Enhanced Catalytic Activity of Nickel Complexes of an Adaptive Diphosphine–Benzophenone Ligand in Alkyne Cyclotrimerization

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Supporting Information

ABSTRACT: Adaptive ligands, which can adapt their coordination mode to the electronic structure of various catalytic intermediates, offer the potential to develop improved homogeneous catalysts in terms of activity and selectivity. 2,2’-Diphosphinobenzophenones have previously been shown to act as adaptive ligands, the central ketone moiety preferentially coordinating reduced metal centers. Herein, the utility of this scaffold in nickel-catalyzed alkyne cyclotrimerization is investigated. The complex 1[(PhL1)Ni[(BPI)] (PhL1 = 2,2’-bis(di(para-tolyl)phosphino)benzophenone; BPI = benzophenone imine) is an active catalyst in the [2 + 2 + 2] cyclotrimerization of terminal alkenes, selectively affording 1,2,4-substituted benzenes from terminal alkenes. In particular, this catalyst outperforms closely related bi- and tridentate phosphate-based Ni catalysts. This suggests a reaction pathway involving a hemilabile interaction of the C=N unit with the nickel center. This is further borne out by a comparative study of the observed resting states and DFT calculations.

KEYWORDS: alkyne cyclotrimerization, nickel complexes, adaptive ligand, π–acceptor ligand, hemilabile ligand

INTRODUCTION

The search for improved activity and selectivity in transition-metal based homogeneous catalysts strongly relies on the development of steering ligands to tune the steric and electronic properties of the metal center to the requirements of particular transformations. Recent years have seen the development of more sophisticated adaptive or cooperative ligands that can adjust their binding modes or engage in chemical transformations along a catalytic cycle.1–4 The use of such ligands also plays an important role in the development of catalysts based on inexpensive and nontoxic first-row transition metals that can compete with, or even surpass, their counterparts based on precious metals, contributing to a more sustainable chemistry.5 Perhaps one of the simplest implementations of the concept of adaptive ligands are hemilabile ligands, which are polydentate ligands featuring a weakly binding moiety that can reversibly (de)coordinate the metal center.6 Since their introduction in synthetic chemistry by Jeffrey and Rauchfuss,7 hemilabile ligands have played a significant role in the current transition from noble to base metals in homogeneous catalysis. The hemilabile interaction is important not only for opening up a masked coordination site but also to stabilize catalytic intermediates, by allowing the supporting ligand to adapt its binding mode throughout the reaction coordinate. Most commonly, weak donor groups, such as ether (OR),7a amine (NR),9 or imine derivatives (R₂C=NR),9b,10 are employed as the labile unit, often resulting in enhanced catalytic activity for different kinds of reactions. Examples include olefin oligomerizations and polymerizations,8b,11 (cyclo)trimerization,9c,11 carbynolation of methanol and methyl acetate,12 (transfer) hydrogenation of ketones or dehydrogenation of alcohols,9b,13,14 hydroacylation of alkenes and alkynes,8d,15 and coupling reactions.9c,11–19

In addition to weak σ-donor moieties, σ-acceptor groups20 (e.g., triarylborane)21 or π-ligands2 (e.g., C=C double bond)22 can also act as hemilabile fragments. Our group recently reported the hemilabile character of the ligand 2,2’-bis(diphenylphosphino)benzophenone23 (PhL1) bound to nickel24 and other first-row transition metals.25 PhL1 was shown to function as a hemilabile π-acceptor ligand, with the central C=O bond coordinating to the metal center in its more reduced forms (Figure 1). Ru,23,26 Rh,27–29 Os,30 and Ir31 complexes of PhL1 were also studied, more specifically in the catalytic hydrogenation of ketones,32,26,28,30 in which the formation of a hydroxalkyl species was accessible via the hydrogenation of the ketone moiety of the ligand.28

