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Mechanistic investigation of well-defined cobalt catalyzed formal $E$-selective hydrophosphination of alkynes

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Abstract: A formal $E$-selective hydrophosphination of terminal and internal alkynes catalyzed by well-defined [Co(PMe$_3$)$_4$] (A) complex is achieved under mild conditions in good-to-excellent yield. The reaction does not require any additives and/or external base for an efficient hydrophosphination reaction. The reaction provided excellent scope and good functional tolerance. Detailed spectroscopic analysis (NMR, EPR, and UV-Vis) revealed that the low valent cobalt(0) complex undergoes oxidative addition with diphenylphosphine followed by hydrometallation with alkyne and subsequent reductive elimination led to the expected product. The detailed spectroscopic analyses along with the isotopic labelled experiments facilitate to intercept the active intermediates that are involved in the catalytic cycle, which are detailed. It
was revealed that the suprafacial \textit{(vide infra)} delivery of H and phosphorus to $\pi$-alkynes in \textit{syn}-fashion lead to formal $E$-vinyl phosphine.

\textbf{Introduction}

Addition of X-H bond (where X is a heteroatom) to alkyne is of significant importance due to atom and step economy.\textsuperscript{1,2} This waste free method was widely employed for various hydro-functionalization of unsaturated system, especially C-C double -and triple bonds. Among them, hydrophosphination holds an edge over the others, due to the importance of organophosphorus compounds in antibiotic & anti-tumor activity, metal catalysis and organocatalysis as witnessed in recent times.\textsuperscript{3,4} Hydrophosphination reaction, although, can be promoted by acids, bases, radicals,\textsuperscript{5,6} high temperature and organometallic reagents, these reactions suffer drastically from lower selectivity, poor functional groups tolerance and uncontrolled reactivity. The pioneering works of Gleuck et al. and Pringle et al. showed that these problems could be resolved by employing a metal catalyst.\textsuperscript{7,8} The metal catalyst, often tend to provide better regio and stereo selective control compared to the uncontrollable radical initiated reaction.\textsuperscript{3b} However, the sluggish progress in developing new metal catalyst is perhaps due to the resultant trivalent vinyl phosphine is an excellent coordinating ligand, which is likely to poison the catalyst. Hence, the catalyst development for hydrophosphination reaction of unsaturated C-X (where X = C, O, N, S) bonds was not much explored\textsuperscript{9-18} compared to the other hydro-functionalization reactions such as hydroboration, hydrosilylation and hydroamination, etc.\textsuperscript{16,19-40}

Noble metals such as [Pt], [Pd] and [Ru] based catalysts were predominantly employed to promote the hydrophosphination of unsaturated C-X (where X = C, O, S) bonds.\textsuperscript{41-43} Although conscious efforts were made by several research groups to develop cheap, environment friendly, less toxic metal catalyst (such as alkaline metal complexes), the reactions either require high catalyst loading or suffer from poor regio and stereo selectivity of the
Transition metal catalyst developed for the hydrophosphination reaction, on the other hand, often requires other additives, in particular with the late transition metal catalyst. For example, Oshima and co-workers elegantly demonstrated the use of inexpensive copper and [Co(acac)₂] catalyst for provoking hydrophosphination of alkynes but it requires additional strong base Cs₂CO₃ and a reactive n-BuLi respectively.

Therefore, we sought to unveil a robust, cheap and abundant transition metal catalyst for hydrophosphination reaction. We, herein report an efficient, stereo-selective hydrophosphination of alkynes catalyzed by the well-defined cobalt catalyst [Co(PMe₃)₄] (A) and investigated the mechanism of the reaction to intercept the various intermediates involved in the catalytic cycle. Such mechanistic investigations are extremely scarce in the literature. In this process, we have identified various intermediates involved in the catalytic cycle with the aid of multi-spectroscopic analysis, and isotopic labelling experiments, which are described below.

**Results and Discussion**

This well-defined catalyst A yields formal E-selective hydrophosphination of terminal and internal alkynes exclusively under mild reaction conditions and the reaction proceeds smoothly via syn-addition of P-H bond to the alkyne without any additional bases or organometallic reagent (Scheme 1). We began our investigation by screening various reaction parameters using 0.9 mmol of phenylacetylene and dipheylphosphine with 5 mol% of A. The catalytic reaction was optimized to isolate the product with better yield/stereo selectivity by screening solvent, temperature and catalyst loading. A better stereo selectivity (E) was obtained in low polar solvent compared to the polar solvents presumably due to the sluggish isomerization process of the product in low polar solvent compared to the polar solvent. Such scenario witnessed in the literature, for example solvent polarity dependent stereo selective product obtained for hydrogenation of alkynes.
Scheme 1. Cobalt catalyzed hydrophosphination of alkynes.

