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Highly efficient monophosphine platinum catalysts for alkyne diboration

Rhodri Ll. Thomas,[a] **Fabio E. S. Souza**[b] **and Todd B. Marder** *[ab]

[a] *Department of Chemistry, University of Durham, South Road, Durham, UK DH1 3LE. E-mail: Todd.Marder@durham.ac.uk*
[b] *Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada*

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Automated parallel screening using a series of *in situ* generated platinum(0) phosphine complexes has allowed the identification of improved catalysts for the diboration of alkynes using bis(pinacolato)diboron ($B_2(pin)_2$, pin = $OCMe_2CMe_2O$). A selection of phosphines were added to $[Pt(NBE)_3]$ (NBE = norbornene), which contains only labile mono-olefin ligands, and the activity of the resulting solutions as catalysts for the diboration of $4\text{-}CF_3C_6H_4C{\equiv}CC_6H_4CF_3\text{-}4'$ **1** by $B_2(pin)_2$ was investigated by *in situ* GC-MS and/or NMR spectroscopy. This allowed the optimum phosphine : platinum stoichiometry to be identified as 1 : 1, and the large differences in catalyst activity depending on the nature of the phosphine to be quantified. The best phosphines employed in the study, PCy_3 and PPh_2(*o*-Tol) (*o*-Tol = C_6H_4Me-*o*), give activities orders of magnitude greater than the worst, such as $P(C_6F_5)_3$ and PBu^t_3. The monophosphine catalysts function much more efficiently than previous catalysts for a range of alkynes allowing diborations to be performed at ambient temperatures. The diboration of strained cyclic alkenes and some vinyl- and allyl-arenes proceeded well, although the catalysts were inactive for other olefinic systems examined. As a result of these studies, the isolable and stable compound $[Pt(PCy_3)(\eta^2\text{-}C_2H_4)_2]$ was identified as an excellent catalyst for alkyne diboration even at room temperature.

Introduction

The utility of organoboranes as intermediates in organic synthesis is well documented.[1,2] Metal catalysed borylation reactions, including hydroboration,[3] diboration,[4,5] dehydrogenative borylation,[6,7] borylation of aryl and vinyl halides and triflates,[2,8,9] and additions of B–Si,[10] B–Sn[11] and B–S bonds[12] provide new routes to important organoboron compounds. We have reported rhodium[13,14] and gold[14] complexes as catalysts for the diboration of styrenes using $B_2(cat)_2$ (cat = $1,2\text{-}O_2C_6H_4$) to give the expected alkyl 1,2-bis(boronate) esters, and the use of platinum and palladium compounds for catalytic boronations with $B_2(OR)_4$ compounds has been reviewed.[4,5] Recently, it has been shown that copper based compounds also catalyse borylation reactions.[15]

cis-Alkene-1,2-bis(boronate) esters, the product of diboration of alkynes, are a useful class of organoboron compounds. They can be employed as substrates for the Suzuki–Miyaura cross-coupling reaction with aryl halides,[2,16] and have been used in the synthesis of biologically active molecules such as the anti cancer agent Tamoxifen.[17] Their preparation *via* a platinum catalysed diboration reaction was first reported by Miyaura, Suzuki and co-workers,[16] using $[Pt(PPh_3)_4]$ as a catalyst. Subsequent studies showed that this catalyst may be used in the diboration of allenes,[18] methylcyclopropanes[19] and 1,3-dienes.[20] These diboration reactions typically required heating at 80 °C for 24 hours in DMF, and so an improved catalyst was sought. Simultaneous work by our group[21] and by Iverson and Smith[22] showed that using bis(phosphine)platinum based catalysts, either $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$ or $[Pt(PPh_3)_2\{B(OR)_2\}_2]$, reduced the reaction times required and allowed these reactions to be performed in less polar solvents such as toluene. These compounds also catalyse the diboration of enones[23] as well as the formation of the novel hexaboryl- and tetraboryl-ethanes and tetraborylethenes from bis(boryl) alkynes.[24] Phosphine-free platinum(0) species such as $[Pt(NBE)_3]$, $[Pt(COD)_2]$[25] or $[Pt(dba)_2]$[26] (NBE = norbornene; COD = 1,5-cyclooctadiene; dba = dibenzylideneacetone) catalyse the diboration of alkenes, and show very different selectivities from the catalysts that contain phosphines, with, for example, different products found in the diboration of dienes.[20]

Baker and co-workers have recently reported that the commercially available platinum(II) compound $[Pt(COD)Cl_2]$ shows catalytic activity, after an induction period, for the diboration of a range of substrates, including imines;[27] however, this catalyst requires the more active diboron reagent $B_2(cat)_2$ and the reaction failed when $B_2(pin)_2$ was used (pin = pinacolate, $OCMe_2CMe_2O$). As was the case for the phosphine free platinum(0) complexes, alkenes, such as 1-octene and 4-vinylanisole, were diborated far more easily at room temperature than alkynes such as 1-octyne and di(*p*-tolyl)acetylene, which required a temperature of 55 °C. In light of the selectivity displayed and the induction period required by this catalyst, it is likely that the catalytically active species is a phosphine free platinum(0) species generated *in situ.*