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In this context, we set out to assess the potential utility of an \( \eta^2 \)-bound hemilabile \( \pi \)-acceptor moiety incorporated in a pincer type architecture for catalysis, using the cyclotrimerization of alkynes as a benchmark reaction. Since its discovery by Reppe et al.\(^{32} \) using a [Ni(CO)]\(_2\)(PCl\(_3\)) catalyst, intermolecular [2 + 2 + 2] cyclotrimerization of alkynes has been widely studied.\(^{33} \) Metal catalyzed cyclotrimerization is an elegant method for the formation of cyclic frameworks, particularly convenient when the desired product is not accessible via traditional aromatic substitution reactions. Many transition metal systems have been developed (e.g., Ti,\(^{34} \) Fe,\(^{35} \) Co,\(^{36} \) Ni,\(^{37} \) Mo,\(^{38} \) Ru,\(^{39} \) Rh,\(^{40} \) Pt,\(^{41} \) Ir)\(^{42} \). Literature precedents for the nickel-catalyzed conversion of alkynes to substituted benzene regio-isomers are known, both from an intramolecular\(^{36c,37a} \) and intermolecular approach.\(^{36c,37a} \) For the [2 + 2 + 2] intermolecular alkyn cyclotrimerization, it starts from the early example by Reppe et al.\(^{32} \) to the combination of divalent nickel halide salts and alkynes (see below; Scheme 4).\(^{24} \) Using hemilabile \( \pi \)-acceptor tridentate ligand (P,N),\(^{9c} \) or 1,4-diazadiene\(^{37c,e,u,w,y,z} \) ligands, have been introduced to Ni systems in order to improve selectivity and catalytic activity. Phosphine complexes generally favor the formation of benzene derivatives while 1,4-diazadiene complexes yield cyclooctatetraenes.

Besides their synthetic utility, alkyne condensations are also useful probes for ligand effects in catalysis.\(^{43} \) The possible formation of different products and isomers, such as cyclotrimers, cyclotetramers, linear oligomers, polymers, and other compounds, provides useful information about the reactivity of a particular catalyst. For example, Uyeda\(^{37w,44} \) and Ess\(^{44} \) recently applied this approach to the evaluation of the effect of catalyst nuclearity, and Jones\(^{38e} \) applied it to assessing differences in catalytic performance between bidentate PP and PN ligands (Figure 2). In this study, we assess the effect of using hemilabile \( \pi \)-acceptor tridentate ligand \( (\text{P}^{\text{tol}})\text{L1}) \) (Figure 3) in alkyn cyclotrimerization through comparison with diverse nickel systems. Ni(0) adopting a strong tridentate architecture (ligand = \( \text{P}^{\text{tol}}\text{L2}) \) (Figure 3) and Ni complexes supported by a bidentate ligand (\( \text{P}^\text{tol}\text{L3}) \) (Figure 3) were selected for comparison with \( \text{P}^{\text{tol}}\text{L1}) \).

Here we report the synthesis of nickel(0) complexes of \( \text{P}^\text{tol}\text{L1}) \), \( \text{P}^\text{tol}\text{L2}) \), and \( \text{P}^\text{tol}\text{L3}) \) featuring benzophenone imine (BPI) as a labile protecting ligand. Their stoichiometric reactivity with terminal alkynes is investigated, and the resulting Ni–alkyne complexes are thoroughly characterized. Then, a comparative study of these bi- and tridentate Ni(0)-catalysts in the cyclotrimerization of terminal alkynes is described, aiming to study the effect of a hemilabile \( \pi \)-acceptor system. For all tested alkyne substrates, \( \text{P}^\text{tol}\text{L1}) \) outperforms \( \text{P}^\text{tol}\text{L2}) \) and \( \text{P}^\text{tol}\text{L3}) \), as well as the structurally more different diphosphine rac-BINAP (\( \text{P}^\text{tol}\text{L4}) \), in terms of selectivity and activity. Reactivity studies combined with DFT calculations provide insight into the increased catalytic activity, suggesting that \( \text{P}^\text{tol}\text{L1}) \) can adapt its binding mode throughout the reaction pathway, by the labile (de)coordination of its ketone unit.

**RESULTS AND DISCUSSION**

**Ni(0)-Benzophenone Imine Complexes.** The diphosphine–benzophenone pincer-type ligand\(^{35} \) \( \text{P}^\text{tol}\text{L3}) \) was introduced to Ni systems in order to improve selectivity and catalytic activity. Phosphine complexes generally favor the formation of benzene derivatives while 1,4-diazadiene complexes yield cyclooctatetraenes.