It is noticed that, high yield of the product obtained while using toluene as solvent with the catalyst loading of 5 mol% at 80 °C for terminal alkyne (100 °C for internal alkyne; Scheme 1).

Scheme 2. Scope of the terminal alkynes.$^a, b$

$^a$ All reactions were carried out under Argon atmosphere, unless otherwise stated, using 1/PPh2/[Co] in 0.9/0.9/0.045 mmol at 80 °C in toluene (3 mL). $^b$ Isolated yield after sulfidation.
We observed neither dimerization of alkyne nor poisoning of catalyst by the product, which is an added advantage for the efficient product formation. Slightly higher temperature is required as the catalyst is latent and liberation of PMe$_3$ (from A) is effective at higher temperature to access to active catalyst precursor (*vide infra*). Careful analysis of the product indicate that the phosphine and H are added on the same side of the alkyne, which led to formal E-vinyl phosphine (See also tables S1–S4 of ESI).

With the best conditions in hand, we next examined the scope of terminal alkynes (Scheme 2). Electron donating group such as Me, n-pentyl and $t$-Bu substituent at the $p$-position provided good yield with excellent stereo- and regio-selectivity. Further, the crystal structure of 2c unequivocally supports the E-selective product formation (Figure S1, Table S5), where the phosphine and phenyl rings are *trans* to each other. The electronic effect of the substituent (i.e. either electron withdrawing or electron donating groups) on the phenyl ring does not appear to have influence on the progress of the catalytic reaction and hence the yield of product. For example, electron withdrawing groups such as -Br, -F and acetyl-groups as well as electron releasing groups (such as -OMe, -OEt, OC$_5$H$_{11}$) were well tolerated and provide excellent product yield without much variation in yield (2e-2j). The reaction can be further extended to hydrophosphination of fused aromatic ring such as napthyl, anthracyl and pyrenyl substituted acetylene in good yield (2k-2n). To our delight, even heterocycles can be tolerated albeit in moderate yield (2o). Additionally, the reactivity of aliphatic alkynes, namely tetrahydrocyclopentyl propynyl acetylene and 1-pentyne are tested. The expected hydrophosphinated product was isolated in moderate yield (2p-q), but formation of small amount of other regio-isomer ($E'$) is witnessed with the ratio of E:$E'$ ratio = 3:1, see table S6 of ESI). We would like to emphasize that certain transition metal catalyst does not promote hydrophosphination reaction of aliphatic alkyne,$^{12,13}$ those which facilitate smooth progress of
the reaction often lost its regio-selectivity, a common, yet challenging problem known in the literature.\textsuperscript{18,55}

Although hydrophosphination of terminal alkynes reported in the past but their corresponding extension to the internal alkynes often failed to provide the vinyl phosphine or it did not provide any control over stereo-selectivity due to the vinilydene pathway.\textsuperscript{10} Under the optimized experimental conditions (Scheme 1), we further extent the scope of the internal alkynes (Scheme 3). Biaryl acetylene gave moderate isolated yield of the expected product but the product yield is significantly improved (93%; \textit{3c}) when 1-phenylpropyne is used with one single regio-isomer. The regio and stereo selectivity is absolutely preserved in \textit{3a-c}, while in case of electronically biased alkynes \textit{3d} and \textit{3e}, the regio-selectivity is compromised (E:E’ ratio for \textit{3d} (55:45) and \textit{3e} (69:31), see Table S6 of ESI) to some extent. It is witnessed, hitherto, from the literature that promoting hydrophosphination reaction of internal alkynes with hetero-aromatic ring substituent (or electronically biased substrate) is a challenging task. In majority of the cases, reaction does not proceed due to the catalyst poisoning, while in vice-versa scenario, controlling stereo-and regio selectivity of the reaction is a demanding task and an uphill process. The analyses of product (\textit{3c} & \textit{3e}) revealed that the phosphorous atom prefers to add sterically less hindered carbon site of an alkyne.

