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Research paper

The \([\text{Rh(Xantphos)}]^+\) catalyzed hydroboration of diphenylacetylene using trimethylamine-borane

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\textbf{A B S T R A C T}

The rhodium(I) complex \(\text{[Rh}(\text{c}^3-\text{P,O,P-Xantphos})(\text{η}^2-\text{PhC}≡\text{CPh})][\text{BAr}_4]\) \((\text{Ar}^F = 3,5-(\text{CF}_3)_2\text{C}_6\text{H}_4)\) is an effective catalyst for the \(\text{cis}\)-selective hydroboration of the alkyne diphenylacetylene using the amine-borane \(\text{H}_2\text{BNMe}_3\). Detailed mechanistic studies, that include initial rate measurements, full simulation of temporal profiles for a variety of catalyst and substrate concentrations, and speciation experiments, suggest a mechanism that involves initial coordination of alkyne and a saturation kinetics regime for amine-borane binding. The solid-state molecular structure of a model complex that probes the proposed resting state is also reported, \(\text{[Rh}(\text{c}^3-\text{P,O,P-Xantphos})(\text{NMe})(\text{η}^2-\text{PhC}≡\text{CPh})][\text{BAr}_4]\).

\section{1. Introduction}

The transition metal catalyzed hydroboration or diboration of carbon–carbon multiple bonds using three-coordinate boron containing reagents such as HBF\textsubscript{4} or pin\textsubscript{2}B\textsubscript{2} \((\text{cat} = \text{catechol}, \text{pin} = \text{pinacol})\) is an important methodology in organic synthesis as the corresponding organoboranes \([1–3]\), can be functionalized to give products useful in organic and materials synthesis. Examples of hydroboration strategies that use stable four-coordinate boranes are less well established, e.g. \(\text{H}_2\text{B}\text{Li} \, (\text{L} = \text{Lewis base})\) \([4,5]\), despite the potential advantages in air-stability and handling that such reagents offer compared to three coordinate borane reagents, or more traditional reagents such as \(\text{H}_2\text{BH}_3\text{THF}\).

We have previously reported that \(\text{[Rh}(\text{c}^3-\text{P,Xantphos})(\text{η}^2-\text{PhB}(\text{NMe}_3)\text{CH}_2\text{CH}_2\text{Bu})][\text{BAr}_4]\) \((\text{Ar}^F = 4,5-(\text{diphenylphosphino})\text{-9,9-dimethylxanthene}, \text{Ar}^F = 3,5-(\text{CF}_3)_2\text{C}_6\text{H}_4\) Scheme 1) is an effective catalyst for the hydroboration of the hindered terminal alkene tert-butyl ethene \((\text{TBE})\) using \(\text{H}_2\text{BNMe}_3\) to give the linear \((\text{anti}-\text{Marovnikov})\) alkylborane \(\text{H}_2\text{B}(\text{CH}_2\text{CH}_2\text{Bu})\text{NMe}_3\) \([6]\). Mechanistic studies showed that this transformation was competitive with a slower alkene-promoted \(\text{B}−\text{B}\) dehydrogenative homocoupling to give a strongly-bound, diborane \((\text{H}_2\text{B}_2\text{NMe}_3)\) complex, \(\text{[Rh}(\text{c}^3-\text{P-Xantphos})(\text{L},\text{η}^2-\text{PhB}(\text{NMe}_3)_2)][\text{BAr}_4]\) \((\text{L} = \text{THF})\) \([7]\); while binding of the hydroboration product also inhibits catalysis. We now report an extension of this strategy to report the \(\text{cis}\)-selective hydroboration of the internal alkene, \(\text{PhC}≡\text{CPh}\), using \(\text{H}_2\text{BNMe}_3\) to give the vinyl borane, \(\text{PhCH}≡\text{CPh} \, (\text{BH}_2\text{NMe}_3)\), that is promoted by the readily accessible pre-catalyst \(\text{[Rh}(\text{c}^3-\text{P,O,P-Xantphos})(\text{η}^2-\text{PhC}≡\text{CPh})][\text{BAr}_4]\). 1. Complex 1 is also an active catalyst for the carbothiolation of terminal and internal alkyne \([8,9]\). A catalytic cycle is proposed based upon kinetic, resting state and isotope-labelling experiments, in conjunction with the synthesis and characterization of model complexes.

