Generation of σ-Bonded and Ionic C_5H_5 Complexes from η^5-Cyclopentadienyl-palladium and -platinum Precursors and their Involvement in Hydrogen–Deuterium Exchange Phenomena

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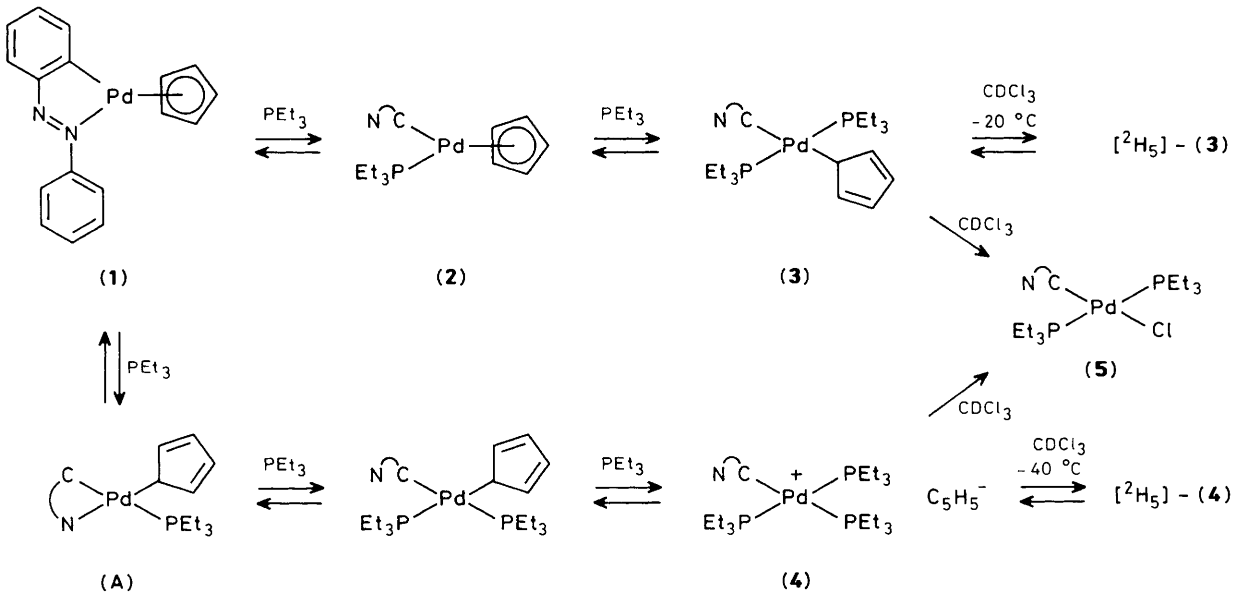
$[\overline{Pd(C_6H_4N{=}N}Ph)(\eta^5\text{-}C_5H_5)]$ (**1**) and its platinum analogue react with PEt_3 in $CDCl_3$ solution to yield σ-bonded and ionic cyclopentadienyl complexes, which undergo partial hydrogen–deuterium exchange with the solvent.

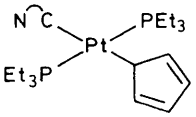
We have previously reported the reversible reaction of $[\overline{Pd(C_6H_4N{=}N}Ph)(\eta^5\text{-}C_5H_5)]$ (**1**) with PBu^n_3 to yield $[Pd(C_6H_4N{=}NPh)(\eta^1\text{-}C_5H_5)(PBu^n_3)]$, a reaction which is accompanied by hydrogen–deuterium exchange between the cyclopentadienyl moiety and a range of deuteriated solvents.[1] We now report a detailed examination of reactions of this type in $CDCl_3$ solution. These involve divergent pathways, each dependent on η^5 to σ rearrangement of the cyclopentadienyl moiety, the generation of ionic cyclopentadienyls from palladium and platinum, and an unexpected reactivity change