Intrigued by this reactivity and stereo-selectivity, we have turned our attention to predict the nature of intermediate formed to better understand the mechanism of reaction. We first carried out deuterium labelling experiments using PPh\textsubscript{2}D (78% deuterium enriched) with 4-\textit{t}-butylphenylacetylene to understand the origin of \textit{E}-selective product formation. Careful analysis of \textsuperscript{1}H and \textsuperscript{2}H-NMR revealed that the intensity of doublet of doublet observed at 7.58 ppm drastically reduced in \textsuperscript{1}H NMR with the concomitant appearance of \textsuperscript{2}H signal in \textsuperscript{2}H NMR at the same ppm implies that deuterium atom (of the PPh\textsubscript{2}D) bound to the internal carbon of the alkyne (Figure S2 of ESI). The coupling constant observed in \textsuperscript{1}H NMR signal (observed at
6.91 ppm (dd $^{3}J_{H-H}=16.3$ Hz, $^{3}J_{P-H}=21$ Hz)) and the peak observed at -11.2 ppm in $^{31}$P NMR of the product confirms the syn-addition results in $E$-selective product formation.

Scheme 3. Scope of the internal alkynes.\(^a\).

We next examined the reaction by following stoichiometric experiment between A and PPh\(_2\)H through various spectroscopic techniques. Prior to the experiment, we have characterized the catalyst A through $^{1}$H and $^{31}$P NMR spectra in C\(_6\)D\(_6\) at room temperature. The characteristic peak for methyl protons and $^{31}$P signal observed at 1.26 and -0.14 ppm respectively. This indicates that all the four –PMe\(_3\) groups bound to the cobalt ion are chemically equivalent (Figure S3 of ESI).

Equimolar amount of the A and PPh\(_2\)H were mixed and the reaction was monitored by $^{1}$H NMR spectrum. A broad signal observed at 0.89 ppm is attributed to a metal free –PMe\(_3\) group in solution, which is likely due to ligand (PMe\(_3\)) dissociation from A followed by $\sigma$-coordination of PPh\(_2\)H. This free PMe\(_3\) group $^{31}$P signal was noted at -62.5 ppm (see green trace in Figure 1; assignment of this signal was based on $^{1}$H and $^{31}$P NMR recorded in C\(_6\)D\(_6\) for commercially available 1 M solution of PMe\(_3\); Figure S4). This further undergoes heterolytic cleavage via 2c-3e$^{-}$ transition state to provide a penta coordinated [Co\(^{II}\)(H)(PPh\(_2\))(PMe\(_3\))\(_3\)]
oxidative addition product B, which is also consistent with EPR, UV-Vis spectroscopy (vide infra).

**Figure 1.** $^1$H NMR (panel 1) and $^{31}$P NMR (Panel 2) of [Co(PMe$_3$)$_4$] treated with PPh$_2$H (green trace) in C$_6$D$_6$. The magenta trace corresponds to substrate added into the [Co(PMe$_3$)$_4$]+HPPh$_2$ reaction mixture. In both cases, the spectra recorded in 400 MHz NMR instrument using C$_6$D$_6$ as solvent. Panel 1 inset: The magnified region of $^1$H NMR spectra observed between -16 to -18 ppm ($^6$silicon grease). Panel 2 (*PPPh$_3$ #PPh$_2$-PPh$_2$).

