% enhancement of the iminomethyl proton in (**3**) on irradiation of *ortho*-aryl protons and no comparable effect in (**4**). Furthermore, one pair of P-Me protons becomes anisochronous in the ¹H n.m.r. spectrum of (**4**) at low temperatures implying proximity to the arene (*vide infra*). The interconver-

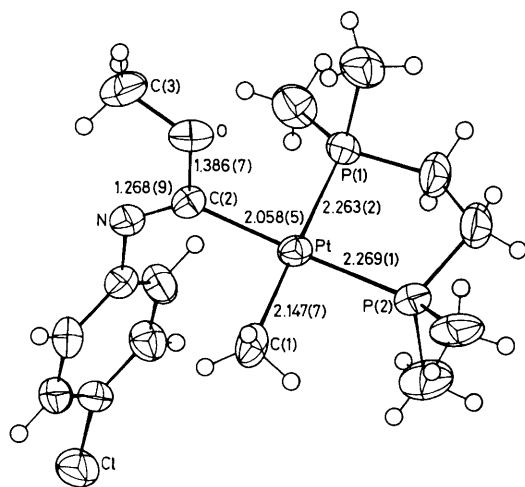
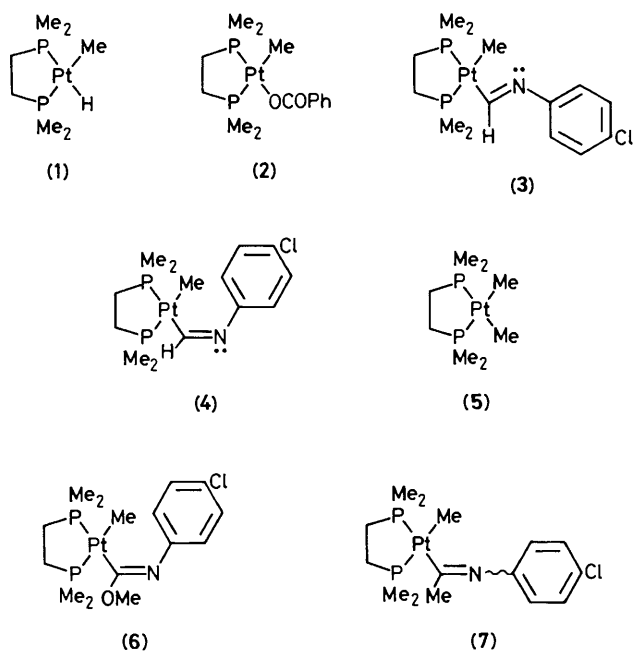


Figure 1: ORTEP drawing of the structure of (6) (thermal ellipsoids to 50% probability) showing principal bond lengths. Heavy atoms were located by Patterson techniques and light atoms found on Fourier synthesis. Hydrogen atoms were inserted at calculated positions with fixed isotropic factors, $U = 0.07 \text{ \AA}^2$, and then refined as CH, CH₂, or CH₃ units. Bond angles: P(1)-Pt-P(2) 85.9(1); P(1)-Pt-C(2) 92.0(2); P(2)-Pt-C(1) 93.1(2); C(1)-Pt-C(2) 89.0(2); Pt-C(2)-N 133.1(4); Pt-C(2)-O 111.6(4); N-C(2)-O 116.2(5)°. Inter-plane angle [Pt-P(1)-P(2)]-[Pt-N-O-C(2)] 115.4°.

sion rate of (3) \rightleftharpoons (4) at 24 °C, $k_{\text{eq.}} = 0.9 \text{ s}^{-1}$ ($\Delta G^\ddagger = 76 \text{ kJ mol}^{-1}$) was measured by ¹H spin-saturation transfer and is comparable to the barrier in typical organic imines.⁸

Comparison with the corresponding dimethylplatinum complex (5) is instructive. This reacted smoothly with *p*-chlorophenyl isonitrile (4 h, MeOH, 20 °C) giving complex (6) quantitatively and not the expected Me-insertion product. The starting material is stable in MeOH solution for protracted periods, and one possible mechanism for the formation of complex (6) involves nucleophilic attack by MeOH on co-ordinated isonitrile, followed by protonation at Pt and CH₄ elimination.⁹ The structure and *Z*-stereochemistry of (6) were

established by *X*-ray crystallography (Figure 1).[†] The ¹H n.m.r. spectrum of complex (6) at 183 K shows that one of the four P-Me groups is strongly shielded by the aryl ring (δ 0.77 vs. 1.37–1.69). At higher temperatures broadening and coalescence with its partner occur ($\Delta G_{213 \text{ K}}^\ddagger = 37 \text{ kJ mol}^{-1}$) through a rotation about the Pt-C bond which when coupled with chelate ring inversion interconverts a molecule of (6) with its enantiomer. Protonation of the imine (CF₃CO₂H, CD₂Cl₂) increases the rotational barrier drastically ($\Delta G_{298 \text{ K}}^\ddagger = \text{ca. } 80 \text{ kJ mol}^{-1}$).

The desired isonitrile insertion reaction of complex (5) could only be achieved under more forcing conditions (C₂H₈, 100–120 °C, 6 h) and gave the 1-iminoethyl complex (7) in admixture with other products.¹⁰ Thus on an intermolecular comparison, reaction of complex (1) with isonitrile is ca. 10⁸ times more rapid than the reaction of (5) with isonitrile in an inert solvent. The former involves exclusive Pt-H rather than Pt-Me migration. These facts will need to be borne in mind in the design of catalytic C-H activation experiments.

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[†] *Crystal data:* C₁₅H₂₆ClN₂OP₂Pt, $M = 528.6$, monoclinic, space group $P2_1/c$, $a = 13.245(2)$, $b = 11.844(3)$, $c = 12.480(3) \text{ \AA}$, $\beta = 97.72(1)^\circ$, $U = 1940.0(7) \text{ \AA}^3$, $Z = 4$, $D_c = 1.81 \text{ g cm}^{-3}$, Mo- K_α radiation, $\lambda = 0.71069 \text{ \AA}$, μ (Mo- K_α) = 76.1 cm^{-1} , $R = 0.026$ for 2992 observed [$I/\sigma(I) > 3.0$] reflections collected by four-circle diffractometer. The atomic co-ordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. Any request should be accompanied by the full literature citation for this communication.