Formation of Unusual Palladium(II) Complexes Containing Metalated Tri-*t*-Butylphosphine and Bidentate Ligands

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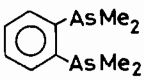
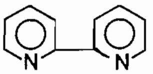
Abstract

The bridge-splitting reactions of chloro-bridged dinuclear palladium(II) complex containing metalated tri-t-butylphosphine, [Pd(μ-Cl)(P-C)]$_2$ (1) (P-C = Bu$_2{}^t$PCMe$_2$CH$_2$), with four types of bidentate ligands, [$\widehat{\text{L L}}$ = Ph$_2$PCH$_2$PPh$_2$(dpm), Ph$_2$AsC$_2$H$_4$-PPh$_2$(ape),  (diars),  (bipy)], have been shown to produce [(P-C)ClPd(dpm)-PdCl(P-C)] (2), [(P-C)ClPd(ape)] (3), [(P-C)ClPd-(diars)] (4) and [(P-C)ClPd(bipy)] (5). Complex (3) has been found to exist in solution as an equilibrium mixture of a neutral four coordinate palladium-(II) complex with 'arphos' acting as a monodentate ligand, [($\overline{\text{P-C}}$)$\overline{\text{Pd}}$Cl(PPh$_2$C$_2$H$_4$AsPh$_2$)] and a cationic complex, [($\overline{\text{P-C}}$)$\overline{\text{Pd}}$(PPh$_2$C$_2$H$_4$AsPh$_2$)]$^+$Cl$^-$. 'Diars' and bipyridyl ligands have been found to behave as mono-dentate ligands, incapable of replacing the chloride ligand to yield the corresponding cationic complexes. Stable cationic complexes, [($\overline{\text{P-C}}$)$\overline{\text{Pd}}$-($\widehat{\text{L-L}}$')]$^+$PF$_6{}^-$ have been prepared from the reaction of AgPF$_6$ with complex 1 followed by the addition of the bidentate ligand.

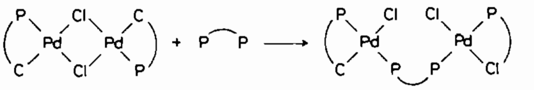
Introduction

In recent years, we have been interested in constructing low symmetry complexes of platinum group metals containing mixed ligands of variable electronic and steric parameters that can be useful in studies like the *trans*-effect of ligands and asymmetric synthesis [1–5]. These complexes can also be useful catalysts since one or more weak donor ligands can be displaced readily by organic substrates [6–10]. Most of the stable mixed ligands complexes of platinum and palladium known in the literature have been obtained by the bridge-splitting reactions of dinuclear complexes with a monodentate ligand. Bridge-splitting reactions using bidentate ligands have been described only rarely and we feel that such systems might result in the formation of some unusual complexes such as mononuclear five coordinate or cationic complexes and dinuclear complexes with bridging bidentate ligands. Here we report the results of our studies on the reactions of four types of bidentate ligands ($\widehat{\text{P P}}$, $\widehat{\text{P As}}$, $\widehat{\text{As As}}$ and $\widehat{\text{N N}}$) with a chloro-bridged dipalladium complex containing metalated t-butylphosphine.

For the present studies, the use of the dinuclear complex containing metalated t-butylphosphine, [Pd(μ-Cl)(Bu$_2{}^t$PCMe$_2$CH$_2$)]$_2$, is preferred in view of the fact that the metalated phosphine occupying two coordination sites eliminates the possible complications such as dissociation and scrambling associated with mono-dentate ligands.

Results and Discussion

Reaction of a bidentate diphosphine ligand, Ph$_2$PCH$_2$PPh$_2$(dpm), with the chloro-bridged dinuclear palladium complex containing metalated tri-t-butylphosphine, [Pd(μ-Cl)(P-C)]$_2$ (1) (P-C = Bu$_2{}^t$PCMe$_2$CH$_2$), in 1:1 molar ratio in benzene resulted in the facile cleavage of chlorine bridges, yielding the diphosphine bridged dinuclear complex (2) (eqn. 1).