\section{2. Results and discussion}

The pre-catalyst complex 1 was prepared as reported previously \([8]\). Initial screening experiments, at 0.5 mol\% catalyst loading, showed that this was an effective – if slow (48 h, unoptimized) – catalyst for the \(\text{cis}\)-hydroboration of diphenylacetylene to give the vinyl base-stabilized borane \(\text{PhCH}≡\text{CPh} \, (\text{BH}_2\text{NMe}_3)\), 2, in greater than 95% spectroscopic yield, and 88% isolated yield \((0.15\text{~g})\) as colorless crystalline material, \(\text{Fig. 1}\). The identity of 2 was ultimately resolved by a single crystal X-ray diffraction study that showed it to be the product of overall \(\text{cis}\)-addition of \(\text{H}_2\text{BNMe}_3\) across the triple bond \((\text{C}−\text{C}, 1.344(2), \text{C}−\text{B} 1.614(2) \text{~ Å})\). In the \(^1\text{H} \text{NMR}\) spectrum of 2 the vinyl signal is observed at \(δ = 6.80\) \((1 \text{~ H relative integral})\) and the NMe\(_3\) groups at \(δ = 2.42\) \(\text{(9H)}\), the former characteristic of the vinyl group of hydroborated diphenylacetylene \([10,11]\). These two signals also show a strong correlation in the NOE difference spectrum, consistent with \(\text{cis}\)-addition. In the \(^{11}\text{B}\) \((\text{H})\) NMR spectrum a single resonance is observed at \(δ = 0.9\), shifted 8.2 ppm downfield from \(\text{H}_2\text{BNMe}_3\), and is consistent with a four coordinate \(^{11}\text{B}\) environment.

With the identity of the product of catalysis identified as the \(\text{cis}\)-...
hydroborated product, the details of the mechanism were probed by combined kinetic and speciation studies. The 48 h reaction time to completion at 0.5 mol% of \( \text{I} \) was not suitable for kinetic studies using in situ NMR spectroscopic monitoring, so higher catalyst loadings were used (1–4 mol%). These conditions resulted in acceptable times to full completion up to 3 h at 298 K at 1 mol%. Fig. 2A shows a representative set of time/concentration data for catalysis when \( \text{[I]} = 2.5 \text{ mol%} \).

Working at the baseline conditions of \([\text{PhC≡CPh}] = [\text{H}_2\text{BNMMe}_3] = 0.435 \text{ M} \), \( \text{I} = 2.5 \text{ mol%} \), the progress of the reaction was monitored by \(^{1}\text{H} \) NMR spectroscopy by following the integrals of \( \text{H}_2\text{BNMMe}_3 \) and product \( \text{2} \), using \([\text{BAr}_2^\text{F}]^- \) (from 1) as an internal standard. Under these conditions the reaction followed a zero-order profile for the first \( \sim 75\% \) of reaction, with some curvature (deceleration) at higher conversions. Initial rate measurements over the first 5% of turnover, in which concentrations of catalyst and substrates were independently varied, reveals that turnover is close to zero order in \( \text{H}_2\text{BNMMe}_3 \). The data suggest that at lower concentrations of \([\text{H}_2\text{BNMMe}_3]\) the initial rate drops slightly (Fig. 2B) — which may be related to the curvature seen at higher conversions, although the deviation from zero order is small. No such attenuation is observed on variation of \( \text{PhC≡CPh} \), which shows a zero-order relationship (Fig. 2C).

The reaction is first order in precatalyst, \( \text{I} \) (D). A KIE measurement using the initial rate method performed on Fig. 2 independent samples using \( \text{D}_2\text{BNMMe}_3 \) (baseline concentration conditions) results in \( k_0/ k_\text{D} = 1.4(1) \). No product inhibition is observed, as addition of 10 or 20 equivalents of 2 to catalysis mixtures resulted in no appreciable change in temporal profile or overall conversion (Fig. 2A inset).

