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Lithium-Aluminate-Catalyzed Hydrophosphination Applications

Victoria A. Pollard, Allan Young, Ross McLellan, Alan R. Kennedy, Tell Tuttle, and Robert E. Mulvey*

Dedication ((optional))

Abstract: Synthesized, isolated, and characterized by X-ray crystallography and NMR spectroscopic studies, lithium phosphidoaluminate $iBu_3AlPPh_2Li(THF)_3$ has been tested as a catalyst for hydrophosphination of alkynes, alkenes, and carbodiimides. Based on the collective evidence of stoichiometric reactions, NMR monitoring studies, kinetic analysis, and DFT calculations, a mechanism involving deprotonation, alkyne insertion and protonolysis is proposed for the $[iBu_3AlHLi]_2$ aluminate-catalyzed hydrophosphination of alkynes with diphenylphosphine. This study enhances further the development of transition metal free, atom economical homogeneous catalysis using common sustainable main group metals.

Introduction

Phosphines are utilized in a range of applications spanning agriculture, medicinal chemistry, and organocatalysis, while their ubiquity as ligands in transition metal catalysis is legend.[1] Hydrophosphination, adding a P–H bond across an unsaturated C–E (E = e.g., C, N) bond, offers atom economy to preparing phosphines.[2] Many transition (e.g., based on Fe, Ni, Pd and Zr) [2b, 2c, 3] and rare earth (e.g., La, Sm, and Yb)[3] metal catalysts have been used for hydrophosphination, while solvent and catalyst-free hydrophosphinations can also be thermally induced under certain circumstances.[4] Developing catalysts based on main group metals is currently trending in homogeneous catalysis including hydrophosphination.[5] K, Ca and Mg complexes have been reported as hydrophosphination catalysts for alkene, alkyne and carbodiimide substrates with diphenyl phosphine ($HPPh_2$), forming alkyl phosphines, vinyl phosphines and phosphaguanidines, respectively.[3a, 3b, 6] Tin complexes are also capable of catalysing hydrophosphination reactions,[2c, 7] though $Cp^*_2SnCl_2$ (Cp^* = pentamethylcyclopentadienyl) required an H_2 atmosphere to inhibit competing phosphine dehydrocoupling of $HPPh_2$.[7b, 8] Attractive industrially due to its high natural abundance and low toxicity, aluminium is gaining prominence in this main group catalysis enlightenment.[9] Work by Roesky, Wright, Cowley/Thomas, Harder, Stephan, and others, have successfully employed Al-based catalysts in hydroboration and hydrogenation.[10] Uhl has also demonstrated that a P/Al geminal FLP can stoichiometrically hydrophosphinate heteroatom substituted nitriles, generating imines incorporated into 5-atom AlCPCN heterocycles.[11] Examples also exist of Al-catalyzed hydrophosphonylation (using P(V) reagents)[12] However, to our knowledge no examples exist of Al-catalyzed hydrophosphination (using P(III) reagents) of alkynes, alkenes or carbodiimides.

Bimetallic ate complexes, which can synergistically enhance stoichiometric reactivities over their neutral monometallic components, are a core theme of our research.[13] Recently expanding this work into the catalytic regime, we used lithium aluminates as catalysts for hydroboration of aldehydes, ketones, imines and acetylenes.[14] In general, the charged bimetallic species proved more active catalysts than their neutral monometallic components.[14b] Here, we probe the ability of our most active lithium aluminate, $[iBu_3AlHLi]_2$, **1**, as a catalyst for hydrophosphination of alkynes, alkenes, and carbodiimides.

Results and Discussion

First, we reacted phenylacetylene with $HPPh_2$ and 10 mol% of dimeric $[iBu_3AlHLi]_2$ in C_6D_6 at 70 °C. This reaction gave a very low 5% conversion after 20 h and it was proposed a higher boiling point solvent would be required to allow the catalysis to proceed. Moving to d_8-toluene at 110 °C yielded 72% conversion (1:8 *E*/*Z* ratio, Fig. 1) within 20 h, to the anti-Markovnikov product consistent with *syn* addition of H–P across the C≡C bond. Changing the solvent to polar d_8-THF (65 °C) lowered the *E*/*Z* selectivity to 1:3. We propose that in d_8-THF solution the resulting lithium aluminium phosphide (*vide infra*) exists in an equilibrium, as observed by the presence of three separate distinct signals for the *iso*-butyl ligands in the ^{1}H NMR spectrum. Using CD_2Cl_2 (40 °C) poisoned the catalyst giving no product. Satisfied this system is a capable hydrophosphination catalyst, a range of alkynes were screened (Table 1). Internal alkynes, diphenylacetylene and 1-phenyl-1-propyne reacted faster than terminal alkynes. However, more challenging unactivated alkynes, 1-hexyne and 3-hexyne did not react, in common with other reports of main group catalysed hydrophosphination.[7b]