For bis(triphenylphosphine)platinum catalysts, alkyne diboration was inhibited by added PPh_3,[21] and the rate was in fact shown to be inverse first order in $[PPh_3]$.[22] Chelating phosphines such as dppe or dppb $[Ph_2P(CH_2)_4PPh_2]$ greatly reduced the catalyst efficiency.[21] The fact that phosphine free platinum complexes are far more active for alkenes than alkynes[27] suggests that the presence of phosphine may be required for efficient alkyne diboration, and that a P : Pt ratio in solution of 1 : 1 would provide the most active catalyst. This could be achieved *via* either an isolable monophosphine platinum(0) complex or *in situ* formation of a similar species. Recent reports by Miyaura and co-workers on the platinum catalysed diboration of allenes[18] have highlighted the marked effect of the nature of the phosphine ligand on the activity of a related catalytic system, with yields varying from 7 to 85% as the phosphine is changed from PMe_3 to PCy_3, and with significant variations in the regioselectivity of the reactions being noted. In

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addition, the development of highly efficient palladium/phosphine based catalysts for a range of coupling reactions by the group of Fu,[28,29] using PBu$^t_3$, and Buchwald and co-workers,[30] using bulky biphenyl based phosphines, led us to consider how the nature of the phosphine might affect platinum catalysed diboration of alkynes.

In this paper we report the use of automated parallel screening techniques for the identification and optimisation of improved catalysts for the diboration of alkynes and simultaneous collection of kinetic data. The effects of the nature and amount of phosphine ligands have been investigated, as have the lifetimes of the catalysts produced.

Experimental

General

All reactions were performed under an atmosphere of dry nitrogen, in a double length glove box (Innovative Technology, Inc., System One), in sealed Young's tap vessels using standard Schlenk line techniques, or in sealed GC autosampler vials, *vide infra*. Solvents were distilled from sodium prior to use or dried and deoxygenated using a modified Innovative Technology Inc. SPS-solvent purification system containing activated alumina followed by an activated BASF R311 copper catalyst under argon pressure, similar to that described by Grubbs and co-workers.[31]

NMR spectra were collected on Varian Mercury 200 (^{1}H, ^{19}F) and Unity 300 (^{11}B) spectrometers at the following frequencies: ^{1}H, 200; ^{19}F, 188; ^{11}B, 96 MHz. Proton NMR spectra were referenced to residual protic solvent resonances, ^{19}F and ^{11}B to external standards ($CFCl_3$ and $BF_3{\cdot}OEt_2$ respectively). All spectra were recorded as solutions in C_6D_6 or mixed C_6D_6/toluene unless stated otherwise. Chemical shifts are reported in ppm and coupling constants in Hz.

GC-MS analyses were performed on a Hewlett-Packard 5890 Series II gas chromatograph equipped with a 5971A mass selective detector and a 7673 autosampler. A fused silica capillary column (12 m cross-linked 5% methylphenylsilicone) was used, and the oven temperature was ramped from 70 to 270 °C at a rate of 20 °C min^{-1}. UHP grade helium was used as the carrier gas. The screw-cap autosampler vials used were supplied by National Scientific Inc. and were fitted with Teflon/silicone/Teflon septa and 0.2 ml micro inserts.

All compounds were either obtained commercially or prepared by literature methods or variants thereof ([Pt(NBE)$_3$],[32] [Pt(dba)$_2$],[33] [Pt(PCy$_3$)(η^2-C$_2$H$_4$)$_2$],[34] B$_2$(pin)$_2$,[35] $4\text{-}CF_3C_6H_4C{\equiv}CH$ [36]), with the exception of **1** which was prepared as described below. All commercial materials were purified by distillation or recrystallisation prior to use, and their purities were confirmed by GC-MS and NMR spectroscopy. Stock solutions of [Pt(NBE)$_3$] and phosphines were prepared immediately prior to use, and were employed in order to achieve accuracy when small quantities of reagent were required, as well as uniformity from run to run.

Synthesis of $4\text{-}CF_3C_6H_4C{\equiv}CC_6H_4CF_3\text{-}4'$ 1

To a mixture of [Pd(PPh$_3$)$_2$Cl$_2$] (65 mg, 0.092 mmol) and CuI (17.5 mg, 0.092 mmol) in triethylamine (150 ml) was added $4\text{-}CF_3C_6H_4I$ (2.5 g, 9.2 mmol) and $4\text{-}CF_3C_6H_4C{\equiv}CH$ (1.7 g, 10.1 mmol). Formation of a solid deposit began immediately, and vigorous stirring at room temperature was required for 45 min, at which time GC-MS analysis indicated that the reaction was complete. After filtration through silica, the solvent was removed from the dark solution under reduced pressure. The oily solid produced was dissolved in Et$_2$O (50 ml) and washed with dilute aqueous HCl (0.2 M, 100 ml) three times [**CAUTION**: if much amine remains, the heat generated may cause a build up of pressure]. The ether was removed from the residue under reduced pressure, and the solid purified by column chromatography on silica gel (4 cm diameter, 10 cm high), using hexane as eluent. Yield = 2.4 g, 84%. NMR: ^{1}H δ 7.02 (d, $J = 7$, 4H), 7.15 (d, $J = 7$, 4H); ^{19}F-{^{1}H} δ −63.3 (s). MS: *m*/*z* 314 (M$^+$, 100), 295 (M$^+$ − F, 17).