Overall these data suggest a saturation-kinetics model for \( \text{H}_2\text{BNMMe}_3 \) binding, which follows on from an essentially irreversible binding of alkyne and precedes the turnover-limiting step. Using these experimental observations, a holistic model was developed using COPASI [12], that combined multiple data sets where the concentrations of the reaction partners were varied. In the absence of specific measured rate constants this model only provides overall relative rates, rather than absolute values, and some consecutive individual steps were telescoped for simplicity and to avoid over-parametrization. Nevertheless, the simulation recreates the experimental data well (Fig. 3), and the model is consistent with: (i) strong — but reversible — binding of \( \text{H}_2\text{BNMMe}_3 \) to \( \text{I} \), (ii) a turnover limiting step that produces product \( \text{2} \) bound to the metal center and (iii) fast displacement of \( \text{2} \) by alkyne to reform \( \text{I} \). The model predicts the steps involved in the turnover limiting process to have \( k_2 = 0.061(2) \text{ s}^{-1} \), which compares favorably with the value that can be estimated from initial rate studies that give \( k_2(\text{obs}) = 0.052(4) \text{ s}^{-1} \), which is calculated assuming an upper bound of \([\text{I} \cdot \text{H}_2\text{BNMMe}_3] \lesssim [\text{Rh}]_{\text{tot}} \), an assumption which is not unreasonable given the saturation kinetics observed.

By following the reaction using \(^{31}\text{P}^{(1}\text{H} \) NMR spectroscopy (2.5 mol \% \( \text{I} \), \([\text{H}_2\text{BNMMe}_3] = [\text{PhC≡CPh}], 1.2-\text{F}_2\text{C}_6\text{H}_4 \)) the resting state was observed, as a broad doublet at \( 37.29 \text{ ppm} \) \((\text{J} \text{RhP}) = 114 \text{ Hz} \), that is distinct from \( \text{I} \) \((\text{J} 20.4, \text{J} \text{RhP}) = 125 \text{ Hz} \). The \(^{1}\text{B} \) NMR spectrum shows a very broad signal that is essentially unshifted from free \( \text{H}_2\text{BNMMe}_3 \). These data are consistent with \( \text{H}_2\text{BNMMe}_3 \) binding to \( \text{I} \), but in rapid equilibrium with unbound amine-borane. Evidence for a \( \eta^3 \)-bound amine-borane comes from combination of \( \text{I} \) and 2 equivalents of \( \text{H}_2\text{BNMMe}_3 \) in \( \text{CD}_2\text{Cl}_2 \) measured at \( -60^\circ \text{C} \). In this experiment a broad signal is observed at \( 0.76 \text{ ppm} \) \((\text{J} \text{H}_2\text{BNMMe}_3, \text{J} 2.27 \text{ Hz}) \) that sharpens in the \(^{1}\text{B}^\text{(H)} \) NMR spectrum, suggestive of a time averaged \( \text{Rh} \cdot \text{H}_2\text{B} \) interaction. We thus propose \([\text{Rh}(\eta^3-\text{P},\text{O},\text{P},\text{Xantphos})(\eta^1-\text{H}_2\text{BNMMe}_3)(\eta^2-\text{PhC≡CPh})][\text{BAR}_2^\text{F}] \) 3, as the resting state (Scheme 2) in which amine—borane and alkyne are bound with the metal center. As formulated
complex 3 is an example of an 18-electron Rh(I) center with Rh...H–B interactions, for which there is precedent [13–15]. At the end of catalysis, the final organometallic product observed is dependent on the ratio of substrates. When alkylene is in excess, or there is a 1:1 ratio, complex 1 is observed. When H₂B-NMe₃ is in excess (i.e. 150 mol%), trace D (Fig. 3) the homocoupled product, H, is the final organometallic product. As this is not a competent catalyst, but catalysis goes to completion under these conditions, we suggest H is formed only when alkylene is consumed, post productive turnover.

Further evidence for complex 3 being the resting state comes from addition of MeCN to the catalysis mixture at the early stages of turnover (10% conversion). ³¹P(¹H) NMR spectroscopy showed the immediate and quantitative formation of a new organometallic product [δ 27.4, J (RhB) = 115 Hz], while ¹H NMR spectroscopy showed that the signal due to H₂B-NMe₃ had sharpened, suggesting displacement by MeCN. This ³¹P chemical shift is very similar to that observed for the resting state complex 3. This new complex was a poor catalyst for the hydroboration reaction, promoting only 50% conversion after 24 h, demonstrating that MeCN largely outcompetes the H₂B-NMe₃ for binding to the metal center. The identity of this new species was resolved by a single crystal X-ray diffraction study on independently synthesized material, that comes from addition of MeCN to 1. Fig. 4 shows the solid-state of the cation, which is a five coordinate Rh(I) complex [Rh(κ³-P₂O₂N-Xanthphos)(NCH)(η²-PhC≡CPh)][BAR₄]. 4. The coordination geometry around the metal center is pseudo trigonal bipyramidal with the two phosphine groups in axial positions. The NCMe ligand has not displaced the alkylene, consistent with the kinetic model, and binds in the equatorial plane. Interestingly these ¹H NMR data show a single Xanthos environment at 298 K, that suggests a rapid, but reversible, decoordination of the MeCN to the metal center to afford time resolved C₂ᵥ symmetry. Such behavior is mirrored in the NMR data observed for 3 and the kinetic model (Fig. 3).

