Reductive Elimination of Alkanes and Arenes from [Pd2R2(μ-H)(μ-dppm)2]PF6 Complexes

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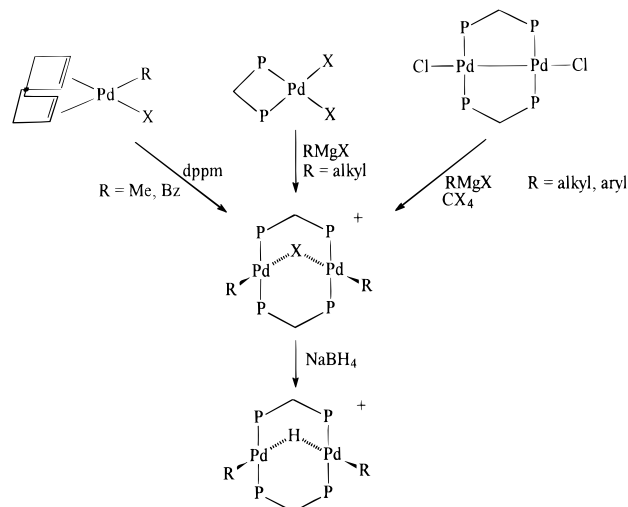*8001 Natural Bridge Road*
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Scheme 1

Whereas the majority of homogeneously catalyzed reactions are believed to involve reactions at a single metal center, there are many instances in which the possibility of a cooperative effect between two or more metals exists, and there are a growing number of cases where such interactions are clear.[1–9] Mechanistic studies of monomeric complexes have established that dinuclear reductive eliminations occur in a few cases,[10] but there have been relatively few studies involving discrete, bimetallic systems. Elimination of H_2 or CH_4 from dppm-bridged diplatinum species has been reported,[11,12] and ethane was formed when solutions of $[Pt_2Me_3(\mu\text{-dppm})_2]^+$ were photolyzed (both intra- and intermolecular mechanisms were involved).[13,14] Both methane and ethane were reported[15] to be eliminated when a solution of $[Pd_2Me_2(\mu\text{-H})(\mu\text{-dppm})_2]BPh_4$ was warmed above ambient temperature. Carbonylation of $[Rh_2Me_2(\mu\text{-CO})(\mu\text{-dppm})_2]$ produced acetone and/or butanedione, depending on the CO pressure employed. The former was shown to be formed by an intramolecular pathway, whereas butanedione was produced by a radical mechanism.[16] In none of these cases was a concerted dinuclear elimination process demonstrated. Stereospecific alkene extrusion from a 1,2-diosmacyclobutane complex has been observed,[17] and evidence against a diradical intermediate was presented.[18] It is clear, however, that the factors that affect the course of elimination reactions in bimetallic systems, as well as their intimate mechanisms, are not yet well understood.

We have prepared a series of halide- and hydride-bridged dipalladium A-frame cations of the type $[Pd_2R_2(\mu\text{-X})(\mu\text{-dppm})_2]^+$,

and these serve as excellent bimetallic substrates from which to study reductive elimination reactions. We have prepared the former by one of three routes, namely, (i) addition of dppm to [PdClR(cod)] or $[Pd_2R_2(\mu\text{-Cl})_2(AsPh_3)_2]$,[19] (ii) reaction of [PdBr2-(dppm)] with RMgBr,[20] or (iii) treatment of the palladium(I) complex $[Pd_2Cl_2(\mu\text{-dppm})_2]$ with RMgBr, followed by CBr4.[21] The halide-bridged species may be isolated as their halide or PF_6^- salts; subsequent treatment with NaBH4 or NaBH3CN gave their hydride-bridged analogues (Scheme 1).[19,20] In contrast to an earlier report,[16] we have found complexes of the type $[Pd_2R_2(\mu\text{-H})(\mu\text{-dppm})_2]PF_6$ to be thermolytically inert at ambient temperature, at least as their PF_6^- salts. We generated the mixed metal complex $[PdPt(4\text{-tolyl})_2(\mu\text{-H})(\mu\text{-dppm})_2]PF_6$ by method iii using [PdPtCl2-$(\mu\text{-dppm})_2$] as the precursor.[22] We had succeeded previously in preparing unsymmetrical platinum-containing A-frames starting from $[PtR(dppm\text{-}PP')(dppm\text{-}P)]^+$,[23] but this approach is not generally applicable to palladium. With a bulky organic group on palladium, however, we were able to produce [Pd(Mes)(dppm-PP')(dppm-P)]$^+$ quantitatively, and further treatment with [PdClMe(cod)], TlPF6, and NaBH4 gave the unsymmetrical dipalladium complex $[Pd_2(Mes)Me(\mu\text{-H})(\mu\text{-dppm})_2]PF_6$.