Formation of B was confirmed further by $^1$H NMR where the methyl protons of -PMe$_3$ groups (coupled with phosphorous of PPh$_2$ group) observed at 1.16 ppm as a doublet and the aromatic protons of the –PPh$_2$ group as multiplets between 6.8 to 7.8 ppm which are coordinated to the Co(II) ion in B (Figure 1; also see inset of panel 1)). Its corresponding $^{31}$P signals are observed at 2.68 (-PMe$_3$) and 32.5 (-PPh$_2$) ppm (green trace in Figure 1 (panel 2)). The weak $^1$H NMR signal observed in -16.1 (doublet of quartet) to -17.6 ppm (quintet) is ascribed to the hydride
ion bound to the Co(II) ion (intermediate B & C (vide infra)), which is consistent with the chemical shift value reported in the literature for a Rh-H complex.\textsuperscript{56} Due to highly reactive nature of B, B presumably reacts with another equivalent of HPh\textsubscript{2} (likely via sigma-bond metathesis), results in the formation of coupled product PPh\textsubscript{2}-PPh\textsubscript{2} and [Co\textsuperscript{II} (H)\textsubscript{2}(PMe\textsubscript{3})\textsubscript{4}] (C, Figure 1, see also scheme 4) complex. The catalytic reaction was carefully monitored again through GC-MS analysis, which clearly reveals that neither H\textsubscript{2} gas evolution nor hydrogenated products (such as alkenes and alkanes) observed in the presence of alkyne substrate (data not shown). This reveals that C is robust and does not undergo any further reaction, which is consistent with NMR observation that the peaks correspond to C (both \textsuperscript{1}H and \textsuperscript{31}P) remain unchanged even after the addition of alkyne substrate (vide infra). The other alternative, reductive elimination pathway for the formation of coupled product (PPh\textsubscript{2}-PPh\textsubscript{2}) from B is omitted, because this will results in Co(0) formation which is an EPR active species. However, experimentally, the products obtained upon addition of PPh\textsubscript{2}H with A found to be EPR silent (vide infra), implies that cobalt remains in +2 state. The quintet signature observed at -17.4 ppm for the hydride ion bound to Co(II) (see inset of Figure 1 (panel 1)) is due to the splitting of its \textsuperscript{1}H NMR signal by four chemically equivalent PMe\textsubscript{3} groups bound to Co(II) ion in C. The \textsuperscript{1}H NMR and \textsuperscript{31}P NMR signals of PMe\textsubscript{3} group coordinated with the Co(II) ion in species C observed at 1.25 ppm and -4.4 ppm (Figure 1) respectively. The existence of both B and C species (in the stoichiometric reaction) further indirectly confirmed by the presence of \textsuperscript{31}P signal at -14.9 ppm, which attributed to the formation of Ph\textsubscript{2}P-PPh\textsubscript{2} coupled product. The observed chemical shift value of this coupled product is consistent with the literature reports.\textsuperscript{57} Not only in stoichiometric reaction, but also in the presence of excess PPh\textsubscript{2}H (A:PPh\textsubscript{2}H = 1:20 (as per in the catalytic reaction condition, but in the absence of alkyne substrate)), formation of small amount of Ph\textsubscript{2}P-PPh\textsubscript{2} (~5%) was observed along with B confirmed through \textsuperscript{31}P NMR (Figure S5 of ESI). Nevertheless, we would like to point out that, the coupled product (Ph\textsubscript{2}P-
PPh₂) formation is prevented during the catalytic reaction, as confirmed through ³¹P NMR, in the presence alkyne substrate (Figure S6 of ESI), reveals the highly reactive nature of B.

To prove the origin of hydride in B and C from PPh₂H upon oxidative addition, we have performed the stoichiometric reaction of deuterated diphenyl phosphine (PPh₂D (60% enriched)) with A in C₆H₆. The ²H NMR spectrum of this benzene solution shows a peak at -16.3 ppm, which is exactly the same chemical shift value observed for the hydride bound to Co(II) ion in B, in ¹H NMR (Figure S7 of ESI). On the other hand, we could not observe deuterium incorporation in species C. The isotopic labelled experiments and detailed NMR analysis unambiguously proves that the oxidative addition is the initial step of the catalytic cycle.

Next, we added the alkyne to the in-situ generated species (B and C), subsequent changes were monitored again through ¹H and ³¹P NMR spectra (Figure 1, magenta trace). The ³¹P signal (2.68 and 32.5 ppm) and ¹H NMR signal (-16.35 ppm) observed for species B is totally disappeared. Further, the intense doublet observed in ¹H NMR at 1.16 ppm for –PMe₃ group coordinated to Co(II) in B, signal intensity drastically decreased. This entire scenario, firmly advocates that the alkyne insert between Co-H followed by reductive elimination lead to styrenyldiphenylphosphine. A new intense ³¹P NMR signal at -11.2 ppm is the characteristic signature of an E-selective styrenyldiphenylphosphine derivative, which is consistent with the other literature reports. The unchanged ¹H NMR signal intensity at 0.86 ppm (which was attributed to the free –PMe₃ originated from A upon oxidative addition) even after the reductive elimination, indicates that Co(0) regenerated after the reductive elimination is not same as A. This regenerated Co(0) is referred as A’ hereafter. This designates that, a concurrent ligand dissociation and oxidative addition of PPh₂H is the first step of catalytic cycle. Formation of A’ further, strongly corroborated with UV-Vis and EPR measurements (vide infra). Further, C remains as the resting state and is not catalytically active under the reaction conditions. This
fact indeed verified from the unchanged $^1$H and $^{31}$P signal even after the addition of alkyne substrate (see magenta trace in Figure 1).