Typical diboration of 1

To a sample of [Pt(NBE)$_3$] (2.4 mg, 5 µmol) dissolved in toluene (0.1 ml) was added a solution of PCy$_3$ in toluene (0.1 ml, 0.05 M), giving a pale orange-yellow solution. This solution was added to a mixture of B$_2$(pin)$_2$ (28 mg, 0.11 mmol) and **1** (31 mg, 0.1 mmol) dissolved in toluene (2 ml), and shaken vigorously to ensure complete mixing. Aliquots of the solution (*ca.* 50 µL) were transferred to micro inserts in GC autosampler vials at ambient temperature. The vials were sealed under N$_2$, removed from the glove box and GC-MS samples taken at 19 minute intervals, each from a fresh autosampler vial, until the reaction was complete, or no further reaction was apparent.

Diboration of 1

Using [Pt(NBE)$_3$]/PPh$_2$(*o*-Tol). A solution of B$_2$(pin)$_2$ (7 mg, 0.028 mmol) and **1** (8 mg, 0.025 mmol) in C$_6$D$_6$ (0.5 ml) was placed in a 5 mm NMR tube sealed with a Teflon tap. This NMR tube was placed in a Mercury 200 NMR spectrometer, and the shim settings were optimised. The tube was removed to a glove box, and to it was added a C$_6$D$_6$ solution of a mixture of PPh$_2$(*o*-Tol) (*o*-Tol = C$_6$H$_4$Me-*o*) and [Pt(NBE)$_3$] (0.025 ml, 0.05M in each component). The NMR tube was replaced in the spectrometer, and ^{19}F-{^{1}H} NMR spectra were collected for 30 seconds every 2 minutes until the reaction was complete.

Using a low catalyst loading. To a solution of **1** (0.62 g, 2.0 mmol) and B$_2$(pin)$_2$ (0.50 g, 2.0 mmol) in toluene (2 ml) was added a catalyst solution containing [Pt(NBE)$_3$] (5 mg, 10 µmol, 0.5 mol% relative to alkyne) and PPh$_2$(*o*-Tol) (2.8 mg, 10 µmol, 0.5 mol%) in toluene (1 ml). The solution was stirred for 10 hours, at which time GC-MS analysis indicated that no **1** remained, with **2** being the only product.

Characterisation of *cis*-$4\text{-}CF_3C_6H_4C(Bpin){=}C(Bpin)C_6H_4CF_3\text{-}4'$ 2

After completion of the above reactions, the combined solutions were filtered through Celite®, and the solvent was removed under reduced pressure leaving an orange oily solid, which was washed with cold hexane to give the product as a white powder. NMR: ^{1}H δ 1.32 (s, 12H), 7.03 (d, $J = 8$, 2H), 7.35 (d, $J = 8$, 2H); ^{19}F-{^{1}H} δ −62.7 (s); ^{11}B-{^{1}H} δ 25.3 (br s). MS: *m*/*z* 568 (M$^+$, <1%), 549 (M$^+$ − F, 3), 84 ($Me_2C{=}CMe_2^+$, 100). Microanalysis: calculated for $C_{28}H_{32}B_2F_6O_4$ 59.19% C, 5.68% H; Found 58.92% C, 5.64% H.

Diboration of other substrates using [Pt(NBE)$_3$]/PR$_3$ catalyst

To a sample of [Pt(NBE)$_3$] (2.4 mg, 5 µmol) dissolved in toluene (0.1 ml) was added a solution of PPh$_3$ in toluene (0.1 ml, 0.05 M), giving a pale orange-yellow solution. This solution was added to a mixture of B$_2$(pin)$_2$ (28 mg, 0.11 mmol) and a substrate (0.1 mmol) dissolved in toluene (2 ml) at ambient temperature. Aliquots were removed at intervals of 30 minutes initially, then at intervals of several hours for the reactions that required significant reaction time. The product mixtures were analysed by GC-MS and ^{1}H NMR spectroscopy, by comparison with previously reported data,[21,22,25,37] except for the diboration products of **1** and 4-allylanisole, which are given below.

Characterisation of $4\text{-}MeOC_6H_4CH_2CH(Bpin)CH_2(Bpin)$. NMR: ^{1}H δ 1.31 (s, 12H, Bpin), 1.37 (s, 12H, Bpin), 1.70 (m, 2H, C*H*$_2$Bpin), 2.20 (apparent quintet, $J = 7$, 1H, CH$_2$C*H*-BpinCH$_2$Bpin), 2.75 (dd, 1H, $J = 7$, 12, C*H*$_2$CHBpinCH$_2$Bpin), 2.75 (dd, $J = 7$, 12, 1H, $CH_2CHBpinCH_2Bpin$), 3.24 (s, 3H, CH_3O), 6.98 (m, 2H), 7.33 (m, 2H); $^{11}B\text{-}\{^1H\}$ δ 32.3 (br s, 1B), 35.2 (br s, 1B). MS: *m*/*z* 402 (M^+, 5), 387 ($M^+ - Me$, 68), 84 ($Me_2C{=}CMe_2^+$, 100).

Diboration of other substrates using [Pt(PCy$_3$)(η^2-C$_2$H$_4$)$_2$] catalyst

These studies were conducted in an identical manner to the above, except that a sample of [Pt(PCy$_3$)(η^2-C$_2$H$_4$)$_2$] (5.3 mg, 10 μmol) was dissolved in toluene (0.2 ml) and half of this solution was used to catalyse the diboration reaction.