(1)

(where $\widehat{\text{P P}}$ = Ph$_2$PCH$_2$PPh$_2$)

Evidence that reaction 1 proceeds by formation of a symmetrical dinuclear complex 2 is provided by the ^{31}P NMR spectrum which shows two sets of equally intense doublets at δ –17.14 (due to metalated phosphine) and 11.06 ppm (due to 'dpm') with a large phosphorus–phosphorus coupling

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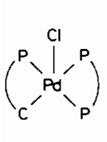
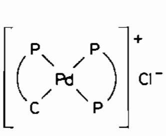
constant (JP_mP = 420 Hz) indicative of a *trans*-geometry. Surprisingly, the attempted reaction of 'dpm' with complex **1** in 2:1 molar ratio to give a five-coordinate complex of the type (**A**) or a mononuclear cationic complex (**B**) or a dinuclear cationic complex (**C**) failed and the only product isolated was complex **2**.



A



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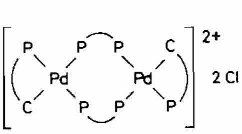


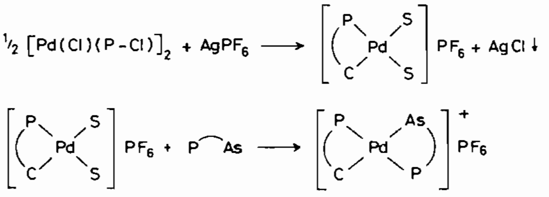
C

A similar bridge-splitting reaction between complex **1** and $Ph_2AsC_2H_4PPh_2$(ape) in 1:1 and 1:2 molar ratios afforded only one complex (**3**), however, contrary to the above 'dpm' reaction, it was found to contain only one 'ape' per palladium.

$$1/2[PdCl(P\text{-}C)]_2 + Ph_2AsC_2H_4PPh_2 \longrightarrow [PdCl(P\text{-}C)(Ph_2PC_2H_4AsPh_2)] \quad (2)$$

(**3**)

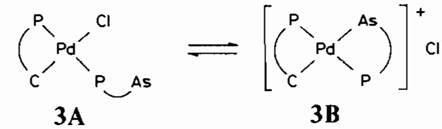
^{31}P NMR spectrum of the complex in $CDCl_3$, unexpectedly, displayed 8 lines as two sets of doublets with large phosphorus-phosphorus coupling constants indicating the presence of two complexes. The doublets at δ −15.28 (due to metalated phosphine) and 20.10 ppm (due to 'ape') (JP_mP = 420 Hz) have been considered to be due to a mononuclear complex, **3A**, with 'ape' behaving as monodentate ligand. The other set of signals at δ −6.23 (metalated phosphine) and 45.03 ppm (JP_mP = 366 Hz) has been suspected of arising from a cationic complex, **3B**. In order to support this, the cationic complex, $[P\text{-}C)Pd(P\text{-}As)]^+PF_6^-$ (**6**), has been prepared by following the reaction Scheme 1.



6

Scheme 1.

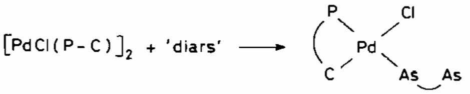
The ^{31}P NMR spectrum of this complex (**6**) has been found to match perfectly with that of **3B**, containing a set of doublets at δ −6.23 and 45.03 ppm (JP_mP = 366 Hz). ^{31}P NMR spectra of two batches of the crystals of complex **3** obtained by the fractional cyrstallization were found to be identical suggesting the possible involvement of an equilbrium in solution (eqn. 3):



3A **3B** (3)

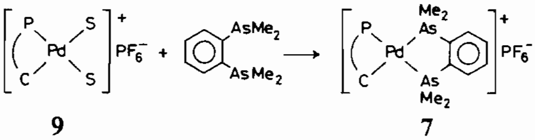
A similar equilibrium has been recently demonstrated by Balch and coworkers [11] in the platinum and palladium complexes of 2-(diphenylphosphino)pyridine ligands utilizing the ^{31}P NMR spectral data.