The ^{1}H NMR spectra of the hydride-bridged A-frames each exhibit a quintet around −8 ppm due to the bridging hydride. The dppm CH2 hydrogens appear as a single resonance, indicating that the molecules are fluxional. This fluxionality is likely to result from inversion of the A-frame unit, where the hydride, unlike a halide, is small enough to pass between the metal centers via a

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(21) In a typical procedure, a CH_2Cl_2 solution (30 mL) of $[Pd_2Cl_2(\mu\text{-dppm})_2]$ (0.10 g, 0.095 mmol) was cooled to −78 °C, and PhMgBr (0.5 mL of a 3.0 M ether solution) was added. The solution turned dark red immediately, and was stirred for 4 h. Methanol (1.0 mL), CBr4 (0.10 g, 0.30 mmol), and TlPF6 (0.034 g, 0.097 mmol) were added, then the mixture was allowed to warm to 25 °C. The solvents were removed. The resulting solid was washed with ether and hexane, then extracted with CH_2Cl_2 and passed through a short alumina column. The solvent was removed to leave the product as a pale yellow solid (0.12 g, 92%). Anal. Calcd for $C_{62}H_{54}BrF_6P_5Pd_2$: C, 54.71; H, 3.97. Found: C, 54.24; H, 4.04. ^{1}H NMR (acetone-d_6): δ 4.44 (dq, 2H, $^2J_{HH}$ = 14.2 Hz, J_{HP} = 3.7 Hz, PC*H*), 4.61 (dq, 2H, $^2J_{HH}$ = 14.2 Hz, J_{HP} = 5.2 Hz, PC*H*), 6.54–6.58 (m, 10H, Pd*Ph*), 7.05–7.90 (m, 40H, P*Ph*2). ^{31}P{^{1}H} NMR: δ 11.5 (s).
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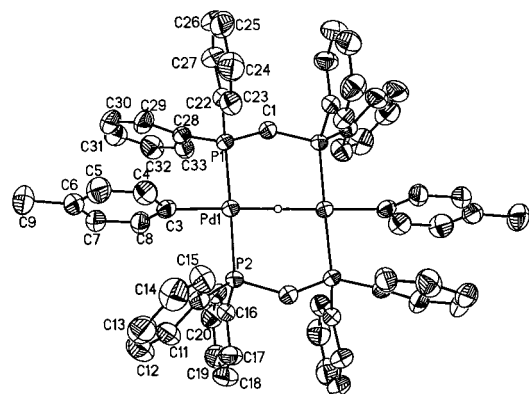
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Figure 1. Projection view of the molecular structure of the $[Pd_2(C_6H_4\text{-}Me\text{-}4)_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$ cation showing the atom-labeling scheme.

linear R−M−H−M−R intermediate.[24] We have reported previously the solid-state structure of $[Pd_2Et_2(\mu\text{-}H)(\mu\text{-}dppm)_2]PF_6$, in which the cation was found to have a bent C−Pd−Pd−C core (C−Pd−Pd angle 158.5°) and a Pd−Pd distance of 2.933(7) Å.[19] In contrast, the $[Pd_2(4\text{-}tolyl)_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$ cation exhibits an almost perfectly linear C−Pd−Pd−C core (C−Pd−Pd angle 178.4°).[25] The complex exists in an elongated chair conformation (Figure 1), and the Pd−Pd distance of 3.0758(4) Å is too long to be described as a direct metal−metal bond. The almost planar $Pd_2P_4C_2$ unit is consistent with the intermediate proposed for the inversion of hydride-bridged A-frames.

Although they were stable at ambient temperature, either in the solid state or in solution, the hydride-bridged complexes did undergo carbon−hydrogen bond-forming reactions at elevated temperatures. The temperatures required for elimination were dependent on the nature of the organic groups present. In DMSO-d_6 solution, $[Pd_2Me_2(\mu\text{-}H)(\mu\text{-}dppm)_2]PF_6$ eliminated CH_4 smoothly at 77 °C, whereas the ethyl derivative produced a mixture of C_2H_6 and C_2H_4 (ca. 4:1). The acyl derivatives lost CH_3CHO or $CH_3\text{-}CH_2CHO$ at 52 °C. The arylpalladium complexes required much higher temperatures to induce elimination (117 °C). The mixed-metal complex $[PdPt(4\text{-}tolyl)_2(\mu\text{-}H)(\mu\text{-}dppm)_2]PF_6$ eliminated toluene at 107 °C; loss of the tolyl group from palladium occurred exclusively. When the unsymmetrical complex $[Pd_2(Mes)Me(\mu\text{-}H)(\mu\text{-}dppm)_2]PF_6$ was heated to 127 °C only methane was formed. The rate of elimination from $[Pd_2(4\text{-}tolyl)_2(\mu\text{-}H)(\mu\text{-}dppm)_2]PF_6$ was unchanged over a 4-fold range of concentration, indicating that the reaction is first order in the A-frame complex. The ionic complexes were soluble in only a limited number of solvents, and in chlorinated solvents decomposition occurred to generate $[PdCl_2(dppm)]$, but reactions carried out in DMSO or dioxane showed no dependence on the nature of the solvent.

