bly intermediates in this reaction, were not detected. The reaction was made possible by the reduction of Pd(II) to Pd(0). The same reduction occurred in our case to produce the conversion of $[1\text{-}(Ph_2PH)B_{10}H_9]^-$ to $(Ph_2PH)_2B_{10}H_8$, but to a limited extend due to the small amount of catalyst used.

1,6-$(Ph_2PH)_2B_{10}H_8$ and 1,10-$(Ph_2PH)_2B_{10}H_8$

Neutral boranes were separated on a silica gel column. 1,10- (20% of neutral boranes) and 1,6-$(Ph_2PH)_2B_{10}H_8$ (80%) isomers were characterised by FAB(–) and electrospray(–) mass spectrometry (*m/z* 486.3 and 487.4, respectively, calculated 488), by ^{11}B NMR (Table I) and ^{31}P NMR (Table II). Additional analysis by COSY ^{11}B-^{11}B was used to elucidate the structure of the isomer 1,6-$(Ph_2PH)_2B_{10}H_8$ (Fig. 2).

^{31}P NMR spectra (^1H decoupled) distinguish between apical and equatorial boron substituted[11]. In the 1,6-isomer spectrum (Fig. 3), while both signals are quartets at +0.50 and –5.61 ppm, the apical signals are sharp and easily recognizable; the equatorial signals are broader.

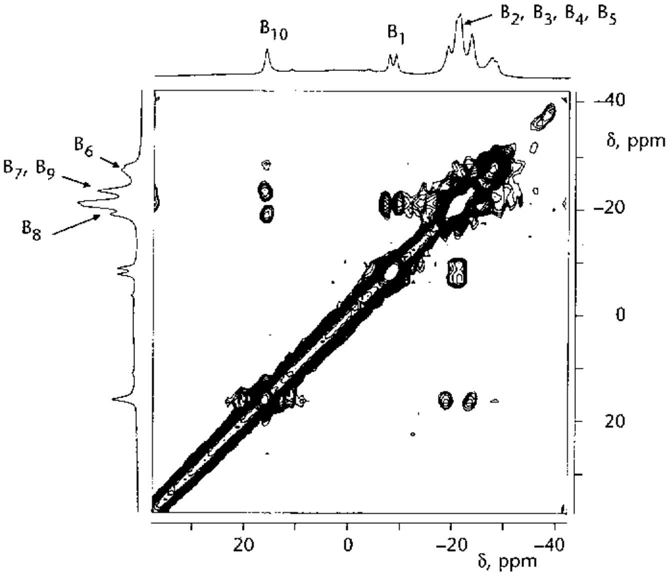

FIG. 2
COSY ^{11}B-^{11}B spectrum of isomer 1,6-$(Ph_2PH)_2B_{10}H_8$

$[1\text{-}(Ph_2PH)B_{10}H_9]^-$ and $[1\text{-}Ph_2P(OH)B_{10}H_9]^-$

The solid product obtained by addition of toluene to the reaction mixture was analysed by FAB(–) mass spectrometry. Three anions were detected: $[B_{10}H_{10}]^{2-}$ (*m/z* 193.2, calculated 192 for $\{(CH_3)_4N[B_{10}H_{10}]\}^-$), $[(Ph_2PH)B_{10}H_9]^-$ (*m/z* 302.2, calculated 303) and $[(PPh_3)B_{10}H_9]^-$ (*m/z* 379.2, calculated 379). An electrospray(–) analysis confirmed the presence of these anions and showed that $[Ph_2P(OH)B_{10}H_9]^-$ was also present (*m/z* 318.4, calculated 319). $[(PPh_3)B_{10}H_9]^-$ formed in low concentration from PPh_3 that $(PPh_3)_2PdCl_2$ contained and could not be detected by ^{11}B NMR analysis. A mixture of $[(Ph_2PH)B_{10}H_9]^-$ and $[Ph_2P(OH)B_{10}H_9]^-$ free of $[B_{10}H_{10}]^{2-}$ was obtained by recrystallization from hot ethanol. The mixture of anions was passed on a column containing DEAE-cellulose, pure $[Ph_2P(OH)B_{10}H_9]^-$ was recovered whereas $[(Ph_2PH)B_{10}H_9]^-$ was not eluted and probably decomposed. The NMR data are reported in Tables I and II. The resonances have been unambiguously assigned to the products by analysis of the COSY ^{11}B-^{11}B spectrum of the crude product and the ^{11}B and ^{31}P NMR spectra of the various fractions.

In spite of several attempts, we have never succeeded in obtaining $[1\text{-}(Ph_2PH)B_{10}H_9]^-$ free of $[1\text{-}Ph_2P(OH)B_{10}H_9]^-$. The formation of this