Besides their synthetic utility, alkyne condensations are also useful probes for ligand effects in catalysis.\(^{43} \) The possible formation of different products and isomers, such as cyclotrimers, cyclotetramers, linear oligomers, polymers, and other compounds, provides useful information about the reactivity of a particular catalyst. For example, Uyeda\(^{37w,44} \) and Ess\(^{44} \) recently applied this approach to the evaluation of the effect of catalyst nuclearity, and Jones\(^{38e} \) applied it to assessing differences in catalytic performance between bidentate PP and PN ligands (Figure 2). In this study, we assess the effect of using hemilabile \( \pi \)-acceptor tridentate ligand \( (\text{P}^\text{tol})\text{L1}) \) (Figure 3) in alkyn cyclotrimerization through comparison with diverse nickel systems. Ni(0) adopting a strong tridentate architecture (ligand = \( \text{P}^\text{tol}\text{L2}) \) (Figure 3) and Ni complexes supported by a
close to that of the free imine at 177.3 ppm, consistent with retention of C=N double bond character. In the $^1$H NMR spectra, slight deshielding of the C=NH proton by 0.24 ppm with respect to free BPI is also in accordance with $\eta^1$ (N) binding. Moreover, the ATR-IR spectrum displays a signal at 3152 cm$^{-1}$ in the region corresponding to the N-H stretch. In contrast, the backbone C=O moiety is bound side-on: the corresponding $^{13}$C NMR signal appears at 119.0 ppm (t, $^3J_{C,P} = 5.1$ Hz), considerably shifted from the value of 197.4 ppm found in the free ligand. This large shift is useful as a diagnostic tool to determine whether the CO moiety is coordinated to the Ni center. The $^{31}$P NMR spectra of p-tol1 consist of a single singlet signal at 15.5 ppm, indicating that the two phosphorus atoms are equivalent on the NMR time scale. However, from $^1$H and $^{13}$C NMR analysis, it appears that the complex contains two chemically different para-tolyl substituents (2.01 and 1.91 ppm in $^1$H NMR, 21.3 and 21.1 ppm in $^{13}$C NMR), as also observed with complex p-tol1.

In a similar fashion, NMR data support $\eta^1$ binding of the BPI ligand in the triphosphine complex p-tol2. The $^{13}$C NMR signal corresponding to the N=C bond is a doublet of triplets at 168.9 ppm ($^3J_{C,P} = 8.1$ Hz, $^3J_{C,P} = 7.4$ Hz). The imine proton appears at 10.25 ppm in the $^1$H NMR spectrum (deshielding of 0.48 ppm compared to the free BPI ligand) and couples with the phosphorus nuclei (dt, $^3J_{H,P} = 3.2$ Hz, $^3J_{H,P} = 2.7$ Hz). The $^{31}$P NMR spectrum is consistent with an AK2 system ($\Delta \nu \approx 5^3J_{A,K}$) with a coupling constant $^3J_{A,K} = 85$ Hz. From $^1$H and $^{13}$C NMR analysis, it appears that the complex contains two chemically different para-tolyl substituents (2.14 and 1.95 ppm in $^1$H NMR, 21.4 and 21.1 ppm in $^{13}$C NMR), as also observed with complex p-tol1.

In the $^1$H NMR of Ph$_3$N, the N-H signal from the coordinated imine appears as a broad singlet at $\delta_H = 9.71$ in the expected 1:3:8 ratio compared to the aromatic region of the spectrum. The $^{31}$P NMR spectrum exhibits a single resonance at 32.4 ppm. No satisfactory $^{13}$C NMR data could be obtained due to the low solubility of the complex and its progressive decomposition, making the assignment of the binding mode of BPI in solution uncertain. The side-on binding of BPI observed in the solid state (see below) may be preserved in solution.
which case fast rotation of BPI ligand on the $^1$H NMR time scale would render the two phosphorus atoms equivalent. The N–H stretch from the bound imine appears as a broad weak band in the ATR-IR spectrum, located at 3200 cm$^{-1}$.

More insights into the structural and electronic properties of nickel complexes $^{p-tol1}$ and $^{Ph3}$ were obtained by X-ray crystal structure determination (Figure 4). Crystals suitable for X-ray diffraction were not accessible with $^{p-tol1}$ but with the structurally related complex $^{Ph1}$, in which the para-tolyl ligand $^{p-tol1}$ is replaced by the phenyl analogue $2,2'$-bis(di(phenyl)-phosphino)-benzophenone ($^{PhL1}$).