In each case the $^{31}P\{^1H\}$ NMR spectrum of the starting material was gradually replaced by two multiplets, consistent with an unsymmetrical species of the form $[Pd_2R(S)(\mu\text{-}dppm)_2]^+$ (S = DMSO-d_6).[26] The palladium-containing product decomposed, however, in less coordinating solvents. Addition of PPh_3 did not appear to affect the rate of elimination, and intractable mixtures of products were formed. With the more nucleophilic phosphine PEt_3, displacement of dppm and cleavage of the dimeric unit took place.

We were able to carry out kinetic studies of the reactions in DMSO solution over a range of temperatures, and these permitted

Table 1. Activation Parameters for Alkane or Arene Elimination from $[Pd_2R_2(\mu\text{-}H)(\mu\text{-}dppm)_2]PF_6{}^a$

complex	$\Delta G^{\ddagger}$, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/(mol·K)
$[Pd_2Me_2(\mu\text{-}H)(\mu\text{-}dppm)_2]PF_6$	25.5	29.9	+10
$[Pd_2(COMe)_2(\mu\text{-}H)(\mu\text{-}dppm)_2]PF_6$	24.8	29.9	+15
$[Pd_2(COEt)_2(\mu\text{-}H)(\mu\text{-}dppm)_2]PF_6$	24.9	29.4	+14
$[Pd_2Ph_2(\mu\text{-}H)(\mu\text{-}dppm)_2]PF_6$	28.7	22.4	−16
$[Pd_2(4\text{-}tolyl)_2(\mu\text{-}H)(\mu\text{-}dppm)_2]PF_6$	27.3	22.1	−15
$[PdPt(4\text{-}tolyl)_2(\mu\text{-}H)(\mu\text{-}dppm)_2]PF_6$	28.1	26.8	−3
$[Pd_2(Mes)Me(\mu\text{-}H)(\mu\text{-}dppm)_2]PF_6$	28.3	36.8	+22

^{a} $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ values are ±1.0 kcal/mol, $\Delta S^{\ddagger}$ values are ±5 cal/(mol·K).

Scheme 2
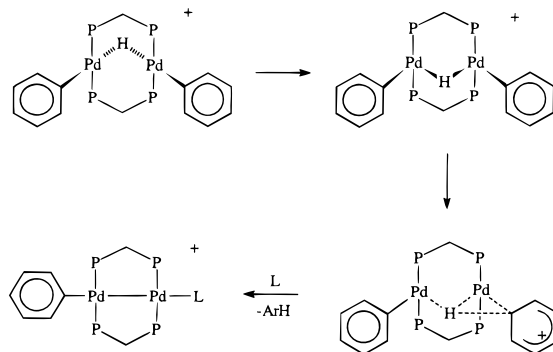
us to determine activation parameters for the eliminations (Table 1). In each case the enthalpy of activation was in excess of 20 kcal/mol, indicating that significant bond breaking has occurred in the transition state. These values ranged from 22 kcal/mol in the arylpalladium species to as high as 37 kcal/mol in $[Pd_2(Mes)\text{-}Me(\mu\text{-}H)(\mu\text{-}dppm)_2]PF_6$. The entropies of activation covered a significant range also, being negative for the arylpalladium species and as high as +22 cal/(mol·K) in the mixed mesityl−methyl compound.[27]

All the hydride-bridged complexes are fluxional in solution, involving reversible inversion of the A-frame unit. As the hydride is likely to migrate between the metals much more rapidly than the larger terminal groups can move, one can easily envisage a short-lived "W-shaped" species, in which the terminal organic fragment and the bridging hydride are mutually cis, as required for reductive elimination. Reductive elimination would then proceed by means of a three-center transition state, in which there is some degree of Pd−C and Pd−H bond-breaking as the new C−H begins to form. The lower $\Delta H^{\ddagger}$ and negative $\Delta S^{\ddagger}$ values suggest a greater degree of bond-forming in the transition state in the aryl complexes, compared with their methyl and acyl analogues. This may be due to the ability of the aromatic ring to promote charge delocalization, as depicted in Scheme 2. The presence of a platinum center appears to increase bond-breaking in the transition state, whereas the bulky mesityl group perhaps inhibits the geometry required for elimination of CH_4 so more positive $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are observed.

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(25) The $[Pd_2(C_6H_4Me\text{-}4)_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$ cation was isolated as its BH_3CN^- salt, due to incomplete replacement with $PF_6{}^-$. The solid-state structure revealed no close contacts between the cations and anions. X-ray: triclinic, $P\bar{1}$, orange, 0.40 × 0.20 × 0.08 mm, a = 11.5028(1) Å, b = 12.4083(1) Å, c = 12.4609(2) Å, α = 106.587(1)°, β = 93.100(1)°, γ = 16.809(1)°, Z = 2, R = 0.0436 (on F_o, $I > 2\sigma(I)$, GOF = 1.069.

(26) For $[Pd_2Me(S)(\mu\text{-}dppm)_2]^+$ two three-line multiplets centered at 10.5 and 17.1 ppm were observed. Similar patterns were found in the other cases.

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