To gain more insight, a 1:1:3 stoichiometric reaction between $[iBu_3AlHLi]_2$, $HPPh_2$, and THF, completely consumed the aluminate giving a solution that deposited crystals of the lithium aluminium phosphide, $iBu_3AlPPh_2Li(THF)_3$, **2**, (isolated yield, 41%) (Fig. 1a). Phosphidoaluminate **2** results from deprotonation of $HPPh_2$

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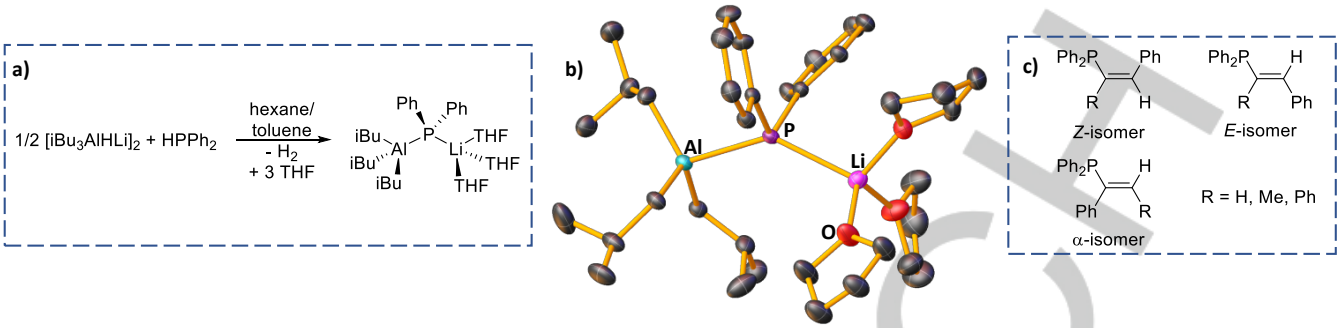

Figure 1. a) Synthesis of $iBu_3AlPPh_2Li(THF)_3$, **2**; **b)** Molecular structure of **2**, H atoms and disordered THF molecules omitted for clarity, thermal ellipsoids drawn at 40% probability; **c)** Depiction of *E*-, *Z*-stereoisomers and α-regioisomers arising from hydrophosphination of alkyne substrates.

by **1**, and importantly, implies this process is the first step in catalytic hydrophosphination. Crystalline **2** (Fig. 1b) is monomeric, with three THF molecules solvating Li. ^{1}H DOSY NMR studies confirm it remains monomeric in d_8-toluene solution.[15] Alternatively, **2** can be made by co-complexing $LiPPh_2$ with iBu_3Al/THF.

Aware that dehydrocoupling can compete with hydrophosphination, a control reaction between $HPPh_2$ and 10 mol% of **2** in d_8-toluene was heated at 110 °C for 20 h. Less than 15% of $HPPh_2$ had undergone dehydrocoupling to form 1,1,2,2–tetraphenyl diphosphine (determined by ^{31}P NMR spectra) signifying that this is unlikely to be a significant problem in this system. Subsequently **2** was tested as a catalyst for hydrophosphination of alkynes, under the previously optimised conditions (10 mol% [Al], d_8-toluene, 110 °C), (Table 1). For phenylacetylene a 95% conversion (1:3 *E*/*Z* ratio) of the anti-Markovnikov product was obtained after 20 h (*cf.* 72% using **1**), albeit with reduced *E*/*Z* stereoselectivity. By contrast, Waterman's tin catalyst $Cp^*_2SnCl_2$ is poorly active for PhC≡CH (10 mol% catalyst, 18 h, 65 °C, 4% yield).[7b] Using **2**, hydrophosphination is much faster with internal alkynes than terminal alkynes, with a 99% yield (10:1 *E*/*Z* ratio) for diphenylacetylene being obtained within just 1 h (**1** takes 5 hours). Similarly, 1-phenyl-1-propyne fully converts to the anti-Markonikov vinyl phosphine product within 1 h. The catalytic activity of **2** with PhC≡CPh compares favourably with the β-diketiminato calcium amide catalyst ^{DIPP}NacNacCa(HMDS)(THF), which required extended reaction times (10 mol% catalyst, 75 °C, 13 h, 94% yield).[6c] However, $[Ca(PPh_2)_2(THF)_4]$ catalytically hydrophosphinated diphenylacetylene after 2 h at room temperature.[6e] Cui used an imino-amidinate ligated Ca catalyst for quantitative hydrophosphination of 1-phenyl-1-propyne after 5 h at 60 °C, using 5 mol% [Ca].[3a]