In accord with NMR data, the structure of $^{Ph1}$ (Figure 4; left) exhibits a side-on bound ketone moiety with Ni1–O11 and Ni1–C71 bond lengths of 2.0217(14) and 1.9760(19) Å, respectively. The C71–O11 bond length (1.320(2) Å) is found between those of unbound $^{PhL1}$ (1.213(3) Å) and a C–O single bond (1.43 Å in ethanol). The ketone is slightly less activated than in $[(^{PhL1})Ni(PPPh_3)]$, which displays a C–O bond length of 1.310(2) Å, consistent with less pronounced π-back-donation arising from the weaker donor character of BPI with respect to PPh$_3$. The sum of bond angles (351.3(3)°) around the carbon atom lies between those expected for sp$^2$ (328.5°) and sp$^3$ (360°) hybridization at the carbon, in accordance with the Dewar–Chatt–Duncanson model. The N12–C12 bond length of 1.289(2) Å is close to the value of a C–N double bond (ca. 1.28 Å) and comparable to the value found by Zhao et al. (1.294(3) Å) for η$^1$-coordination mode in their synthesized NHCl-based nickel(0) complex, $[(^{IPr})Ni(η^2-BPI)(η^1-BPI)]$ ($^{IPr}$ = 1,3-bis(diisopropylphenyl)-imidazolium), showing that the π-back-donation to the BPI ligand is small. Accordingly, the valence angles around the imine carbon add up to 360.0(3)°. Finally, the torsion angle ($\angle$Ni1–N12–C12–CPh) of

Figure 4. Molecular structures of $[(^{PhL1})Ni(BPI)]$ ($^{Ph1}$) and $[(^{PhL3})Ni(BPI)]$ ($^{Ph3}$) in the crystal (50% probability level). Hexane solvent molecules ($^{Ph1}$) and C–H hydrogen atoms are omitted for clarity.

Scheme 3. Ni$^0$-Terminal Alkyne Complexes$^a$

(A) General synthetic route. (B) Generated complexes. $^{p-tol4}$-Ph and $^{p-tol4}$-CH$_2$OMe were characterized in situ in solution, while $^{p-tol5}$-Ph and $^{Ph6}$-Ph were isolated. BPI = benzophenone imine.
analogue of the unbound state of ligand oxygen atom is not coordinated and can be seen as a structural analysis at a B3LYP/def2TZVP level of theory. The distance Wiberg bond index lower than 0.01 calculated by NBO leading to the generation of Ni$^{0}$(111.54(12) Å). Finally, the measured P1 bite angle of 108.59(2)°, revealing the central coordinating unit the C$\equiv$O unit is not bound to the Ni ion (P1$-$Ni$-$P2 112.996(13)°; Ni$-$C = 3.4031(12) Å; Ni$-$O = 3.1012(10) Å), supporting the use of Ph$^{3}$ as a model complex for the unbound state of Ph$^{3}$L$^{1}$.

In summary, complexes Ph$^{3}$L$^{1}$ and Ph$^{3}$L$^{2}$ are geometrically similar and mainly differ by the central coordinating unit the ligand (C$\equiv$O vs P). Complex Ph$^{3}$L$^{3}$ differs in that the central oxygen atom is not coordinated and can be seen as a structural analogue of the unbound state of ligand Ph$^{3}$L$^{1}$ (R = p-tolyl or Ph). Interestingly, moving from tridentate to bidentate mode is coupled to a change in bonding mode of the BPI ligand from end-on to side-on, which can be understood from enhanced $\pi$-back-donation from a d$^{10}$ L$^{3}$Ni fragment (see Supporting Information for more insights by NBO analysis into the different coordination modes of the imine coligand; Table S8).

Ni(0)$-$Alkyne Complexes. With complexes Ph$^{3}$L$^{1}$−Ph$^{3}$L$^{3}$ in hand, their reactivity toward terminal alkynes was investigated, leading to the generation of Ni$-$alkyne complexes [(Ph$^{3}$L$^{1}$)-Ni(HC$\equiv$CPh)] (Ph$^{3}$L$^{1}$-Ph$^{3}$L$^{3}$), [(Ph$^{3}$L$^{1}$)Ni(HC$\equiv$CCH$_{2}$OMe)] (Ph$^{3}$L$^{1}$-Ph$^{3}$L$^{3}$), [(Ph$^{3}$L$^{1}$)Ni(HC$\equiv$CPh)] (Ph$^{3}$L$^{1}$-Ph$^{3}$L$^{3}$), and [(Ph$^{3}$L$^{1}$)Ni(HC$\equiv$CPh)] (Ph$^{3}$L$^{1}$-Ph$^{3}$L$^{3}$) (Scheme 3). Ni-complexes Ph$^{3}$L$^{1}$-Ph$^{3}$L$^{3}$, bearing phenylacetylene as coligand, are sufficiently stable to be isolated and are discussed first.