General procedure for competitive diboration of alkynes

The diboron reagent ($B_2(pin)_2$ or $B_2(cat)_2$, 0.15 mmol), alkynes (0.15 mmol of each) and [Pt(PPh$_3$)$_2$(η^2-C$_2$H$_4$)] (6 mg, 7.5 μmol, 5 mol%) were placed in a vial to which was added toluene (4 ml); samples containing $B_2(cat)_2$ were warmed to ensure complete dissolution. The solutions were transferred to ampoules sealed with a Young's Teflon tap and heated to 80 °C, with regular sampling by GC-MS until the reaction was complete. The solvent was removed under reduced pressure and the remaining solids were analysed by ^1H and ^{19}F NMR spectroscopy as $CDCl_3$ solutions.

Data analysis

The relative amounts of the species present were determined by integration of the GC-MS total ion chromatogram trace. The relative response factors for the compounds studied were determined from the analysis of several mixtures of these compounds of known concentrations. The proportion of substrate remaining was defined as the amount of substrate/(amount of substrate + amount of product), which assumes no by-products are produced from the substrate. This assumption was confirmed by study of the GC-MS and NMR analysis of the final reaction mixtures.

Results and discussion

Automated parallel screening

The development of optimal catalysts is a difficult process. Although general features of a good catalyst may be identified by logical considerations such as kinetics, the fine tuning of the system developed may require the optimisation of many parameters. Automated parallel screening allows the investigation of a range of catalyst precursors to attempt to identify promising catalysts more quickly than by traditional methods. Such approaches to homogeneous catalysis are becoming the subject of more widespread interest.[38] For the process to be successful, it is necessary that one can identify a suitable test reaction, and a method for it to be monitored. It is useful to choose a catalyst system that allows for modification in a straightforward manner, such as a precursor to which different ligands can be added.

The reaction chosen for testing the diboration of alkynes was that of $4\text{-}CF_3C_6H_4C{\equiv}CC_6H_4CF_3\text{-}4'$ **1** with $B_2(pin)_2$ in an aromatic solvent (Scheme 1). This reaction may be monitored by GC-MS, as both reagents and the desired product are readily identified and quantified by this method and, importantly, there are no side products to complicate the analysis. Alternatively, NMR spectroscopy of either the ^{19}F resonance of the alkyne or the ^1H resonance of the boron reagent may be used to monitor the reaction, as both nuclei give sharp singlets for both starting material and product. The time frame of the reaction will govern the technique used: GC requires a modest time delay between each aliquot taken for analysis, typically 19 minutes in our case. For reactions that proceed somewhat more rapidly, NMR spectroscopy is the technique of choice. The use of UV-vis absorbance or fluorescence spectroscopy is efficient for fast reactions,[39] but was not employed in the current work.

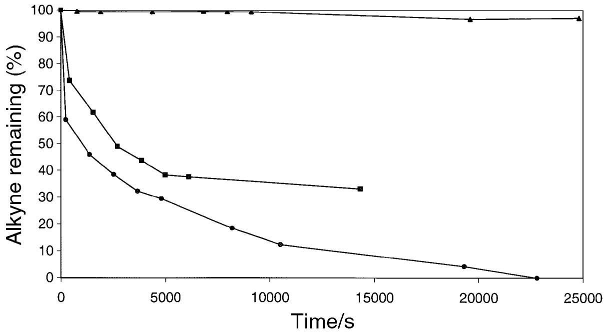
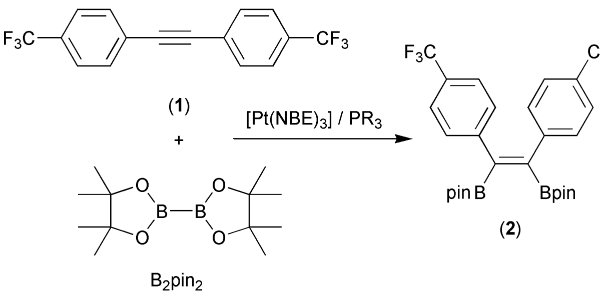


Fig. 1 Effect of [Pt(NBE)$_3$] : PPh$_3$ stoichiometry on the catalytic diboration of **1**. [**1**] = 7.4 mM, [B$_2$(pin)$_2$] = 8.0 mM, [Pt(NBE)$_3$] = 0.37 mM (5 mol%), [PPh$_3$] = 0 (■), 0.37 mM (●) and 0.75 mM (▲).



Scheme 1

The catalysts to be studied were all phosphineplatinum(0) complexes. To generate these species *in situ* it was decided to use a labile platinum(0) precursor complex to which different phosphines could be added in various amounts. Initial studies were attempted using [Pt(dba)$_2$] as a source of platinum; however, this proved problematic. Few of the test reactions went to completion, and deposition of a dark residue was apparent. This was presumably platinum metal due to catalyst decomposition, as seen in previous studies by Miyaura and co-workers.[18] Analysis of the final mixtures also revealed several by-products arising from diboration, hydroboration and dehydrogenative borylation of the dba ligand. The relatively low solubility of this compound also precluded its use for quantitative studies under our conditions.