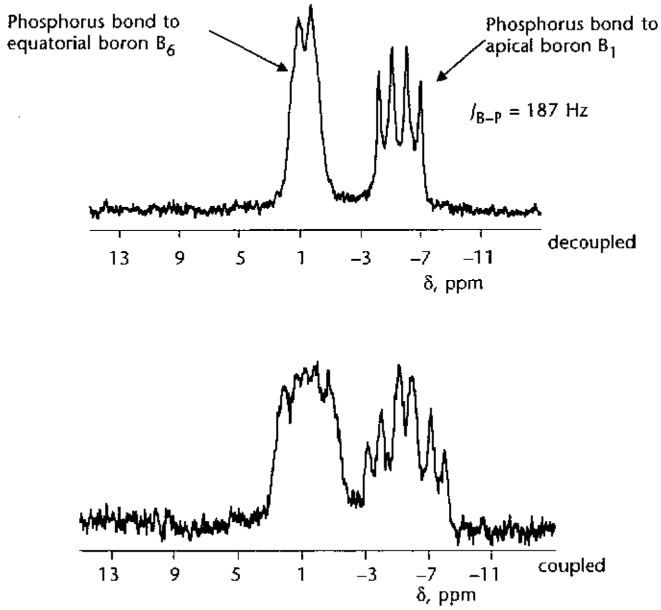

FIG. 3
^{31}P and $^{31}P\{^1H\}$ spectrum of isomer $1,6\text{-}(Ph_2PH)_2B_{10}H_8$ in CD_3CN

hydroxy derivative could be due to the reaction of $[1\text{-}N_2B_{10}H_9]^-$ with $Ph_2P(OH)$ (the tautomeric form[12–17] of $Ph_2(H)P{=}O$) or to the degradation of $[1\text{-}(Ph_2PH)B_{10}H_9]^-$ in contact with traces of oxygen or humidity during the reaction. However the most probable cause of the formation of the hydroxy derivative was our failure to dry completely $[(CH_3)_4N][N_2B_{10}H_9]$. According to the IR spectrum of this product and TGA measurements, the presence of a very low water amount was suspected. However, we were limited in the possibility to dry it: when the product was heated at 90 °C for 8 h, we observed its partial decomposition to $[B_{20}H_{18}]^{2-}$.

Influence of the Catalyst

The catalyst obviously favoured the formation of $[\text{phosphine-}B_{10}H_9]^-$ anions and generated the neutral boranes, but other points deserve to be mentioned.

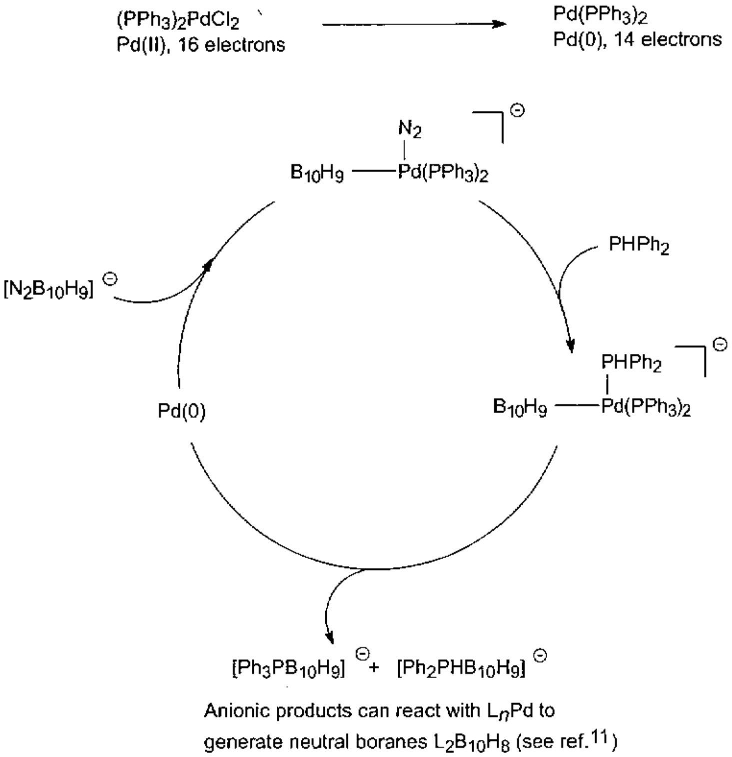

FIG. 4
Possible mechanism of formation of anionic $[\text{phosphine-}B_{10}H_9]^-$ and neutral $L_2B_{10}H_8$

A) $[B_{20}H_{18}]^{2-}$ did not form at 150 °C by thermal decomposition of $[1\text{-}N_2B_{10}H_9]^-$ because of the presence of the palladium catalyst. This indicates that the catalyst interacts with $[1\text{-}N_2B_{10}H_9]^-$.

B) $[(PPh_3)B_{10}H_9]^-$ is formed by the exchange of PPh_3 and N_2 groups between the catalyst and the $B_{10}H_9$ moiety.

Based on recent work on the utilization of *trans*-$(PPh_3)_2PdCl_2$ as catalyst in the reaction of $[B_{12}H_{11}I]^{2-}$ with Grignard reagents[2], it can be assumed that an oxidative addition on Pd leads to $B_{10}H_9\text{-Pd-}N_2$ and that $[(Ph_3P)B_{10}H_9]^-$ is generated by a reductive elimination. $[1\text{-}(Ph_2PH)B_{10}H_9]^-$ could be obtained by the same process provided that Ph_2PH exchanges for diazo leaving ligands bound to palladium. Possible mechanism based on such interpretation is shown in Fig 4.

The formation of $1,6\text{-}(Ph_2PH)_2B_{10}H_8$ and $1,10\text{-}(Ph_2PH)_2B_{10}H_8$ from $[1\text{-}(Ph_2PH)B_{10}H_9]^-$ could proceed through a PdLBH four-centered intermediate[11] (L = Ph_2PH).

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