From the reaction of one or two mol equivalent of 'diars' with complex **1**, colorless needles of a complex corresponding in analysis to [PdCl(P-C)(diars)] (**4**) were obtained (eqn. 4):



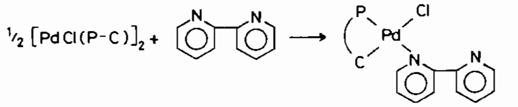
(4)

The ^{31}P NMR spectrum of the crystals showed only one peak at −1.83 ppm indicating the presence of only one complex. Although this signal was found at a position comparable to that of the cationic complex, $[(P\text{-}C)Pd(As\text{-}As)]^+PF_6^-$ (**7**) (δP = −1.72 ppm), the large variation in the NMR spectra [complex **4**: di-t-butyl protons at δ 1.40 (d), JPH = 14 Hz; dimethyl protons at 1.48 ppm (d), JPH = 12.5 Hz; methyl group protons of 'diars' at 1.60 ppm (s) and complex **7**: di-t-butyl protons at δ 1.48 ppm (d), JPH = 14.8; dimethyl protons at δ 1.57 ppm (d); J PH = 12 Hz; methyl group protons of 'diars' at 1.68 ppm (s)] suggested these complexes had different structures. The cationic complex (**7**) was obtained by the reaction of 'diars' with complex **9** (eqn. 5).

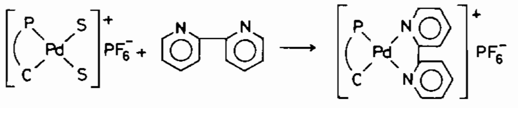


9 **7** (5)

The elemental analysis of the product of the reaction of bipyridyl with complex **1**, (eqn. 6) suggested it contained one mol of bipyridyl per palladium. ^{31}P NMR of this complex (**5**) showing a singlet at δ −10.66 ppm was found to differ from that of cationic complex (**8**) (δP = −15.57 ppm) (eqn. 7).

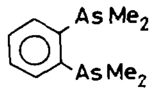


(6)



(7)

Experimental

Solvents used were of spectroanalyzed grade. Reactions involving diars  and ape ($Ph_2AsCH_2CH_2PPh_2$) were carried out under nitrogen, however, other reactions and manipulations such as purifications were carried out under open conditions. The chloro-bridged dinuclear palladium complex, $[Pd_2(\mu\text{-}Cl)_2(Bu_2{}^tPCMe_2CH_2)_2]$, was prepared as reported earlier [4].

Elemental analyses were performed by M.H.W. Laboratories, Phoenix, Arizona. Proton and ^{31}P NMR spectra were recorded on a Bruker PW-60 Fourier transform spectrometer. TMS as internal standard for proton NMR and phosphoric acid (85%) as external standard for ^{31}P NMR were used. ^{31}P chemical shifts to high field (low frequency) are reported as negative.

Preparation of $[Pt_2Cl_2(Bu_2{}^tPCMe_2CH_2)_2]$ (1)

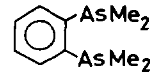
The title compound was prepared from the metalation reaction of $(Bu_3{}^tP)_2Pd(H)Cl$ as reported earlier [4]. Alternatively, it was prepared from the reaction of bis[(2-methoxy-5-cyclooctenyl)chloropalladium] (1.12 g; 2 mmol) in deoxygenated methanol (20 ml) with tri-t-butyl phosphine (0.81 g, 4 mmol) at room temperature for 2 hr. The precipitate formed in the reaction was filtered, washed with methanol and dried. The solid was recrystallized from benzene/hexane to give prism-shaped crystal (yield ~80%). *Anal.* Calcd. for $[Pd_2(Cl)_2[Bu_2{}^tPCMe_2CH_2)_2]$: C, 42.0; H, 7.59; Cl, 10.4%. Found: C, 41.9; H, 7.67; Cl, 10.4%. m.p. 172–73 °C (dec.) ^{31}P NMR ($CDCl_3$): $\delta P = -12.97$ ppm.