The platinum(0) complex thus chosen was [Pt(NBE)$_3$] as it contains only very labile mono-olefin ligands. This complex and the desired phosphine ligand were mixed in solution prior to addition to the substrate mixture to provide ample time for generation of the phosphineplatinum complex before exposure to the reactants which ensured consistent, comparable data. Slightly different data were obtained when the platinum and phosphine were added sequentially to the reaction mixture, presumably due to the increased time required for the phosphine ligand and platinum atom to interact with each other in this more dilute solution.

Phosphine : platinum stoichiometry in the catalyst

The effect of varying the ratio of phosphine to platinum from 2 : 1 to 1 : 1 and then to 0 : 1 was investigated using PPh_3. The amount of alkyne remaining was monitored by automated GC-MS, and the results are displayed in Fig. 1. It is apparent that while the use of a catalyst formulated as 'Pt(PPh$_3$)$_2$' is known to be effective at elevated temperatures, at room temperature the reaction is too slow to be of general use, with only a few percent reaction in seven hours. The reaction does proceed to completion; however, this takes fifteen days. The reaction using [Pt(NBE)$_3$] is much more rapid in the absence of added phosphine compared with 2 molar equivalents of added

Table 1 Effect of phosphine size and basicity on the [Pt(NBE)$_3$]/phosphine catalysed diboration of **1**

Phosphine	Cone angle^a/°	pK_a^{b}	k_{eff}^{c}/10^{-5}
PBu$^t_3$	182	11.40	2.8
P(o-Tol)$_3$	194	3.08	9.2
P(C$_6$F$_5$)$_3$	184	^{d}	9.6
No phosphine	—	—	13
PPh$_3$	145	2.73	15
PMePh$_2$	136	4.57	19
PMe$_2$Ph	122	6.50	61
PBu$^n_3$	132	8.43	63
PCy$_3$	170	9.70	82
PPh$_2$(o-Tol)	^{d}	^{d}	232

Reaction conditions: 1.5 μmol of **1** (7.4 mM), 1.1 equivalent B$_2$(pin)$_2$ (8.0 mM) in 0.2 ml toluene with 5 mol% of an equimolar mixture of [Pt(NBE)$_3$] and PR$_3$ at ambient temperature. ^{a} See reference 47. ^{b} pK_a of the conjugate acid. See reference 48. ^{c} Rate = k_{eff}[alkyne]/[alkyne]$_0$. ^{d} No value reported for this parameter.

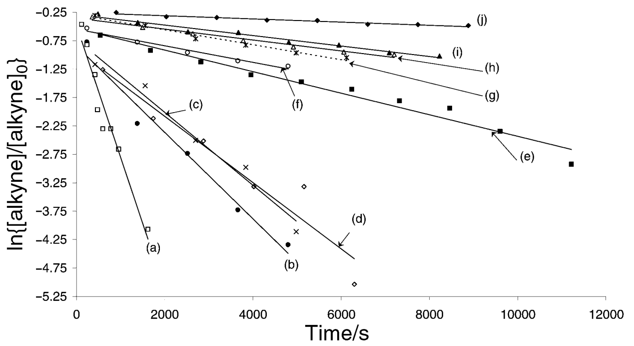


Fig. 2 Effect of phosphine on the [Pt(NBE)$_3$]/phosphine catalysed diboration of **1**. [**1**] = 7.4 mM, [B$_2$(pin)$_2$] = 8.0 mM, [Pt(NBE)$_3$] = [phosphine] = 0.37 mM (5 mol%). Phosphine = PPh$_2$(o-Tol) (a, □), PCy$_3$ (b, ●), PMe$_2$Ph (c, ×), PBu$^n_3$ (d, ◇), PMePh$_2$ (e, ■), PPh$_3$ (f, ○), None (g, *), P(C$_6$F$_5$)$_3$ (h, △), P(o-Tol)$_3$ (i, ▲), PBu$^t_3$ (j, ◆).

PPh$_3$; however, the reaction does not proceed to completion, and the formation of colloidal platinum is apparent in the reaction mixture. The most effective catalyst stoichiometry was found to be phosphine : platinum = 1 : 1, with the reaction being more rapid than either of the other systems tested, and proceeding to completion without any obvious precipitation of platinum metal. Similar results were found using other phosphines such as PCy$_3$ and PPh$_2$(o-Tol), with the 'Pt(PR$_3$)$_1$' stoichiometry producing a significantly faster reaction than that using 'Pt(PR$_3$)$_2$' as the catalytic species.

Nature of phosphine added

Since the optimal catalyst appeared to be a monophosphine platinum species, as predicted by the previous studies, this stoichiometry was investigated for a range of commercially available phosphines to determine the effects of basicity and/or cone angle on the rate of diboration. The results are displayed in Fig. 2. It is apparent from the linearity of the plots that the reaction is overall first order with respect to the product [alkyne][B$_2$(pin)$_2$], as had been reported.[21,22]

