# Novel Synthesis of Platinum(II) Alkenyl Compounds *via* Organoboration of Platinum(II) Acetylides

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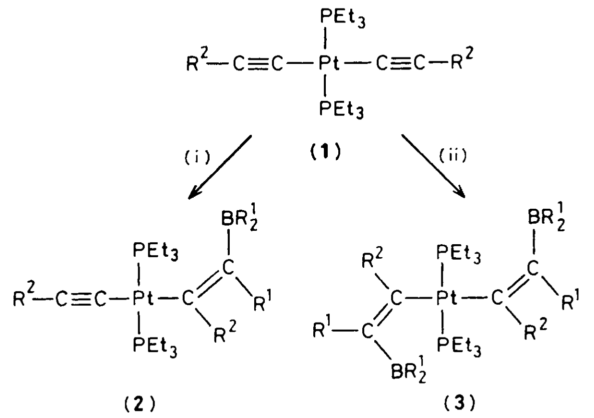
High-yield syntheses of two new types of platinum(II) alkenyl compounds are described: (i) organoboration of *trans*-$[\mathrm{Pt(C{\equiv}C{-}H)_2(PEt_3)_2}]$ with $\mathrm{R^1{}_3B}$ ($\mathrm{R^1}$ = Me, Et, or $\mathrm{Pr^i}$) leads to (*E,E*)-*trans*-$[\mathrm{Pt(CH{=}CR^1BR^1{}_2)_2(PEt_3)_2}]$ and (ii) organoboration of *trans*-$[\mathrm{Pt(C{\equiv}C{-}Me)_2(PEt_3)_2}]$ with $\mathrm{R^1{}_3B}$ ($\mathrm{R^1}$ = Me or Et) leads to (*E*)-*trans*-$[\mathrm{Pt(C{\equiv}C{-}Me)(CMe{=}CR^1BR^1{}_2)(PEt_3)_2}]$.

The reactivity of metal–carbon bonds M–C≡ in metal acetylides towards organoboranes appears to be unique, as has been shown when M = Sn or Pb.[1-3] The reaction of the platinum(II) acetylides (**1**) with triorganoboranes which we have now studied (Scheme 1) provides the first example of transition metal acetylides undergoing organoboration. Compounds (**2**) are formed exclusively in the case of $\mathrm{R^2}$ = Me, and they do not react with excess of $\mathrm{R^1{}_3B}$. For $\mathrm{R^2}$ = H the attempted synthesis of (**2**) results in a mixture consisting mainly of (**1**) and (**3**) and a minor quantity of (**2**). Compounds (**3**) are formed quantitatively in the presence of excess of $\mathrm{R^1{}_3B}$ which is readily removed when the reaction is completed. Compounds (**2**) and (**3**) are pale yellow solids which are extremely air- and moisture-sensitive and should be stored in the dark. The n.m.r. spectra of (**3**) show the presence of a small amount of the (*E,Z*)-isomer (**4**). The amount of (**4**) increases when (**3**) is exposed to light. It is, therefore, not clear at present whether (**4**) is formed in the initial reaction between (**1**) and $\mathrm{R^1{}_3B}$ or by isomerization of (**3**). In any case the structure of the compounds (**2**) and (**3**) [and (**4**)] are suggestive of a borate-like intermediate (**5**) which has also been proposed for alkynylstannanes and triorganylboranes.[1,2]

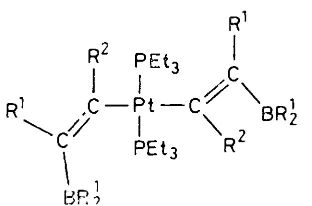
The high stereospecifity of this organoboration is in accord with the attack of a bulky electrophile at one side of the triple bond and the transfer of the group $\mathrm{R^1}$ from boron to the $\alpha$-carbon from the other side. The decreased reactivity of (**1**) and (**2**; $\mathrm{R^2}$ = Me) can be explained in terms of steric hindrance of the electrophilic attack at the $\beta$-carbon atom. In fact, reaction



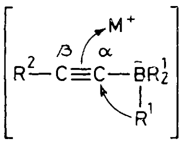
**Scheme 1.** Reagents and conditions: (i) $R^1_3B$ in benzene or toluene; $R^1$ = Me or Et, $R^2$ = Me, 60 °C, 10 h; (ii) 2 $R^1_3B$ in benzene or toluene; $R^1$ = Me, Et, or $Pr^i$, $R^2$ = H, 25 °C, 2 h.

of (**1**) with $R^1_3B$ does not take place if the substituents $R^2$ are bulky (*e.g.* $Bu^t$). Similarly, the bulkiness of $R^1_3B$ is important since (**1**; $R^2$ = Me) fails to react with $Pr^i_3B$ in contrast to (**1**; $R^2$ = H).

The reactions between (**1**) and $R^1_3B$ are readily monitored by i.r., and $^1H$, $^{11}B$, $^{31}P$, and $^{195}Pt$ n.m.r. spectroscopy. The structural elucidation was based finally on n.m.r. data.† The relative positions of $R^1$ and $R^2$ at the C=C double bond were determined by $^1H$ nuclear Overhauser enhancement difference spectroscopy.[4,5]



(**4**)



(**5**)

This novel route to platinum(II) alkenyl compounds offers a new entry into organoplatinum chemistry since both the acetylides[6,7] and many triorganylboranes[8,9] are conveniently accessible in high yields.

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† Representative n.m.r. data (Bruker WP 200) for (**2**) and (**3**), 0.5 M in [$^2H_8$]toluene at 28 °C; chemical shifts for $^1H$, $^{11}B$, $^{13}C$, $^{31}P$, and $^{195}Pt$ relative to internal $Me_4Si$, external $BF_3 \cdot OEt_2$, external $Me_4Si$, external 85% $H_3PO_4$, and $\Xi(^{195}Pt)$ = 21.4 MHz, respectively. Coupling constants, *J*/Hz, to $^{195}Pt$ are given in parentheses and those to $^{31}P$ in square brackets: (**2**; $R^1 = R^2$ = Me), $\delta(^{31}P)$ 6.6 p.p.m. (2855); $\delta(^{11}B)$ 73.4 p.p.m.; $\delta(^{195}Pt)$ 137.4 p.p.m. [*ca.* 2860]; $\delta(^{13}C)$ 184.9 (663) [9.4], Pt-*C*=; 146.7, Pt-C=*C*; 100.7 (208), Pt-C≡*C*; 92.1 (778) [16.8], Pt-*C*≡; 30.7 (52.3) [1.5], Pt-C(*C*H$_3$); 20.1 (46.0), B-C(*C*H$_3$); 6.4 p.p.m. (17.5), =C-*C*H$_3$; (**3**; $R^1$ = Me, $R^2$ = H), $\delta(^{31}P)$ 4.6 p.p.m. (2917); $\delta(^{11}B)$ 74.0 p.p.m.; $\delta(^{195}Pt)$ 432.0 p.p.m. [*ca.* 2920]; $\delta(^1H)$ 9.56 (29.0), =C-*H*; $\delta(^{13}C)$ 188.5 (556.6) [12.9], $^1J(^{13}C-^1H)$ 117.0 Hz; 151.0, Pt-C=*C*; 32.2 p.p.m. (64.7), =C-*C*H$_3$.