The $^{31}$P NMR spectrum of Ph$^{3}$L$^{1}$-Ph$^{3}$L$^{3}$ displays two signals at 78.7 ppm (t, $^{3}J_{\beta\beta} = 35.4$ Hz) and at 28.1 ppm (d, $^{3}J_{\beta\beta} = 35.4$ Hz) in a ratio of 2:1, indicating that the ligand binds in a tridentate fashion. Two $^{1}$H NMR singlets of the same intensity at 2.12 and 1.91 ppm correspond to the methyl group from diastereotopic para-tolyl substituents bound to the same phosphorus atom. A single alkyne is bound to Ni as indicated by the terminal proton signal at 6.30 ppm, which appears as a doublet of triplets ($^{3}J_{\beta\beta} = 25.6$ Hz, $^{3}J_{\beta\beta} = 7.2$ Hz) and couples with a carbon nucleus at 92.9 ppm in HMQC ($^{1}$H$\rightarrow^{13}$C). Further confirmation of this assignment is provided by treatment of Ph$^{3}$L$^{1}$-Ph$^{3}$L$^{3}$ with d-phenylacetylene, resulting in the disappearance of the signal at 6.30 ppm in an otherwise identical $^{1}$H NMR spectrum (Supporting Information; Figure S68 and S76). In agreement with the spectroscopic characterization, the solid-state structure of Ph$^{3}$L$^{1}$-Ph$^{3}$L$^{3}$ (Figure 5, left) reveals a pseudo-tetrahedral geometry in which the alkyn moiety is coordinated in $\eta^{2}$ fashion.

Compound Ph$^{3}$L$^{1}$-Ph$^{3}$L$^{3}$, supported by the bidentate diphosphine ether ligand Ph$^{3}$L$^{3}$, displays two signals at 29.2 ppm and at 27.3 ppm coupling to each other ($^{3}J_{\beta\beta} = 14.0$ Hz) and in a ratio of 1:1 in the $^{31}$P NMR spectrum. This is consistent with a triligational planar geometry in which rotation of the alkyne ligand is slow on the $^{1}$H NMR time scale; warming up the sample to 100 °C does not result in coalescence of the two $^{31}$P NMR signals. This interpretation is supported by reaction of Ph$^{3}$L$^{3}$ with 1 equiv of the symmetric alkyne diphenylacetylene, resulting in a symmetrical analogue of Ph$^{3}$L$^{1}$-Ph$^{3}$L$^{3}$ displaying a single $^{31}$P NMR singlet at 28.1 ppm (Supporting Information; Figure S98). The proton from the alkyne gives a $^{1}$H NMR signal at 6.9 ppm, as revealed by HMQC ($^{1}$H$\rightarrow^{13}$C) and comparison with deuterated analogue. The solid state structure (Figure 5, right) of Ph$^{3}$L$^{1}$-Ph$^{3}$L$^{3}$ is in accord with the NMR data and reveals a triliganal planar geometry with a P1$-$Ni$-$P2 bite angle of 100°. The crystal structure of Ph$^{3}$L$^{1}$-Ph$^{3}$L$^{3}$ shows that the nickel atom is slightly out of the plane of BPI, which is probably sterically driven.

In contrast to that of Ph$^{3}$L$^{1}$, the crystal structure of Ph$^{3}$L$^{3}$ (Figure 4, right) reveals a triliganal planar complex in which the imine coligand is coordinated to the nickel in an $\eta^{2}$ fashion (Ni1$-$C37 = 2.018(2) Å, Ni1$-$N1 = 1.8985(19) Å; C$\equiv$N bond axis is parallel to the metal coordination plane, which is thought to maximize $\pi$-back-donation from the high-lying in-plane d orbital with significant $\sigma^{*}$(P$-$Ni) character. Accordingly, strong $\pi$-back-donation into the $\pi^{*}$(N$-$C) orbital is evidenced by an elongated C37$-$N1 bond (1.373(3) Å vs 1.28 Å (in the free imine) and the pyramidalization of the coordination sphere, which displays a sum of valence angles of 355.3(3)°, in line with known $\eta^{2}$-imine coligands; Table S8).

Interestingly, moving from tridentate to bidentate mode is coupled to a change in bonding mode of the BPI ligand from end-on to side-on, which can be understood from enhanced $\pi$-back-donation from a d$^{10}$ L$^{1}$Ni fragment (see Supporting Information for more insight by NBO analysis into the $\pi^{*}$-coordination mode, the C37$-$C38 axis being in the Ni coordination plane.