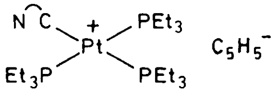
Scheme 1

between (**1**) and its platinum analogue. Although $C_5H_5^-$ has been displaced from a rhenium complex,[2] and [Ir(dppe)$_2$]C$_5$H$_5$ [dppe = bis(diphenylphosphino)ethane] has very recently been prepared by reaction of [Ir(dppe)$_2$]Cl with LiC$_5$H$_5$,[3] there have been no previous reports of $C_5H_5^-$ displacement from a late transition metal. The chemistry of palladium and platinum cyclopentadienyls is already known to be complicated, and includes coupling of cyclopentadienyl with itself[4] or other groups,[5] metal–metal bond formation,[4,6] η^5 to σ conversions,[7] and transfer of cyclopentadienyl between metals.[8] The elimination of ionic cyclopentadienyls described here represents another important reaction pathway available to complexes of this type.

Addition of 1 mol equiv. PEt$_3$ to a CDCl$_3$ solution of (**1**) at 20 °C results in near quantitative conversion into (**2**)† which, on standing, produces a 1 : 1 mixture of (**1**) and (**5**) (Scheme 1) in addition to a significant quantity of CHCl$_3$. Treatment of (**2**) with further PEt$_3$ yields the novel σ-cyclopentadienyl complex (**3**).† Complex (**3**) remains in equilibrium with (**2**), but either addition of excess of PEt$_3$ or reduction of the temperature to −50 °C displaces the equilibrium to (**3**) almost quantitatively. At room temperature (**3**) reacts with the CDCl$_3$ solvent to produce CHCl$_3$ and the (known) complex[9] *trans*-[PdCl(C$_6$H$_4$N=NPh)(PEt$_3$)$_2$], (**5**). Allowing a solution of (**3**) to warm in stages from −50 °C permits the operation of two distinct processes to be observed. At −20 °C the ^{1}H cyclopentadienyl resonances of (**3**), and the small amount of (**2**) with which it equilibrates at this temperature, diminish to zero intensity over 5 h, whilst the CHCl$_3$ signal dramatically increases. During this period the ^{31}P n.m.r. signals of (**3**) and (**2**) remain practically unaltered; the amount of (**5**) produced is very small. At ambient temperature, (**5**) is produced almost quantitatively over a similar time span.



(**6**)



(**7**)

When the reaction of (**1**) with PEt$_3$ is performed at −50 °C the ionic species (**4**)† is generated in addition to (**2**) and (**3**). The amount of (**4**) produced increases with PEt$_3$ concentration; with 4 mol equiv. PEt$_3$, (**3**) and (**4**) are formed in a 2 : 1 ratio. Raising the temperature to −40 °C causes a reduction in the intensity of the $C_5H_5^-$ resonance at δ 6.07, with a concomitant increase in the CHCl$_3$ signal, whereas the intensities of the ^{31}P n.m.r. signals due to the [Pd(C$_6$H$_4$N=NPh)(PEt$_3$)$_3$]$^+$ cation remain unchanged. This indicates that H–D exchange occurs between $C_5H_5^-$ and CDCl$_3$ at this temperature. {Reaction with the solvent to liberate Cl$^-$ does not occur, since [Pd(C$_6$H$_4$N=NPh)(PEt$_3$)$_3$]$^+$ reacts with chloride to give (**5**).} Further warming to −20 °C then converts [^{2}H$_5$]-(**4**) into (**5**).

We have been unable to convert (**3**) into (**4**), even with an 11-fold excess of PEt$_3$, and it is apparent that divergent pathways must operate from (**1**) (Scheme 1). Low temperatures would favour the route to (**4**) if an initial rapid equilibrium involving the intermediate (A) was displaced to the right under such conditions. Whilst the participation of $C_5H_5^-$ in H–D exchange reactions is to be expected,[2,10] the failure to produce (**4**) from (**3**) indicates that another mechanism not involving $C_5H_5^-$ generation must operate in the H–D exchange of the cyclopentadienyl hydrogens in (**3**).