We propose a catalytic cycle as shown in Scheme 3. Addition of H₂B-NMe₃ to 1 reversibly forms 3, with the equilibrium biased towards the adduct and away from 1. B–H activation to form a boryl hydride, A, is followed by turnover limiting irreversible [16] alkyne insertion into the Rh–H bond to give the vinylborane species B. While this is consistent with the measured KIE of 1.4 [17], we cannot discount an alternative rapid and reversible [6,18] B–H activation followed by turnover limiting irreversible alkyne insertion into the Rh–B bond [19]. Equilibrium isotope effects would certainly be operating in both these processes, making a definitive interpretation of the measured KIE more difficult [20,21]. While the precise nature of the steps involved in the turnover limiting manifold (i.e. 3 to B) remain to be delineated, subsequent reductive coupling forms C, in which the product, 2, can then be rapidly displaced by alkylene to reform 1. As addition of 2 to 1 does not result in the observation of a new species, and there is no product inhibition, we propose this process is fast and essentially irreversible.

In conclusion we report a cis-hydroboronation of diphenylacetylene using H₂B-NMe₃ to provide the vinyl borane, PhCH = CPh(BH₂NMe₃). A detailed kinetics analysis reveals the essential elements of the mechanism, that follows a saturation kinetics model for amine–borane addition. While the current substrate scope is limited to one alkyne (diphenylacetylene), the elementary steps revealed are relevant to other process involving amine–borane activation, such as dehydropolymerization [22], and we suggest our observations may be helpful in helping delineate these significantly more complex processes.

3. Experimental

All manipulations, unless otherwise stated, were performed under an atmosphere of argon using standard Schlenk and glovebox techniques. Glassware was oven dried at 130 °C overnight and flamed under vacuum prior to use. CH₂Cl₂, MeCN, Et₂O, pentane and hexane were dried using a Grubbs-type solvent purification system (MBraun SPS-800) and degassed by successive freeze-pump-thaw cycles. 1,2-C₆H₄F₂.
(pretreated with alumina) and Cd₂Cl₂ were dried over CaH₂, vacuum distilled and stored over 3 Å molecular sieves. NMR spectra were recorded on Varian Unity 500 MHz, Bruker AVIII500, Bruker DPX250 or Bruker AVIII400 spectrometers at room temperature, unless otherwise stated. Residual proto solvent was used as a reference for ¹H NMR spectra in deuterated solvent samples. For ¹,²-CCl₃H₄, were referenced externally against 85% H₃PO₄ and BF₃·OEt₂, respectively. Chemical shifts are quoted in ppm. Coupling constants are quoted in Hz. Electrospray ionization mass spectrometry (ESI-MS) data were recorded using Bruker MicrOTOF instrument directly connected to a modified Innovative Technology glovebox [23]. Samples were diluted to a concentration of approximately 1 x 10⁻⁶ M before analysis. Elemental microanalyses were performed by Stephen Boyer at London Metropolitan University (UK). The starting materials D₂B·NMe₃ [24], and mer-[Rh(κ²-P,Ο-P,Xanthos)(η⁶-PhC≡CPh)][BAR₅] [1] [8], were prepared by literature methods or variations thereof. H₂B·NMe₃ was purchased from Boron Specialties and sublimed twice prior to use. Crystallographic data have been deposited with the CCDC as 1887954 (version 2018/3) in combination with the Cambridge Crystallographic Data Centre via http://optimized.ccdc.cam.ac.uk/data_request/cif.