To provide additional support for the oxidative addition of PPh$_2$H with [Co(PMe$_3$)$_4$] (A), we have recorded UV-Visible spectrum for both A and in-situ generated products (stoichiometric amount of A and PPh$_2$H) in a sealed cuvette (Figure 2). The spectral features of both A and in-situ generated complexes are distinctly different. For A there is no significant absorption feature, whereas for the in-situ generated product two distinct d-d transitions centered at 404 nm and 473 nm is observed,$^{58,59}$ for intermediate species B and C.

Upon addition of 4-bromophenylacetylene to the reaction mixture results in no absorption features as like A, with the synchronous disappearance of the absorption bands observed earlier. The UV-Vis spectrum upon addition of alkyne into the in-situ generated species, however, is not exactly resembles that of A. This suggests that A is not a catalytically active species, but A' which is confirmed by its spin Hamiltonian parameters extracted from EPR measurement compared to A (vide infra).

In order to shed light on the electronic structure of the various species involved in the hydrophosphination catalytic cycle low temperature, X-band EPR measurements were performed on A by dissolving in toluene, as a frozen toluene glass at 5 K. The EPR spectrum

![UV-Vis spectrum of A (red trace), in-situ generated intermediate B upon PPh$_2$H addition to A (blue trace) and magenta trace represents the alkyne added to B measured in toluene (2.8×10$^{-8}$ mmol) at room temperature.](image-url)

Figure 2. UV-Vis spectrum of A (red trace), in-situ generated intermediate B upon PPh$_2$H addition to A (blue trace) and magenta trace represents the alkyne added to B measured in toluene (2.8×10$^{-8}$ mmol) at room temperature.
of A measured at 5.0 K shows nicely resolved hyperfine fine structures due to the interaction of unpaired electron spin on cobalt with the nuclear spin of $^{59}$Co ($I(^{59}\text{Co}) = 7/2$). The cobalt hyperfine couplings are clearly visible in the $g_{||}$ region, whereas it is severely overlapped and poorly resolved in the $g_{\perp}$ regions. Simulation of the experimental EPR spectrum of A gave principal values of the $g$-tensor and components of hyperfine coupling for $^{59}$Co nucleus; $g = [2.1626, 2.1601, 1.9832]$, $A(^{59}\text{Co}) = [130 70 179]$ MHz with isotropic hyperfine coupling, of $a_{\text{iso}}(^{59}\text{Co}) = 126.3$ MHz (see black trace in Figure 3). The Gaussian line width of 3.89 mT was used to reproduce the experimental line shape. The observed EPR line shape and the extracted spin-Hamiltonian parameters are in good agreement with the previously reported Co(0) complexes with organophosphorous ligands in the coordination sphere with distorted tetrahedral geometry.

Figure 3. X-band CW-EPR spectra of [Co(PMe$_3$)$_4$] (black trace; A), in-situ generated products upon PPh$_2$H addition to A (red trace; B). Alkyne treated with B (blue trace) measured at 5.0 K in toluene solution. The solid magenta traces represent the simulations of the experimental spectra using the parameters described in main text. * denotes the signal from the resonator
cavity. # represents the EPR signals originate from a radical impurity (<3%). See main text for details.

When diphenylphosphine (HPPh\textsubscript{2}) is added into the solution of A, the characteristic EPR features of A are completely disappeared (see red trace in Figure 3). Similar trend has been observed previously when Co(0) complex [Co(C\textsubscript{2}H\textsubscript{4}O\textsubscript{2})\textsuperscript{2-}Al(c\textsubscript{2}H\textsubscript{5})\textsubscript{3}] was treated with dihydrogen gas.\textsuperscript{84} This implies that ligand exchange takes place (oxidative addition) at the expense of valence state of the cobalt centre in A. However, literature precedents are known for some reactions that there is no change in oxidation state of Co(0) upon ligand substitution.\textsuperscript{61,66-68} Oxidative addition leads to the formation of species B and C, which are EPR silent, in contrast to A. This suggests that cobalt ion in both B and C (Scheme 4) exist in a high-spin divalent oxidation state presumably. The rationale for EPR silent signature of Co(II) ion in a high-spin state (\(S = 3/2\)) is well established already in the literature.\textsuperscript{58,69-74}