Adding a catalytic amount (30 mol%) of THF to 10 mol% of **1** resulted in hydrophosphination of diphenylacetylene within the same time as that using pre-formed **2**, suggesting that deaggregation of dimeric **1** by THF is advantageous in catalysis. Again attempted catalysis with unactivated 1-hexyne or 3-hexyne and $HPPh_2$ by **2** proved unsuccessful. Deaggregation aside, the coordination shell surrounding a metal cation can play a key role in modulating the Lewis acidity of the metal, thereby providing a potential route to modify reactivity. Thus, we explored the effect of the Lewis donor on hydrophosphination of PhC≡CPh. A range of Lewis donor additives were added to the hydrophosphination reactions of diphenylacetylene catalysed by **1**. Adding either two equivalents (with respect to the catalyst) of bidentate donor TMEDA (N,N,N',N'-tetramethylethylenediamine) or one equivalent of 12-crown-4 result in quantitative conversions in 1 hour, the same time as when 3 equivalents of THF are used. The molecular structure of the organometallic compound in the presence of polydentate 12-crown-4 was determined *via* X-ray crystallography as the contacted ion pair structure, iBu_3AlPPh_2Li(12-crown-4), with the phosphorus atom bridging the Al and Li centres (see ESI). Unfortunately, due to poor quality data no geometric parameters can be discussed, however the structure provides unequivocal proof of atomic connectivity. The use of isolated *i*Bu_3AlHLi(PMDETA) also results in quantitative product formation within 1 h (tridentate PMDETA = *N,N,N',N''N''*-pentamethyldiethylenetriamine). This complex was crystallographically characterised (Fig. 2), but all organic ligands exhibit significant disorder which precludes a discussion of geometric parameters beyond atomic connectivity.

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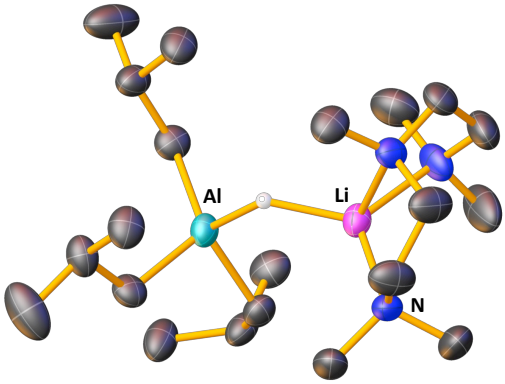
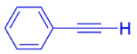
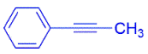
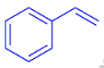
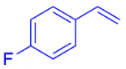
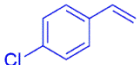
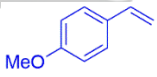
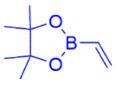
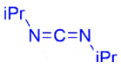
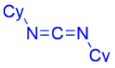


Figure 2. Molecular structure of $iBu_3AlHLi(PMDETA)$. Thermal ellipsoids are drawn at 40% probability, and disordered iBu groups, disordered PMDETA, and hydrogen atoms, except hydride, have been removed for clarity.