Synthesis of 2: To a J. Young’s ampoule containing trimethylamine-borane H₂B·NMe₃ (50.0 mg, 0.685 mmol, 1 equiv), diphenylacetylene (134.3 mg, 0.754 mmol, 1.1 equiv) and 1 (5.90 mg, 3.43 µmol, 0.5 mol %) was added 1 mL 1,2-C₄H₈F₂ and the resulting solution was stirred for 2 d at room temperature. The solvent was removed in vacuo resulting in an oil which was triturated with pentane to give a colorless solid. The solid was washed with further pentane and recrystallized from Et₂O giving PhCH = CPh(BH₂NMe₃) as colorless crystals. (Yield = 88%, 151 mg).

¹H NMR (400 MHz, CD₂Cl₂, r.t., ppm): δ = 7.24–7.15 (m, 4H, Ar-H), 7.12–6.95 (m, 4H, Ar-H), 6.95–6.89 (m, 2H, Ar-H), 6.80 (s, 1H), 2.42 (s, 9H, NMe₃), 2.40 (br s, BH₂, overlapping).

¹³C(H) NMR (100 MHz, CD₂Cl₂, r.t., ppm): δ = 148.5 (CₛAr), 140.4 (C₋Ar), 136.7 (C(Ph2)-H), 129.6 (C₆Ar-H), 129.1 (CₛAr-H), 128.4 (CₛAr-H), 127.8 (C₋Ar-H), 125.6 (CₛAr-H), 125.1 (CₛAr-H), 52.7 (NMe₃) (one C not observed, likely that attached to B).

¹¹B(H) NMR (128 MHz, CD₂Cl₂, r.t., ppm): δ = 0.86. ESI-MS (CH₂Cl₂) [C₁₇H₁₃BNH] + m/z = 252.1919 (calc. 252.1918).

Microanalysis C₁₇H₁₃BN (251.18) requires: C 81.29, H 8.83, N 5.58; found: 81.17, H 8.96, N 5.59.

Synthesis of 4: To a J. Young’s crystallization tube containing 1 (30.0 mg, 0.0174 mmol, 1 equiv) was added 0.5 mL of CD₂Cl₂ at ~78 °C (dry ice/acetone). MeCN (9 µL, 0.174 mmol, 10 equiv) was added, the reaction mixture was warmed up to room temperature, layered with pentane and stored at room temperature for 3 d giving [[Rh(κ²-P,O,P-Xanthos)(NMe₃)(η⁶-PhC≡CPh)][BAR₅]] as red crystals. (Yield = 78%, 24 mg).

¹H NMR (400 MHz, CD₂Cl₂, r.t., ppm): δ = 7.89 (dd, J₁ = 7.7 Hz, J₂ = 1.5 Hz, 2H, Ar – H), 7.75–7.70 (m, 8H, BAR₃), 7.55 (br s, 4H, BAR₄), 7.42 (t, J = 7.7 Hz, 2H, Ar–H), 7.39–7.31 (m, 6H, Ar–H), 7.26 (t, J = 7.3 Hz, 4H, Ar–H), 7.22–7.07 (m, 22H, Ar–H), 1.89 (s, 6H, Xanthos CH₃), 1.44 (br s, 3H, H₂CCN).

¹³B(H) NMR (128 MHz, CD₂Cl₂, r.t., ppm): δ = −6.6 (s, BAR₃), ³¹P(H) NMR (162 MHz, CD₂Cl₂, r.t., ppm): δ = 27.4 (d, J₁BAR₃ = 115 Hz).

ESI-MS (CH₂Cl₂) Positive Ion [C₅₅H₄₅N₂OP₂Rh]⁺ m/z = 900.21 (calc. 900.20).

Microanalysis C₅₅H₄₅BF₂NOP₂Rh (1764.04) requires: C 59.24, H 3.26, N 0.79; found: 59.22, H 3.37, N 0.80.

3.1. General procedure for kinetic measurements

In a J. Young’s high-pressure NMR tube diphenylacetylene, H₂B·NMe₃ and 1 were combined and the tube was sealed. To a second J. Young’s high-pressure NMR tube 0.4 mL 1,2-C₄H₈F₂ was added and the tube was sealed. Using a J. Young’s glass bridge, the solvent was vacuum-transferred from one NMR tube to the other. The NMR spectrometer was set up for the kinetic measurements and the NMR tube was thawed, shaken thoroughly and immediately put in the NMR spectrometer. The reaction progress was monitored by ¹¹B NMR spectroscopy.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.sci.2019.03.032.

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