The wide variation in activity with different phosphines is apparent. The effective rate constants, given in Table 1, vary by two orders of magnitude. The order of activity of the phosphines may be summarized as: PPh$_2$(o-Tol) > PCy$_3$ > PBu$^n_3$ ≈ PMe$_2$Ph > PMePh$_2$ > PPh$_3$ > no phosphine ≈ P(C$_6$F$_5$)$_3$ ≈ P(o-Tol)$_3$ > PBu$^t_3$. A general trend is apparent, with the catalyst being improved by use of basic phosphines; however there are two notable exceptions. The catalytic system based on PBu$^t_3$, the most basic phosphine tested, showed little activity. This may be due to the extreme bulk of the phosphine, preventing the approach or reaction of the catalyst and reagents. The major differences in the catalytic activity of PCy$_3$ and PBu$^t_3$ illustrate how sensitive catalysts may be to small changes in phosphine size and basicity, with phosphines larger than a threshold value being inactive. Similar differences in activity have been seen in the palladium catalysed Suzuki–Miyaura coupling reaction, where Fu and co-workers[28] have shown that, in the reaction of TfOC$_6$H$_4$Cl (TfO = CF$_3$SO$_3$) with aryl boronic acids, different products are obtained when PCy$_3$ is used (TfO substitution) in place of PBu$^t_3$ (Cl substitution).

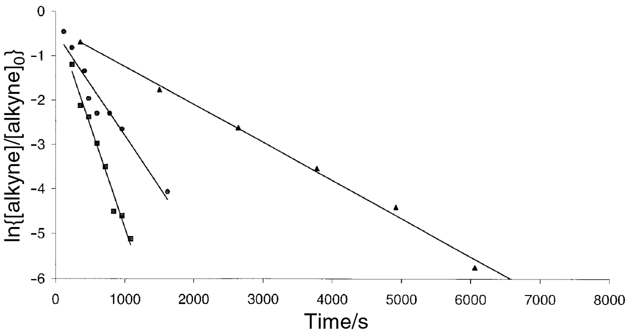


Fig. 3 Effect of [catalyst] on the [Pt(NBE)$_3$]/phosphine catalysed diboration of **1**. [**1**] = 7.4 mM; [B$_2$(pin)$_2$] = 8.0 mM; [Pt(NBE)$_3$] = [phosphine] = 0.14 (2, ▲), 0.37 (5, ●), 0.69 mM (10 mol%, ■).

The phosphine which generated the most active catalyst was PPh$_2$(o-Tol), which is not expected to have significantly greater basicity than triphenylphosphine, although the additional methyl group would increase the cone angle of the phosphine significantly. The substantially enhanced activity of this catalyst was therefore surprising. It is possible that there is an alternative mechanism in action in this case, as has been found for the Heck reaction, where the introduction of *ortho*-tolyl groups into the phosphines used also increases the catalytic activity of systems dramatically.[40] This has been postulated to be due to the formation of metallacyclic intermediates, and indeed such metallacycles[41] and related compounds containing 'PCP pincer' ligands[42] have been shown to be very active catalysts in that reaction.

If similar alkyne diboration activity were observed for tri-(o-tolyl)phosphine, which is known to form palladacycles readily,[43] the suggestion of platinacyclic catalysts would be reinforced. The activity found with this phosphine, however, is comparable to that with P(C$_6$F$_5$)$_3$, both of which show no greater rate for diboration than is found for the phosphine free platinum species. The lower basicity and large size of P(o-Tol)$_3$ and P(C$_6$F$_5$)$_3$ may disfavour the formation of a catalytically active platinum–phosphine complex in the presence of other competing ligands in the reaction mixture. This would give the same phosphine-free catalytically active species in the presence or absence of these two phosphines. The reason for the enhanced activity of the PPh$_2$(o-Tol) catalyst remains elusive.

Concentration of catalyst

The above studies were conducted using identical catalyst concentrations of 0.37 mM, corresponding to 5 mol% with respect to the alkyne. At this concentration only 20 catalyst turnovers are required for complete reaction; however, higher turnover numbers and hence lower catalyst loadings would be preferable for preparative use. Using concentrations of [Pt(NBE)$_3$]/PPh$_2$(o-Tol) of 0.14 and 0.69 mM, corresponding to 2 and 10 mol% respectively, we obtained the kinetic data shown in Fig. 3. From the gradients of the three lines (Table 2), we obtain k_{eff} for the reactions, demonstrating that $k_{eff} \propto$ [catalyst], *i.e.* the reaction is first order in catalyst concentration. This also illustrates that the reaction can proceed with only 2 mol% catalyst, equivalent to 50 turnovers per platinum atom. In further studies the reaction proceeded to completion in 10 hours using only 0.5 mol% catalyst, with a consequent turnover number of *ca.* 200.

Reactions with other substrates

To test the general applicability of monophosphine catalysts, as well as the relative reactivity of various unsaturated substrates, the diboration of a selection of alkynes and alkenes was attempted. The catalytic system used was $[Pt(NBE)_3]/PPh_3$, as the reactions involving this catalyst were slow enough for relative reaction rates to be determined with greater confidence than would be the case for the extremely active catalysts. Table 3 lists the substrates utilised and the time required for completion of the diboration reaction.

Amongst the alkynes it is seen that the diboration reaction of phenylacetylene is unusually slow, as has been observed previously with both '$Pt(PPh_3)_2$'[21] and $Pt(PPh_3)_4$ catalysts.[16] The π-acceptor substituted $4\text{-NCC}_6H_4C{\equiv}CH$ substrate proved even less reactive, but the π-donor substituted $4\text{-MeOC}_6H_4C{\equiv}CH$ was readily diborated. All other alkyne substrates were diborated cleanly at room temperature, *i.e.* the catalyst is successful for both alkyl- and aryl-alkynes, and for terminal and internal alkynes. From the comparison of the reactions of the substituted diphenylacetylenes, **1**–**3**, we can see that for these compounds the reaction rate is enhanced by electron withdrawing substituents such as CF_3, and retarded by those that are electron donating, such as Me or OMe.