Figure 5. Molecular structure of [(Ph$^{3}$L$^{1}$)Ni(HC$\equiv$CPh)] (Ph$^{3}$L$^{1}$-Ph$^{3}$L$^{3}$) and [(Ph$^{3}$L$^{1}$)Ni(HC$\equiv$CPh)] (Ph$^{3}$L$^{1}$-Ph$^{3}$L$^{3}$) in the crystal (50% probability level). Toluene solvent molecules (Ph$^{6}$-Ph) and hydrogen atoms (except alkyne) have been omitted for clarity.
While stable tricoordinate Ni(0) alkyne complexes with formally 16 valence electrons analogous to $p^\text{tol}$-Ph are well documented, $p^\text{tol}$-5-Ph represents an unusual example of tetracoordinate, 18 VE Ni(0)—alkyne complex, to the best of our knowledge the first to be structurally characterized. Spectroscopic and structural data point toward a considerably weaker activation of the C=C triple bond in this geometry (Table 1). First, the $^{13}$C NMR chemical shifts of the two alkyne carbons ($\delta_2 = 77.5$ and 83.3) indicate relatively weak rehybridization from sp to sp$^2$. This contrasts with a stronger activation of the C≡C triple bond of phenylacetylene in $p^\text{tol}$-6-Ph evidenced by the $^{13}$C NMR signals from the coordinated phenylacetylene at 125.7 ppm (C≡C–H, d, $J_{CH} = 40.1$ Hz, $J_{CP} = 7.1$ Hz) and 136.4 ppm (C≡C–Ph, d, $J_{CP} = 38.9$ Hz, $J_{CP} = 8.4$ Hz), which were assigned as having the assistance of APT $^{13}$C NMR and by comparison with the diphosphine phenylacetylene complex. Second, the acetylic hydrogen signal of $p^\text{tol}$-5-Ph ($\delta_1 = 92.9$) is less shifted than that of $p^\text{tol}$-6-Ph ($\delta_1 = 79.2$), consistent with a stronger rehybridization toward sp$^2$. Third, the C≡C stretch vibration from the alkyne in $p^\text{tol}$-5-Ph is found at 1823 cm$^{-1}$ in the FT-IR spectrum versus 2126 cm$^{-1}$ for free phenylacetylene and 1749 cm$^{-1}$ for $p^\text{tol}$-6. Ph. Finally, the slightly elongated C47–C48 distance at 1.231(8) Å (vs 1.182–1.190 Å in free phenylacetylene) and the rather large C47–C48–C49 angle at 152.0(6)$^\circ$ are also consistent with a relatively weak activation of the C–C triple bond, contrasting with the longer C37–C38 bond length (1.269(3) Å) and the more acute the C37–C38–C39 angle (144.07(19)$^\circ$) found for $p^\text{tol}$-6-Ph. The C47–C48–C49 bond length in $p^\text{tol}$-5-Ph is the shortest we are aware of for nickel(0)–alkyne complexes. Together, these data suggest that the $\pi$-back-donation from the nickel to phenylacetylene is more pronounced in $p^\text{tol}$-6-Ph, resulting in a stronger rehybridization toward sp$^2$.

The observations made for complex $p^\text{tol}$-6-Ph parallel those reported for mononuclear, 16 valence electron, tricordinate Ni–alkyne, in which the C–C bond is significantly more elongated than in $p^\text{tol}$-5-Ph, regardless of substituent groups on the alkyne. For example, strong activation of the alkyne is observed for bidentate diimine and mixed P,N supported species (up to 1.296(6)$^\circ$) while bidentate phosphorus ligands afford C=C bond lengths from 1.260(4) to 1.283(3)$^\circ$ while bidentate phosphorus ligands afford C=C bond lengths from 1.260(4) to 1.283(3)$^\circ$. The substantially weaker rehybridization observed in $p^\text{tol}$-5-Ph can be assigned to its unique coordination geometry (i.e., tetracoordinate complex; 3 donor ligands; pseudo-$T_g$ geometry) compared to $p^\text{tol}$-6-Ph and the reported Ni–alkyne complexes (i.e., tetracoordinate complex; 2 donor ligands; trigonal planar geometry). The weak activation of phenylacetylene in $p^\text{tol}$-5-Ph is presumably a consequence of the smaller splitting of the d-orbitals in its pseudo-tetrahedral geometry (3 donor ligands), resulting in less pronounced $\pi$-back-donation from Ni to the antibonding orbitals of the alkyne. Similar considerations were used by Lee and co-workers to explain the rather weak activation of CO in the tetracoordinate pseudo-tetrahedral nickel complex ([P$^{\text{Me}}$MeP]$^2$Ni(η$^2$-CO)$_2$) (P$^{\text{Me}}$MeP = PMe$_2$-PPh$_2$-CH$_2$)$_2$) with respect to tricordinate Ni-η$^2$-CO$_2$ adducts supported by bidentate phosphines such as ([dtbpe]Ni(η$^2$-CO$_2$)) (dtbpe = 1,2-bis(di-tert-butylyphosphino)-ethane).