When an alkyne is added to the \textit{in-situ} generated species, the EPR signal is re-generated, with characteristic features of an \(S = \frac{1}{2}\) spin state i.e. Co(0) (see blue trace in Figure 3). The regeneration of the EPR signal due to Co(0), unambiguously suggest that reductive elimination is the final step of the hydrophosphination catalytic cycle. The EPR spectrum of the final step was simulated by considering \(S = \frac{1}{2}\) spin state with the spin-Hamiltonian (SH) parameters; \(g = [2.1622\, 2.1317\, 2.002]\), \(A^{(59}\text{Co}) = [136\, 48\, 104]\) MHz, with isotropic hyperfine coupling, of \(a_{\text{iso}}^{(59}\text{Co}) = 96\) MHz; The SH parameters extracted for Co(0) regenerated from the final step (A’) are slightly different from the SH parameters of extracted for A. This suggests that the regenerated catalyst precursor (A’) possess slightly modified coordination environment than A. Similar trend has been reported previously when one/two of the organophosphorous ligands in the coordination environment of Co(0) complexes were replaced by other ligands/solvents.\textsuperscript{61,65} The vacant coordination site formed after the reductive elimination,
conceivably, occupied by the solvent molecule with the tentative molecular formula of [Co(PMe$_3$)$_3$(L)] (where L = solvent).

The spin Hamiltonian parameters extracted for A', reproduce only part of the experimental spectrum, which leave out some of the spectral features in 320-350 mT range (see Figure 3 marked with # symbol). Origin of these EPR signals is due to an unknown radical impurity. The SH parameters extracted for this from simulation described in ESI (see Figure S8 and its related text). The entire experimental spectral features in the final step were reproduced by considering two different $S = \frac{1}{2}$ spin states with the weighted factor of 0.96 (for A'):0.04 (radical $S = 1/2$) (blue trace in Figure 3). At this moment, we do not know the origin of radical impurity (<4 %). Overall, the modified coordination environment for the regenerated catalytic precursor (compared to A) is well supported by EPR, NMR and UV-Vis data undisputedly.

**Scheme 4. Proposed mechanism.**
Based on the various spectroscopic observations (NMR, UV-Vis, and EPR (vide supra)), we have proposed the working mechanism as depicted in Scheme 4. Complex A undergo initial ligand dissociation followed by oxidative addition of P-H led to the intermediate B. Intermediate B in the absence of alkynes reacts with HPPh₂ and leads to the formation of C along with the minor coupled product (PPh₂)₂. Initial coordination of alkyne to the intermediate B followed by insertion between Co-H led to intermediate D, which then proceeded to reductive elimination to produce vinylphosphine and regenerate an active species A’ for next catalytic cycle.

**Conclusions**

In conclusions, we have shown hydrophosphination of internal and terminal alkynes for the first time using well-defined low valent cobalt(0) complex. The suprafacial addition of P-H bonds across the alkyne in syn-fashion result in regio and stereo selective vinylphosphine as product. Deuterated labelled experiments undisputedly unveil the origin of regio and stereo selectivity of the isolated products. The reaction is general, applicable for both terminal and internal alkynes with good functional groups tolerance. The detailed NMR, UV-Vis, and EPR spectroscopic methods apparently discloses the presence of species B ([Co⁰(H)(PMe₃)₃(PPh₂)]) in solution upon oxidative addition of PPh₂H with A. Further in the absence of alkyne, B reacts with HPPh₂ and leads to C ([Co⁰(H)₂(PMe₃)₄]). Addition of alkyne substrate into the in-situ generated species B facilitate reductive elimination which concomitantly regenerate presumably a tricoordinated naked Co(0) active species. This extensive study allows us to further extend the catalytic system to activate other X-H bonds including inert C-H bonds, which is currently underway in our laboratory.