These results are in agreement with a series of competition experiments using $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$ as a catalyst, in which solutions of equimolar amounts of differently substituted diphenylacetylenes were treated with sufficient diboron reagent to react with only half of the triple bonds present. The results of these studies are listed in Table 4, and it can be seen that diboration of the CF_3 substituted compound is faster than the reaction of the more electron rich substrate. This preference is much less marked when $B_2(cat)_2$ is used in place of $B_2(pin)_2$, with the lower selectivity presumably due to the greater reactivity of the former diboron reagent.[21,44] Stoichiometric diborations of similar *para* substituted diphenylacetylenes using $[Pt(PPh_3)_2(Bcat)_2]$ led to a similar order of reactivity, with rates in the order R = $CF_3 \gg H > OMe$.[22]

Interestingly, the order of reactivity of the diphenylacetylenes is apparently reversed from that of the *para*-substituted terminal phenylacetylenes, *vide supra*, where donor moieties enhance the reaction rate. The reasons for this are still not clear, although it seems reasonable that ≡C–H activation processes may become an important factor when the pK_a of the alkynyl proton drops below a certain level, with such processes present in phenylacetylene ($pK_a = 29.1$[45]) but absent in 4-methoxyphenylacetylene ($pK_a = 29.7$[45]).

Alkene substrates were also examined (Table 3), and it was found that diboration of NBE proceeded rapidly and cleanly. This was as expected as diborated NBE was observed in some of the slower alkyne diborations reactions, derived from the ligands of the catalyst used. It was most apparent in the diboration of 1-heptyne and 4-octyne, although traces were observed in the diborations of the arylacetylenes. The diboration of styrene derivatives could also be catalysed at room temperature; however, these reactions were not clean, with some hydroboration and dehydrogenative borylation[6,7] also occurring giving the monoborylated alkane and the vinyl boronate ester respectively in equal amounts. Surprisingly, 4-allylanisole was cleanly and rapidly diborated. Other alkenes, including *cis*- and *trans*-stilbene, *trans*-4-octene and 1-heptene, failed to react under these conditions.

The $[Pt(NBE)_3]/PCy_3$ mixture has been shown to be a much better catalyst than $[Pt(NBE)_3]/PPh_3$ in our test reaction, the diboration of **1**. This catalyst was then tested for a range of

Table 2 Effect of [catalyst] on $[Pt(NBE)_3] : PPh_2(o\text{-Tol})$ catalysed diboration of **1**

Catalyst concentration/mM	Catalyst loading/mol%	$k_{eff}/10^{-3}$	k_{rel}
0.14	2	0.82	1.8
0.37	5	2.32	5.0
0.69	10	4.63	10

Reaction conditions: 1.5 µmol of **1** (7.4 mM), 1.1 equivalents $B_2(pin)_2$ (8.0 mM) in 0.2 ml toluene solution of given concentration in $[Pt(NBE)_3]/PPh_2(o\text{-Tol})$ (1 : 1).

Table 4 Product distributions in the competitive diboration studies of alkyne mixtures

Diboron reagent	Substrates $4\text{-RC}_6H_4C{\equiv}CC_6H_4R\text{-}4'$ R	R	Reaction time	Diboration ratio
$B_2(pin)_2$	CF_3	H	2 days	6 : 4
$B_2(pin)_2$	CF_3	OMe	1 week	9 : 1
$B_2(cat)_2$	CF_3	H	1 day	1 : 1
$B_2(cat)_2$	CF_3	OMe	1 week	7 : 5

Reaction conditions: 0.15 mmol of each alkyne, 0.15 mmol diboron reagent in 4 ml toluene with 7.5 µmol $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$ as catalyst at 80 °C.

Table 3 Time required and product distribution for the catalysed reaction of $B_2(pin)_2$ with selected substrates

Substrate	Reaction time/hours	Product distribution[a] (%) Diboration	Hydroboration	Dehydrogenative borylation
$4\text{-CF}_3C_6H_4C{\equiv}CC_6H_4CF_3\text{-}4'$ **1**	4.3	100		
$4\text{-MeC}_6H_4C{\equiv}CC_6H_4Me\text{-}4$	5.0	100		
$4\text{-MeOC}_6H_4C{\equiv}CC_6H_4OMe\text{-}4$	5.5	100		
4-Octyne	9	100		
1-Heptyne	12	100		
$4\text{-MeOC}_6H_4C{\equiv}CH$	1.3	100		
$C_6H_5C{\equiv}CH$	36	30		
$4\text{-NCC}_6H_4C{\equiv}CH$	65	11		
Norbornene	2	100		
Styrene	2.5	78	12	10
4-Vinylanisole	3	74	14	13
4-Allylanisole	5	98	1	1
trans-Stilbene	36	0		
cis-Stilbene	36	0		
trans-4-Octene	36	0		
1-Heptene	36	0		

Reaction conditions: 0.1 mmol of substrate, 1.1 equivalents $B_2(pin)_2$, 2.3 µmol $[Pt(NBE)_3]$, 2.3 µmol PPh_3 in 2.2 ml toluene at ambient temperature. [a] Does not include NBE diboration product arising from $[Pt(NBE)_3]$.