Finally, reaction of the diphosphine-ketone complex $p^\text{tol}$1 with terminal alkynes generally led to a mixture containing the alkyne complex, [(p$^\text{tol}$1)Li(NC≡CR)] ($p^\text{tol}$4-R$^1$: R$^1$ = substituent on the alkyne), the starting material $p^\text{tol}$-1, BPh$_3$, the substrate, and cyclotrimerization products. This indicates that cyclotrimerization occurs concomitantly with ligand exchange, precluding the isolation of pure alkyne complexes. Nonetheless, in situ characterization of alkyne complexes was possible. Interestingly, $^{13}$C NMR of $p^\text{tol}$-4-Ph indicates that the ketone moiety is not bound to the metal center: addition of phenylacetylene to $p^\text{tol}$-1 causes the disappearance of the triplet at 119.0 ppm, characteristic of the η$^2$(C=O) coordination to nickel and the appearance of a triplet at 202.7 ppm ($J_{CP} = 4.9$ Hz). In addition, all the para-tolyl groups in $p^\text{tol}$-4-Ph are equivalent at room temperature, with singlets appearing at 2.00 and at 21.2 ppm in $^1$H and $^{13}$C NMR, respectively. This is consistent with an unbound ketone allowing fast ring inversion of the chelate macroring. A single $^{31}$P NMR singlet at 33.0 ppm down to $-80 \, ^\circ$C indicates fast rotation of the alkyne, exchanging the two phosphorus atoms on the NMR time scale even at low temperature (Supporting Information; Figure S59).

The C≡C–H $^1$H NMR signal of the coordinating phenylacetylene could not be located, presumably hidden in the crowded aromatic region of the spectrum. In contrast, the assignment of the acetylic proton of the bound alkyne was possible in the $^1$H NMR spectrum of $p^\text{tol}$-4-CH$_2$OME where it appears as a triplet of triplets at 6.34 ppm ($J_{CH} = 15.6$, $J_{HH} = 1.6$ Hz) and integrates in a ratio of 1:12 compared to the four CH$_2$ groups of the ligand, confirming that a single alkyne molecule is bound. The integrals, coupling constants, and multiplicity of CH$_3$ groups (4.63 ppm, d, $J_{HH} = 1.6$ Hz) and OCH$_3$ (3.32 ppm, s) of the bound alkyne are in agreement with the proposed structure. Similar to $p^\text{tol}$-4-Ph, both $^1$H and $^{13}$C NMR of $p^\text{tol}$-4-CH$_2$OME reveal that the ketone moiety is not bound to the metal center: the ketone resonance appears as a triplet at 203.1 ppm ($J_{CP} = 4.7$ Hz) and the methyl groups from the para-tolyl are all equivalent, with a singlet at 2.03 and a doublet 22.2 ppm ($J_{CP} = 2.3$ Hz) in $^1$H and $^{13}$C NMR, respectively. A singlet $^{31}$P NMR signal at 32.7 ppm at room temperature is consistent with fast rotation of the methyl propargyl ether group similar to $p^\text{tol}$-4-Ph. However, gradually cooling the sample down to $-85 \, ^\circ$C first shows the appearance of a new unsymmetrical species at ca. $-10 \, ^\circ$C, as characterized by two doublets ($J_{PP} = 23.3$ Hz) at 32.1 and 34.1 ppm (Supporting Information; Figure S67). The central signal corresponding to $p^\text{tol}$-4-CH$_2$OME does split into two new doublets ($J_{PP} = 23.3$ Hz) with a coalescence temperature between $-50$ and $-60 \, ^\circ$C. This indicates that the rotation of methyl propargyl ether can be frozen on the NMR time scale, but also that two distinct species are formed at low temperature. This is tentatively attributed to a secondary interaction of the oxygen atom from