Interestingly, the *E*/*Z*-isomer ratio is dependent on the donor used. PMDETA and 12-crown-4 are less selective (*E*/*Z* 2:1; and 5:1 respectively, versus 10:1 with 3 THF), whereas 2 TMEDA donors result in enhanced *E*/*Z*-selectivity of 19:1. Adding one equivalent of bulky tetradentate Me_6-TREN, takes 3 h for quantitative conversion (*E*/*Z* 10:1). Adding two equivalents of bidentate dppe (diphenylphosphinoethane) results in conversion in 5 hours, albeit with good *E*/*Z* selectivity (16:1). Interestingly it appears that when two bidentate donors are added, TMEDA or dppe, marked improvements in selectivity occur. Finally, adding three equivalents of PPh_3 to preformed **2** results in both slower catalysis (1.5 h) and poorer selectivity (*E*/*Z* 4:1) than those observed with the THF variant, indicating the phosphine Lewis donor may inhibit the hydrophosphination process.

Next, the more challenging hydrophosphination of alkenes was examined using **2** (Table 1). Styrene undergoes hydrophosphination in 6 h, at 110 °C, yielding 84% of the anti-Markovnikov product. Halo-substituted styrenes are also tolerated (Table 1, entries e-f). 4-Vinyl anisole undergoes hydrophosphination to the alkyl phosphine product in 87% yield after 20 h at 110 °C. Bulkier substrates such as α-methyl styrene, trans-β-methyl styrene, and the less activated alkene 1-hexene did not undergo hydrophosphination with **2** as the catalyst. Similar failures with both Ca and Sn based catalysts have been noted for these substrates.[6c, 7b] Hydrophosphination of vinyl boronic acid pinacol ester (vinyl Bpin) achieved a 93% yield after 4 h at 110 °C, producing linear phosphine boronic ester $Ph_2P(CH_2)_2Bpin$. To our knowledge this is the first time $Ph_2P(CH_2)_2Bpin$ has been made *via* a hydrophosphination route, since earlier published methods required hydroboration of diphenyl vinyl phosphine.[16]

Table 1. Hydrophosphination of alkynes, alkenes and carbodiimides using **1** – **6** as catalysts.

Alkynes[a]		
a) 	b) 	c) 
Catalyst; yield (%); *E*/*Z*/*α*-isomer ratio; time (h)		
1 72%, 1:8:0, 20 h **2** 95% (78%), 1:3:0, 20 h **3** 86%, 1:3:0, 20 h **4** 72%, 1:8:8, 20 h **5** 62%, 1:12:4, 20 h **6** 62%, 1:12:4, 20 h	**1** 98%, 10:1, 5 h **2** 99% (80%), 10:1, 1 h **3** 98%, 10:3, 3 h	**1** 99%, 1:1:0, 6 h **2** 99% (79%), 1:1:0, 1 h **3** 95%, 1:3:0, 10 h
Alkenes[b]		
d) 	e) 	f) 
1 89%,6 h **2** 84% (60%), 6 h **3** 72%, 6 h	**2** 84%, 20 h	**2** 86%, 18 h
g) 	h) 	
2 87%, 20 h	**2** 93%, 4 h	
Carbodiimides[c]		
i) 	j) 	
2 99% (80%), 0.25 h	**2** 86%, 20 h	

General conditions: 0.6 mmol substrate, 0.5 mmol $HPPh_2$, d_8-toluene. Conversions based against ^1H NMR internal standard hexamethylcyclotrisiloxane. E/Z/α stereoselectivity based on ^{31}P NMR spectra. Selected isolated yields in parenthesis. [a]/[b] 10 mol% [Al] catalyst, 110 °C [c]: 5 mol% [Al] catalyst, RT.

Phosphidoaluminate **2** is also an able catalyst for hydrophosphination of carbodiimides at room temperature. Thus, using 5 mol% catalyst loading (Table 1, entries i-j), diisopropylcarbodiimide is converted fully to the phosphaguanidine product within 15 minutes; while bulkier dicyclohexylcarbodiimide required 20 h, to achieve 86% conversion. Hill reports quantitative yields for diisopropyl– and dicyclohexyl–carbodiimides within 1 h and 4 h,

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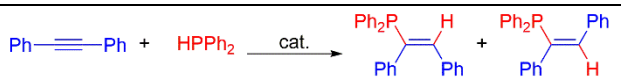
Table 2. Effect of Lewis donor upon hydrophosphination catalysis of diphenylacetylene.