Reaction of Complex 1 with $Ph_2PCH_2PPh_2$ (dpm)

To a magnetically stirred solution of 200 mg (0.29 mmol) of complex 1 in benzene was added 84 mg (0.29 mmol) of 'dpm' and the reaction mixture was stirred at room temperature for 6 hr. The solution was concentrated and hexane was added dropwise to precipitate the solid which was collected by filtration (Yield ≈ 89%). It was recrystallized from a solvent mixture of CH_2Cl_2/hexane. *Anal.* Calcd. for $[Pd_2Cl_2(Bu_2{}^tPCMe_2CH_2)_2(Ph_2PCH_2PPh_2)]$ (2): C, 55.0; H, 6.92; Cl, 6.64%. Found: C, 55.1; H, 7.20; Cl, 6.83%. ^1H NMR ($CDCl_3$): $Bu_2{}^t = 1.486$ (d) ppm ($JPH = 13.5$ Hz); $Me_2 = 1.222$ (d) ppm ($JPH = 12.4$ Hz); $Pd\text{–}CH_2\text{–}C = 0.484$ (t) ppm ($JPH = 6.9$ Hz); $P\text{–}CH_2\text{–}P = 3.65$ (br) ppm; Ph = 7.37 ppm. ^{31}P NMR ($CDCl_3$): metalated phosphine $\delta P_m = -17.14$ ppm; dpm $\delta P' = 11.06$ ppm; $JPP' = 420$ Hz.

Reaction of Complex 1 with $Ph_2PCH_2CH_2AsPh_2$ ('ape')

To a magnetically stirred benzene solution of complex 1 (188 mg; 0.27 mmol) was added 242 mg (0.55 mmol) of 'ape' and the reaction solution was stirred at ~40 °C for 5 hr. The solution was concentrated and addition of hexane afforded the solid which was filtered, washed with ether and vacuum dried (yield ~86%). *Anal.* Calcd. for $[PdCl(Bu_2{}^tPCMe_2CH_2)(ape)]$ (3): C, 53.2; H, 6.74; Cl, 6.30%. Found: C, 52.9; H, 6.83; Cl, 6.87%. ^{31}P NMR ($CDCl_3$): Four sets of doublets (8 lines). Two doublets at $\delta P_m = -15.28$ ppm and $\delta P = 20.10$ ppm with $JP_mP = 420$ Hz. Other two doublets at $\delta P'm = -6.23$ ppm and $\delta P' = 45.03$ ppm with $JP'_mP' = 366$ Hz.

Reaction of Complex 1 with  *('diars')*

1:2 Molar Ratio

274 mg (0.4 mmol) of complex 1 was dissolved in benzene (~50 ml) and the solution was degassed by bubbling dry nitrogen. To this was added dropwise 230 mg (0.8 mmol) of diars under nitrogen and the reaction mixture was stirred at room temperature overnight. The solution was concentrated and addition of hexane afforded colorless needles (yield ~68%). *Anal.* Calcd. for $[PdCl(Bu_2{}^tPCMe_2CH_2)(Me_2AsC_6H_4AsMe_2)]$ (4): C, 42.0; H, 6.68; Cl, 5.65%. Found: C, 41.3; H, 6.77; Cl, 5.93%. ^1H NMR (CH_2Cl_2): $Bu_2{}^t = 1.40$ (d) ppm ($JPH = 14$ Hz); $Me_2 = 1.48$ (d) ppm ($JPH = 12.5$ Hz); Diars = $Me_2 = 1.60$ (s); and Ph = 7.75 (m) ppm. ^{31}P NMR ($CDCl_3$): Singlet at $\delta P_m = -1.83$ ppm.

1:1 Molar Ratio

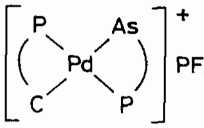
The above reaction was repeated by adding 84 mg (0.29 mmol) of diars to the benzene solution of 200 mg (0.29 mmol) of complex 1 under nitrogen atmosphere. The reaction mixture was stirred overnight at R.T. and the solution was concentrated. Addition of ether to the solution afforded the colorless needles of complex 4 which gave the same elemental analysis, ^1H and ^{31}P NMR spectra as above.

Reaction of Complex 1 with Bipyridyl

Bipyridyl (63 mg; 40 mmol) was added to a stirred solution of complex 1 (280 mg; 0.4 mmol) in benzene. The reaction mixture was stirred at 40 °C for 8 hr and the solution was concentrated. Addition of ether to the concentrated solution resulted in the precipitate which was collected by filtration and dried under reduced pressure (yield ~74%). *Anal.*: Calcd. for $[PdCl(Bu_2{}^tPCMe_2CH_2)(C_{10}H_8N_2)]$ (5): C, 53.0; H, 6.82; N, 5.62; Cl, 7.12%.