**Experimental Section: General Remarks.**
All the reactions were carried out under argon atmosphere unless otherwise mentioned. All the alkyne substrate was purchased from commercially available source, except (1j-1n), (1ab-1ad) is synthesized as per the literature reports. 75-77 Toluene was purified by means of distillation under dry nitrogen atmosphere over benzophenone/sodium ketyl. [Co(PMe$_3$)$_4$] was synthesized as per literature procedure.14 Chromatography purification was carried out using silica (mess size 60-120) for isolation of the products, additionally thin layer chromatography was performed using Merck TLC silica gel 60 F$_{254}$ plates. All the NMR ($^1$H, $^{13}$C, $^{31}$P) were recorded on Bruker 400 AVANCE or 500 AVANCE and referenced to CDCl$_3$ or C$_6$D$_6$ residual peak. 85% H$_3$PO$_4$ was used as external reference for recording $^{31}$P NMR. UV-Vis. spectra were recorded on a Shimadzu (UV-NIR-3600) at room temperature. Variable temperature EPR was recorded using a Bruker EMS plus series instrument and the EPR spectra were simulated using easy spin software.60

**Synthetic procedure:**

**General procedure for the hydrophosphination of terminal alkyne**

In an argon filled glove box 16.5 mg of [Co(PMe$_3$)$_4$] and 0.16 ml (0.9 mmol) of HPPh$_2$, 3 ml of toluene was added in an Schlenk tube and the mixture was stirred at room temperature for 10 minutes before adding various alkyne (0.9 mmol) into the reaction mixture. The resultant mixture was heated at 80°C for 1-2 hrs. Reaction was followed by $^{31}$P NMR and consumption of HPPh$_2$ (-40.5 ppm) was monitored. Reaction tube was cooled and 60 mg of S8 was added into the reaction mixture. This was heated at 80 ⁰C 15 min before the reaction was quenched with water. The mixture was transferred in to a separatory funnel and the compound of interest was extracted in ethyl acetate. The pure product of interest was isolated through column chromatography (pet. ether/ethyl acetate (ratio: 99:1). The Purity of the resultant product were
confirmed through the $^1$H and $^{31}$P NMR where we had obtained only single peak corresponding to product.

**General procedure for the hydrophosphination of internal alkyne**

The same reaction procedure was followed as above, but the reaction mixture was heated at 100° C for 12 hours.

**Procedure for the NMR follow up**

To follow the intermediates generated in the catalytic cycle, we performed several NMR experiments in a J-Young NMR tube. The general procedure followed described below. 10 mg (0.0275 mmol) of [Co(PMe$_3$)$_4$] was dissolve in 0.5 ml of C$_6$D$_6$, in the resulting homogeneous solution 4.7 µL of (0.0275 mmol) HPPh$_2$ was added. Upon addition, the reaction mixture turns into dark brown and the tube was sealed and heated for 15 min. at 70 °C. The resultant mixture was cooled to room temperature and $^1$H, $^{31}$P NMR was recorded. The tube was brought inside the glove box and 5mg (0.0275 mmol) of 4-Bromophenyl acetylene was added into it, sealed and heated at 80 °C for 30 min. $^1$H, $^{31}$P NMR was recorded for resulting solution. A similar procedure was followed for the isotopic labelled experiments (reaction of A with DPPh$_2$) as well, but the NMR was recorded in C$_6$H$_6$.

**Procedure for UV-Vis. follow up**

A similar synthetic method was followed as in NMR follow up, but the reactions were performed in a Schlenk tube fitted with septa in a 1.0 ml toluene solvent. With the help of syringe 0.05 mL of aliquot was taken from the reaction mixture which is then transferred to a sealed UV-Vis cuvette (containing 3.5 mL of dry toluene) under inert atmosphere.

**Procedure for EPR follow up**
A similar synthetic method was followed as in NMR follow up, but the reactions were performed in a Schlenk tube fitted with septa in a 1.0 ml toluene solvent. With the help of syringe 0.05 mL of aliquot was taken from the reaction mixture which is then transferred to a sealed EPR tube (containing 0.15 mL of dry toluene) under inert atmosphere.

ASSOCIATED CONTENT

Crystallographic data obtained for 2c and relevant NMR of the isolated products are given in ESI. CCDC number: 1509786

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Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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ABBREVIATIONS
NMR, nuclear magnetic resonance; EPR, electron paramagnetic resonance, UV-vis., ultraviolet visible; ESI, electronic supplementary information.

REFERENCES


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A well-defined cobalt(0) catalyst ([Co(PPh$_3$)$_4$]; A) promotes hydrophosphination reaction of both terminal and internal alkynes with excellent stereo and regio-selectivity ($E$-isomer). In addition, we report, through detailed spectroscopic (NMR, UV-Vis and EPR) analyses and isotopic labelling methods various intermediates involved in the catalytic cycle identified.