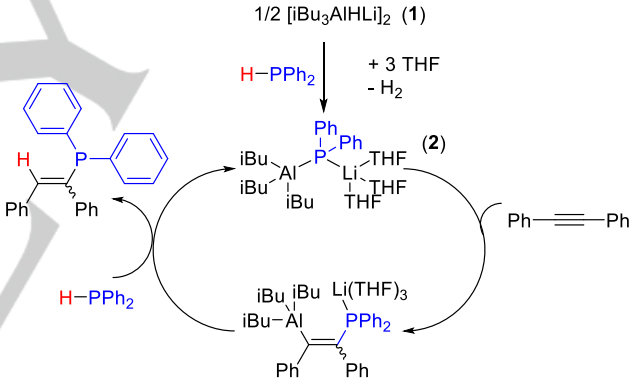
Lewis donor additive	Time (h)	Yield(%) / (*E*:*Z* ratio)
None [*i*Bu$_3$AlHLi]$_2$, **1**	5	98 / 10:1
1 + 3 equiv. THF	1	99 / 10:1
*i*Bu$_3$AlHLi(PMDETA)	1	99 / 2:1
1 + 1 equiv. 12-crown-4	1	99 / 5 : 1
1 + 2 equiv. TMEDA	1	99 / 19:1
1 + 1 equiv. Me$_6$-TREN	3	95 / 10:1
1 + 2 equiv. dppe	5	95 / 16:1
*i*Bu$_3$AlPPh$_2$Li(THF)$_3$	1	99 / 10:1
2 + 3 equiv. PPh$_3$	1.5	99 / 4:1

General conditions: 0.6 mmol substrate, 0.5 mmol HPPh$_2$, d$_8$-toluene, 10 mol% [Al] catalyst, 110 °C. Conversions based against ^{1}H NMR internal standard hexamethylcyclotrisiloxane. E/Z/α stereoselectivity based on ^{31}P NMR spectra.

respectively, using 2 mol% Ca(HMDS)$_2$ as catalyst, also at room temperature. Significantly longer reaction times were seen when using ^{DIPP}NacNacCa(HMDS)(THF) as a catalyst (1.5 mol%) (iPr, 6 h, 99%: Cy, 28 h, 85%).[6d] KHMDS is also found to be a good catalyst for carbodiimides requiring low catalyst loadings and short reaction times,[6a] while a sodium magnesiate also catalyses hydrophosphination of carbodiimides.[6f]

Attempting to pinpoint the active catalyst, four compounds LiPPh$_2$ (**3**), iBu$_3$Al (**4**), iBu$_2$AlH (**5**) and iBu$_2$AlPPh$_2$ (**6**),[17] were screened for catalytic viability using PhC≡CH as a model substrate (Table 1). Using LiPPh$_2$ as a catalyst yields 86% conversion to the vinyl phosphine after 20 h, with anti-Markovnikov regioselectivity, similar to that of **2**. Compounds **4**-**6** afford different product regio- and stereo-selectivities as well as lower yields for PhC≡CH hydrophosphination. Interestingly when **4** is used as catalyst (72%; 1:8:8 *E/Z/α*) the major isomer products are the *Z*- anti-Markovnikov isomer, and equally the Markovnikov [*α* – isomer; Ph(Ph$_2$P)C=CH$_2$]. In contrast, **2** does not give any appreciable *α*–isomer, suggesting **2** is not disproportionating in solution at high temperature into LiPPh$_2$ and iBu$_3$Al. In order to ascertain whether LiPPh$_2$ is implicated in the catalytic profile we conducted another stoichiometric reaction (see ESI). Monitoring reaction of **2** and PhC≡CPh, in d_8-toluene, by ^{31}P NMR shows that after 2 h at 110 °C full consumption of **2** occurs with concomitant growth of two new signals at 3.4 and -16.5 ppm. Unable to isolate these species despite several attempts, we tentatively assign them as two isomers resulting from insertion of diphenylacetylene into **2**. Subsequent addition of HPPh$_2$ and further heating at 110 °C allows for product formation [8.9 ppm (*E*-isomer) and -7.3 ppm (*Z*-isomer)] and regeneration of **2** (-49.3 ppm). We rationalise the intermediate (at 3.4 ppm) reacts onwards to form the *E*-stereoisomer as it is consumed faster than the other intermediate. Significantly there are no resonances corresponding to LiPPh$_2$ in the spectrum (-52 ppm) further reinforcing the view that **2** is the catalytically active species. We propose a catalytic cycle (Scheme 1) that begins by deprotonation of HPPh$_2$ by [iBu$_3$AlHLi]$_2$, releasing H$_2$ and forming compound **2**. Next, a substrate molecule inserts into the Al–P bond. Subsequent protonolysis by a second equivalent of HPPh$_2$ accesses the hydrophosphinated product whilst regenerating the active catalytic species **2**.