Found: C, 53.1; H, 6.92; N, 5.37; Cl, 6.46%. ^1H NMR ($CDCl_3$): $Bu_2{}^t$ = 1.639 (d) (JPH = 13.7 Hz); Me_2 = 1.566 (d) (JPH = 13.7 Hz); $CH_2{-}Pd$ = 1.353 (t) (4 Hz) ppm. Bipyridyl: (a) 9.153 (d) (JHH = 7.8 Hz); (b) 8.37 (m) and (c) 7.657 (t) (JHH = 6.5) ppm. a:b:c = 1:2:1. ^{31}P NMR ($CDCl_3$): Singlet at δ P = −10.66 ppm.

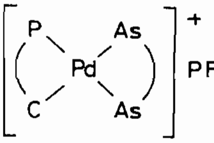
Preparation of



PF_6^- *(6) [(P-C) = ($Bu_2{}^tPCMe_2CH_2$) and (As P) = ($Ph_2AsC_2H_4PPh_2$)]*

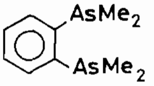
Addition of a methanolic solution of two mol equivalent amount of $AgPF_6$ (0.13 g; 0.5 mmol) to a rapidly stirred CH_2Cl_2 solution of complex **1** (0.17 g; 0.25 mmol), resulted in the white precipitate formation of AgCl. The reaction mixture was stirred for 30 min and the solid was centrifuged and filtered. To the filtrate was added 0.22 g (0.5 mmol) of $Ph_2AsC_2H_4PPh_2$(ape) and the reaction mixture was stirred at room temperature for 4 hr. Addition of ether to the concentrated solution afforded the crystals of the title complex **6** (yield ~78%). *Anal.* Calcd. for [Pd($Bu_2{}^tPCMe_2CH_2$)($Ph_2AsC_2H_4PPh_2$)PF_6]: C, 51.0; H, 5.59%. Found: C, 50.6, H, 5.74. ^{31}P NMR ($CDCl_3$): Two doublets at δ P_m = −7.60 and δ P′ = 45.78 ppm with JP_mP' = 360 Hz.

Preparation of



PF_6^- *(7)*

[(As As) =



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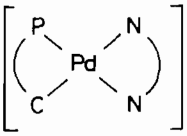
To a vigorously stirred solution of complex **1** (0.17 g; 0.25 mmol) in CH_2Cl_2 was added a methanolic solution of $AgPF_6$ (0.13 g; 0.5 mmol). The reaction mixture was stirred at R.T. for 30 min and the precipitated AgCl was centrifuged and removed. The filtrate was allowed to react with diars (0.14 g; 0.5 mmol) at room temperature for 5 hr. To the concentrated solution, was added dropwise ether to give the crystals of complex 7. Yield ~74%. *Anal.* Calcd. for [Pd($Bu_2{}^tPCMe_2CH_2$) ($Me_2AsC_6H_4AsMe_2$)PF_6]: C, 39.8; H, 6.37%. Found: C, 40.1; H, 6.52%. ^{31}P NMR ($CDCl_3$): Singlet at δ P_m = −1.716 ppm. ^1H NMR: $Bu_2{}^t$ = 1.48 (d) ppm (JPH = 14.8 Hz); Me_2 = 1.57 (d) ppm (JPH = 12 Hz); Diars Me_2 = 1.68 (s) ppm; Ph = 7.77 (m) ppm.

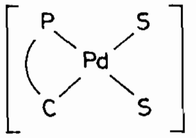
Preparation of



PF_6^- *(8)*

[N͡N = Bipyridyl]

To the solution of the cationic complex:



PF_6^-, (**9**) (0.5 mmol) with $AgPF_6$ (0.13 g; 0.5 mmol) was added 79 mg (0.5 mmol) of bipyridyl. Reaction mixture was stirred for 5 hr and addition of ether to the concentrated solution precipitated the title complex 8 (yield ~69%). *Anal.* Calcd. for [Pd($Bu_2{}^tPCMe_2CH_2$)($C_{10}H_8N_2$)PF_6]: C, 43.4; H, 5.63; N, 4.6%. Found: C, 42.9; H, 5.7; N, 4.4%. ^{31}P NMR ($CDCl_3$): Singlet at δ P_m = −15.57 ppm.

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