Table 5 Reaction times required for the catalytic diboration of a range of substrates using [Pt(NBE)$_3$]/PPh$_3$, [Pt(NBE)$_3$]/PCy$_3$ and [Pt(PCy$_3$)-(η^2-C$_2$H$_4$)$_2$] as catalysts

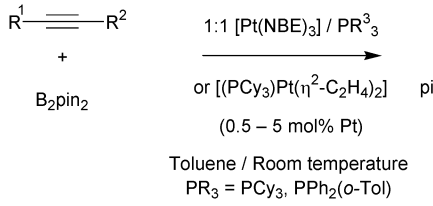
	Time required for complete reaction/h		
Substrate	[Pt(NBE)$_3$]/PPh$_3$	[Pt(NBE)$_3$]/PCy$_3$	[Pt(PCy$_3$)(η^2-C$_2$H$_4$)$_2$]
4-CF$_3$C$_6$H$_4$C≡CC$_6$H$_4$CF$_3$-4′ **1**	4.3	1.4	1.2
4-MeC$_6$H$_4$C≡CC$_6$H$_4$Me-4	5.0	1.6	1.6
4-MeOC$_6$H$_4$C≡CC$_6$H$_4$OMe-4	5.5	1.6	1.8
4-Octyne	9.0	3.0	2.5
1-Heptyne	12	3.5	3.3
MeOC$_6$H$_4$C≡CH	1.3	0.4	0.6
Norbornene	2.0	0.8	0.7

Reaction conditions: 0.1 mmol of substrate**,** 1.1 equivalents B$_2$(pin)$_2$ in 2.2 ml toluene with 2.4 µmol [Pt(NBE)$_3$] and 2.4 µmol PR$_3$ or 2.4 µmol [Pt(PCy$_3$)(η^2-C$_2$H$_4$)$_2$] as catalyst.

alkyne substrates to ensure that the effect was not specific to just one compound. The results, given in Table 5, show that the greater activity of the PCy$_3$ containing catalyst in our test reaction was repeated for all the alkynes studied, and also for the strained alkene, NBE. It can be seen that diboration reactions using the PCy$_3$ system typically take one third of the time needed using PPh$_3$ as the phosphine.

Preformed catalysts

The use of [Pt(NBE)$_3$] for the *in situ* preparation of diboration catalysts is hampered by the thermal instability of the compound; it must be stored in an inert atmosphere at low temperatures. An ideal catalyst would be a thermally stable, and preferably air-stable, solid that matched the properties elucidated above. A literature search reveals that the compounds [Pt(PR$_3$)(η^2-C$_2$H$_4$)$_2$], which match the desired catalyst stoichiometry, were reported in the 1970s by the group of Stone.[46] Importantly, [Pt(PCy$_3$)(η^2-C$_2$H$_4$)$_2$] was reported to be sufficiently stable to be handled in air and stored under an inert atmosphere at room temperature. This stability was greater than that reported for compounds containing the less basic phosphines, such as PPh$_3$, and so the cyclohexyl compound was chosen for study (Scheme 2).



Scheme 2

We prepared this compound and studied its catalytic activity in our test reaction. The activity of the isolated catalyst is the same within experimental error as that of the catalytic mixture of [Pt(NBE)$_3$]/PCy$_3$ containing the same amount of platinum, with $k_{\text{eff}} = 79$ for [Pt(PCy$_3$)(η^2-C$_2$H$_4$)$_2$] *vs.* 82 for [Pt(NBE)$_3$]/PCy$_3$. This suggested that both form identical species in the reaction solution, and that the stable [Pt(PCy$_3$)(η^2-C$_2$H$_4$)$_2$] can be used as a convenient alkyne diboration catalyst. Studies on a range of alkynes and NBE showed no significant difference in reaction times (Table 5) between preformed and *in situ* generated monophosphine species.

Conclusion

The results of this study indicate that the catalysts presently employed for the diboration of alkynes may be improved substantially, and that the reaction may be effected under much milder conditions than previously reported. Previous kinetic and mechanistic studies suggested that a monophosphineplatinum species was the active catalyst when two or more equivalents of phosphine were present. The above results confirm this finding and demonstrate conclusively that a PR$_3$: Pt ratio of 1 : 1 is more efficient than that of 0 : 1 which in turn is much more efficient than 2 : 1. Parallel screening of a series of *in situ* generated monophosphineplatinum catalysts using 0.2 ml sample size and automated GC-MS techniques allowed identification of two particularly effective phosphines, namely PCy$_3$ and PPh$_2$(*o*-Tol). While a general trend of enhanced activity with increased phosphine basicity was observed, PPh$_2$(*o*-Tol) does not fit this trend, pointing to the importance of using empirical screening methods as a complement to rational design based on kinetic and mechanistic study. These studies led to the hypothesis that the known stable, isolable monophosphine complex [Pt(PCy$_3$)(η^2-C$_2$H$_4$)$_2$] would also be an excellent alkyne diboration catalyst. This has now been verified, and both the isolated PCy$_3$ compound and the *in situ* generated PPh$_2$(*o*-Tol) system provide high catalytic activity for alkyne diboration at room temperature.

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