Since after the facile room temperature deprotonation step, alkyne insertion and protonolysis are the other key steps, we performed a deuterium labelling study to investigate the cycle further. Catalytic hydrophosphination between PhC≡CPh and DPPh$_2$ favoured formation of the *E*-stereoisomer and deuterium was incorporated into the vinyl



Scheme 1. Proposed reaction mechanism for hydrophosphination of diphenylacetylene by pre-catalyst **1**, showing formation of active species **2**.

phosphine product, Ph(Ph$_2$P)C=C(D)Ph, as confirmed by ^{2}H NMR spectra and GC-MS (see ESI). Also, in a stoichiometric reaction between [iBu$_3$AlHLi]$_2$ and DPPh$_2$, HD was detected in the ^{1}H NMR spectrum (triplet at 4.45 ppm, ^{1}J = 42.8 Hz), confirming the initial deprotonation step.

A kinetic isotope effect experiment (KIE) was conducted for hydrophosphination of diphenylacetylene by recording the reaction profile in duplicate for HPPh$_2$ and DPPh$_2$ at 100 °C, in d$_8$-toluene, with 10 mol% of **2**. By monitoring the consumption rate of phosphine by ^{31}P NMR, rates were obtained, and in each case the overall reaction rate is pseudo–first order. From these rates a KIE of 1.38 ± 0.13 was determined (see ESI). This is a small value, compared with other literature reports, and suggest that cleavage of the

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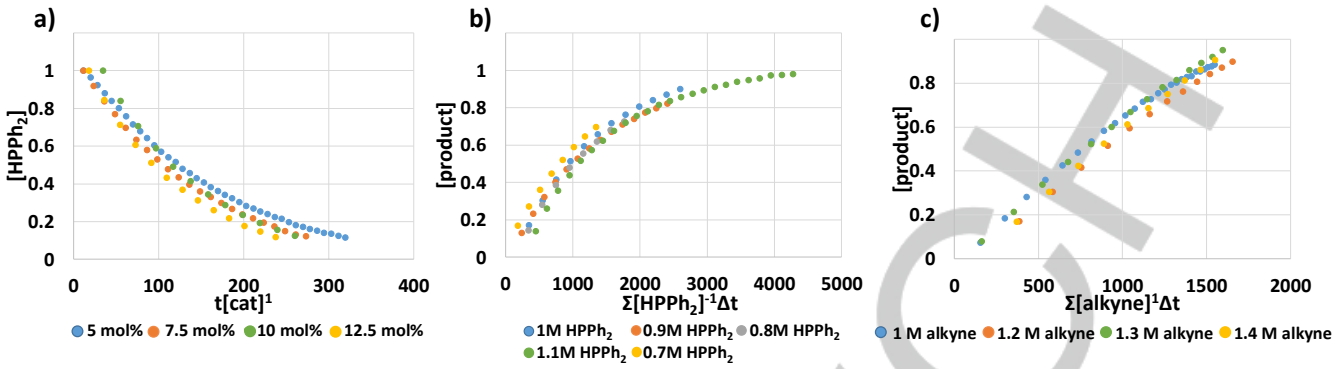

Figure 3. Variable Time Normalisation Analysis (VTNA) plots illustrating the order in a) catalyst (first order); b) phosphine (inverse first order); c) diphenylacetylene (first order).

P–H bond is only involved to a minor extent in the rate determining step.[7b] This also indicates that alkyne insertion into **2** is rate determining, which given the rather congested structure of **2** and bulky nature of the alkyne is unsurprising.