The platinum analogue of (**1**) reacts with 1 or 2 mol equiv. PEt$_3$ in CDCl$_3$ solution at room temperature to produce *trans*-[PtCl(C$_6$H$_4$N=NPh)(PEt$_3$)$_2$], accompanied by a signifi-

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† *Selected n.m.r. spectroscopic data* (CDCl$_3$, *J* in Hz): (**2**): ^{1}H (300 MHz, 20 °C) δ 5.70 [d, *J*(H,P) 1.6, cp]; ^{13}C{^{1}H} (75 MHz, 20 °C) δ 95.77 [d, *J*(C,P) 3.8, cp]; ^{31}P{^{1}H} (121 MHz, 20 °C) δ 34.07 p.p.m.

(**3**): ^{1}H (300 MHz, −50 °C) δ 6.23 (s, cp); ^{13}C{^{1}H} (75 MHz, −50 °C) δ 109.46 (s, cp), 12.74 [t, *J*(C,P) 12.0, PCH$_2$CH$_3$], 8.09 (s, PCH$_2$CH$_3$); ^{31}P{^{1}H} (121 MHz, −50 °C) δ 9.24 p.p.m.

(**4**): ^{1}H (300 MHz, −50 °C) δ 6.07 (s, cp); ^{13}C{^{1}H} (75 MHz, −50 °C) δ 103.25 (s, cp); ^{31}P{^{1}H} (121 MHz, −50 °C) δ 2.80 [t, *J*(P,P^1) 36.3, PEt$_3$ *trans* to C], 9.66 p.p.m. [d, *J*(P,P^1) 36.3, PEt$_3$ *cis* to C].

(**6**): ^{1}H (300 MHz, −30 °C) δ 6.12 [*J*(H,Pt) 21.4, cp]; ^{13}C{^{1}H} (75 MHz, −30 °C) δ 112.72 [*J*(C,Pt) 37.6, cp]; ^{31}P{^{1}H} (121 MHz, −30 °C) δ 7.08 p.p.m. [br, *J*(P,Pt) 2810].

(**7**): ^{1}H (300 MHz, −30 °C) δ 5.87 (s, cp); ^{31}P{^{1}H} (121 MHz, −30 °C) δ 3.89 [d, ^2J(P,P^1) 22.0, ^1J(P,Pt) 2547, PEt$_3$ *cis* to C], 0.13 p.p.m. [t, ^2J(P,P^1) 22.0, ^1J(P,Pt) 1799, PEt$_3$ *trans* to C].

cant quantity of $CHCl_3$. When the reactants are mixed at −50 °C the reaction is extremely slow, but warming to −30 °C allows gradual formation of *trans*-[Pt(σ-C_5H_5)(C_6H_4N=NPh)$(PEt_3)_2$] (**6**)† and [Pt(C_6H_4N=NPh)$(PEt_3)_3$]C_5H_5 (**7**).† The ^1H resonance due to $C_5H_5^-$ diminishes above −30 °C owing to H–D exchange with the solvent, and above 0 °C (**6**) and (**7**) are converted largely into *trans*-[PtCl(C_6H_4N=NPh)$(PEt_3)_2$]. A mechanism similar to that for palladium appears to be operative, but the analogue of (**2**), [Pt(η^5-C_5H_5)(C_6H_4N=NPh)(PEt_3)], cannot be detected, presumably because it reacts rapidly (at −30 °C) with PEt_3 to form (**6**). Although the overall reaction occurs at much lower temperatures for palladium, the ready observation of (**2**), even at room temperature, and the failure to detect its platinum analogue represent an unusually large change of reactivity for these two metals.

In the platinum case unidentified olefinic resonances are observed in the ^1H n.m.r. spectrum on warming to 20 °C, and in both cases cyclopentadiene is produced. The reactions are being studied in other solvents in order to determine the origin of these species.

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