Next, we conducted a kinetic analysis of the reaction using the Variable Time Normalisation Analysis (VTNA) method reported by Burés, allowing us to obtain valuable mechanistic detail under synthetically relevant conditions to three half-lives (see Fig. 3 and ESI).[18] The reaction order with respect to [catalyst] was determined by conducting reactions using different catalyst concentrations, while keeping [alkyne] and [phosphine] constant. These data showed the reaction rate increases with increasing [catalyst], and that the order in catalyst is 1. This situation is consistent with the reaction proceeding *via* a monomeric rate determining step during the reaction. Variation of [phosphine] under synthetically relevant conditions revealed that increasing concentration of phosphine inhibits the reaction, giving a phosphine order of -1. This inhibition likely results from pre-coordination of the phosphine, blocking off the alkyne for insertion. Also, we have already established that bulky mono- and bidentate phosphines slow down reactivity in our Lewis donor study (*vide supra*). Lastly, variation of [alkyne] revealed a first order dependence in [alkyne], indicating that the alkyne is involved in the rate limiting step.

Finally, in order to reinforce our experimental insight, we turned to DFT calculations. Run on the full system with the internal alkyne, diphenylacetylene, used as the model substrate, the calculations were performed at the B3LYP-D3/[19] 6-311G(d,p)[20] level of theory employing a continuum solvent with the dielectric constant of toluene within the IEFPCM model.[21] The relative stability of the formation of **2** from $[iBu_3AlHLi]_2$ with 2 $HPPh_2$ and 6 THF molecules was initially investigated. Formation of the catalyst (**2**) is thermodynamically favourable despite the entropic penalty associated with THF coordination, with a calculated ΔG = -63.8 kcal/mol (ΔH = -130.8 kcal/mol). The activation barrier for the formation of the catalyst was challenging to isolate as a result of the complex potential energy surface associated with the large dimer species. However, a bond scan along the coordinate associated with the formation of H_2 provided an indicative barrier (ΔE^*) of ~38 kcal/mol, which would be achievable under the reaction conditions and lead irreversibly to **2** given the exothermic nature of this step. In contrast to the induction step, the first step in the catalytic cycle (adding diphenylacetylene to **2**) is mildly endergonic for both the *E* and *Z* isomers of the intermediate shown in Scheme 1. However, the *E* isomer is more stable in the intermediate state of the reaction (ΔG = 6.9 kcal/mol), with the *Z*-isomer (ΔG = 8.3 kcal/mol) being further destabilised by 1.4 kcal/mol, relative to the *E*-isomer. Finally, generation of the product and reformation of the catalytic species occurs in an exergonic reaction. In this step, the formation of the *Z*-isomer (ΔG = -25.3 kcal/mol) is favoured over the *E*-isomer (ΔG = -20.4 kcal/mol). The reversal of the relative stabilities of the isomers in the intermediate state versus the product state suggests that the formation of the intermediate is deterministic for the final product distribution, which favours the experimentally determined *E*-isomer. The rate-limiting step for the reaction could not be located as the calculation of transition states proved elusive for these bulky compounds. However, the relative stabilities of the intermediates and products determined for this pathway indicate that the mechanism proposed is achievable under the reaction conditions employed.

Conclusion

Previously lithium aluminates have been shown to be active catalysts for hydroboration of aldehydes, ketones, imines and acetylenes. This new study extends the catalytic chemistry of these bimetallic main group compounds by reporting the first example of Al-catalysed hydrophosphination of alkynes, alkenes

and carbodiimides, using the lithium aluminate (pre)catalyst $[iBu_3AlHLi]_2$. A mechanism is proposed for the alkyne catalysis, elucidated by stoichiometric reactions, thought to proceed *via* formation of the crystallographically defined lithium aluminium phosphide, $iBu_3AlPPh_2Li(THF)_3$, **2**, followed by insertion of the alkyne into the Al-P bond, then protonolysis of a second equivalent of the phosphine to generate the vinylphosphine product and regenerate the catalyst. While intuitively the formation of an anionic aluminium centre saturated by four anionic ligands as in an aluminate might be expected to have insufficient Lewis acidity to engage in hydrophosphination processes, it is clear from the different results obtained using a number of Lewis donor solvent molecules that the presence of the lithium helps to circumvent this apparent handicap so pointing to bimetallic synergistic behaviour.

Experimental Section

Full experimental characterisation and synthetic procedures are described in the supporting information.

Synthesis of $iBu_3AlPPh_2Li(THF)_3$, 2: method a) To a stirred solution of $[iBu_3AlHLi]_2$ (0.412 g; 1 mmol) in hexane (10 mL) was added $HPPh_2$ (0.34 mL; 2 mmol) and the reaction stirred 1 h. THF (0.5 mL; 6 mmol) was added then the volatiles were removed. The residue was taken up in hexane (5 mL) and toluene (1 mL). Subsequent cooling to – 30 °C yielded the desired product as pale-yellow crystals. Crystalline yield 0.494 g; 0.82 mmol; 41 %. **method b)** To a stirred solution of $HPPh_2$ (0.17 mL; 1 mmol) in hexane (5 mL) was added dropwise nBuLi (0.63 mL; 1.6 M/hexane; 1 mmol) and the resulting bright yellow suspension stirred for 1 h. Addition of iBu_3Al (1 mL; 1 M/hexane; 1 mmol) generated a clear pale-yellow solution, which was stirred for 1 h. THF (0.3 mL; 3 mmol) was added and the pale-yellow solution cooled at – 30 °C overnight. Crystalline yield 0.150 g; 0.25 mmol; 24%. ^{1}H NMR (400.1 MHz, d_8-toluene, 300 K): δ 0.48 (d of d, J = 6.93 Hz, 2.88 Hz, 6H, iBu CH_2); 1.31 (d, J = 6.29 Hz, 18H, iBu CH_3); 1.41 (m, 12H, THF CH_2); 2.26 (m, 3H, iBu CH); 3.44 (m, 12H, THF CH_2); 7.00 (m, 2H [overlapping solvent], Ph); 7.17 (m, 4H [overlapping solvent], Ph); 7.14 (m, 4H, Ph) ppm. ^{31}P NMR (104.2 MHz, d_8-toluene, 300 K): δ - 49.2 ppm. ^{13}C{^{1}H} NMR (151 MHz, d_8-toluene, 300 K): δ 25.4 (THF CH_2); 25.5 + 25.6 (iBu CH_2); 28.3 (iBu CH); 29.5 (iBu CH_3); 68.6 (THF CH_2); 124.9 (Ar C–H); 127.3 (d, J = 6.17 Hz, Ar C–H); 134.0 (d, J = 13.04 Hz, Ar C–H); 144.1 (d, J = 13.08 Hz, ipso Ar) ppm. ^{7}Li NMR (155.5 MHz, d_8-toluene, 300 K): δ 0.21 (s) ppm. ^{27}Al NMR: no signal was observed.

General Catalytic Reaction: The desired catalyst loading was added to 0.5 mL of d_8-toluene solution (unless alternative solvent specified) containing the substrate precursor (0.6 mmol) and $HPPh_2$ (0.5 mmol, 0.09 mL). The reaction mixture was transferred to a sealed J. Young's tap NMR tube and the reaction was regularly monitored by ^{1}H and ^{31}P NMR spectroscopy until the formation of the products was completed as determined by integration versus an internal capillary standard (hexamethylcyclotrisiloxane). For alkynes and alkenes, the hydrophosphination catalysis was performed at 110 °C with 10 mol% [Al] catalyst loading. For carbodiimides the hydrophosphination catalysis was performed at room temperature with 5 mol% [Al] catalyst loading. The yields reported are based on ^{1}H NMR and ^{31}P relative to the internal standard. In all cases, the bulk of the NMR solution can be attributed to either product compounds or starting materials. Isolated yields are provided for example substrates, isolated via either recrystallization methods or column chromatography, as reported in the ESI.

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Keywords: Aluminate • Homogeneous Catalysis • Hydrophosphination • Lithium • Phosphine

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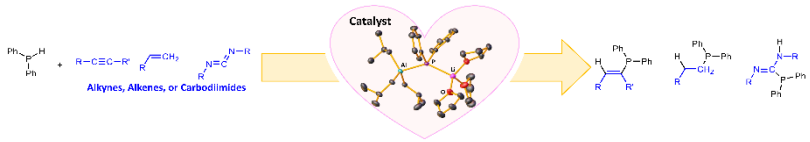

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Alluring Aluminium: catalytic hydrophosphination of unsaturated organic substrates is usually associated with transition metals, but here aluminium is found to be an attractive catalytic partner