Table 1. Selected Spectroscopic and X-ray Crystal Structure Values of Phenylacetylene, $p^\text{tol}$-5-Ph and $p^\text{tol}$-6-Ph

|          | $p^\text{tol}$-5-Ph | $p^\text{tol}$-6-Ph |
|----------|---------------------|---------------------|
| $\delta_1\text{ (C≡C–H)}$ (ppm) | 77.5                | 92.9                |
| $\delta_1\text{ (C≡C–Ph)}$ (ppm) | 83.3                | 101.1               |
| $\delta_1\text{ (C≡C–H)}$ (ppm) | 2.73                | 6.30                |
| C=C [Å] | 1.182–1.190         | 1.231(8)            |
| C≡C–C=CP [deg] | 177.39–179.49      | 152.0(6)            |
| $J_{CP}$ (Hz) | 2126                | 1823                |

“Vibrational frequencies are measured with ATR-IR (near). NMR chemical shifts are given in C$_6$D$_6$. 
Ph−ketone state is characterized by the coordination of the ketone moiety, which contrasts with the observed behavior of the tricoordinate state, involving Ni coordination of the ketone moiety to the Ni center, resulting in a low overall rotation energy barrier of 5.5 kcal/mol (Figure 6). Optimized geometry of transition states reveals that the rotation of acetylene is assisted by transient conformer or an isomeric structure in which the central ketone fragment binds to the nickel center.

The fast rotation of the alkyne fragment in complex Ph4-H(TS1) contrasts with the observed behavior of the tricoordinate Ph6-Ph. DFT calculations on the acetylene complex Ph4-H reveal that the rotation of acetylene is assisted by transient coordination of the ketone moiety to the Ni center, resulting in a low overall rotation energy barrier of 5.5 kcal/mol (Figure 6). The first transition state, Ph4-H(TS1), from the unbound ketone state Ph4-H to the bound state Ph4-H(I1), is characterized by the coordination of the ketone moiety (\( \nu = 113 \text{ cm}^{-1} \); \( \Delta G^{TS1} = 4.3 \text{ kcal/mol} \)) to generate a four-coordinate intermediate Ph4-H(I1). The second transition state, Ph4-H(TS2), corresponds to the rotation of acetylene (\( \nu = 95 \text{ cm}^{-1} \); \( \Delta G^{TS2} = 4.1 \text{ kcal/mol} \)) accompanied by partial decoordination of one of the phosphine arms. The low overall energy barrier of \( \Delta G^{TS,overall} = 5.5 \text{ kcal/mol} \) is in qualitative agreement with the observed fast rotation of alkynes at room temperature. For comparison, a rotation energy barrier of 25.0 kcal/mol was calculated for the rotation of acetylene in the diphosphine ether complex Ph6-H (Supporting Information; Figure S112), in qualitative agreement with the observation of two \(^{31}P\) NMR signals for Ph6-Ph up to 100 °C.

The differences in electronic and structural properties of Ni−alkyne complexes Ph4-Phe−Ph6-Ph were further investigated by DFT calculations (geometry optimization and NBO analysis), as summarized in Table 2. The optimized geometries of Ph4-Phe, Ph5-Phe, and Ph6-Phe (Table 2, entries 1−4) are consistent with the obtained crystal structures in which the C1−C2 bond length, C1−C2−C3 angle and Ni−C1 and Ni−C2 distances calculated for Ph5-Phe indicate weaker activation of the HC=C=O-HCl substrate. Accordingly, Wiberg bond indexes (WBI) calculated in the NBO basis at a B3LYP/def2TZVP level of theory show that the binding of phenylacetylene induces a decrease of the C1−C2 WBI (Table 2, entry 5) from 2.82 to 2.30 in Ph4-Phe versus 2.20 in Ph5-Phe and 2.17 in Ph6-Phe.
Table 2. Selected DFT Bond Distances and Angles and Wiberg Bond Indexes (WBI)*

| entry | property | HC≡CPh | Ph4-Ph | Ph5-Ph | Ph6-Ph |
|-------|----------|--------|--------|--------|--------|
|       | DFT Bond Length and Angle [in Å and deg] |        |        |        |        |
| 1     | C1–C2   | 1.21   | 1.29   | 1.26   | 1.30   |
| 2     | C1–C2   | 180    | 141    | 150    | 141    |
| 3     | Ni–C1   | 1.84   | 1.84   | 1.94   | 1.84   |
| 4     | Ni–C2   | 1.89   | 1.97   | 1.97   | 1.89   |
|       | Wiberg Bond Index (WBI) |        |        |        |        |
| 5     | C1–C2   | 2.82   | 2.20   | 2.30   | 2.17   |
| 6     | Ni–C1   | 0.43   | 0.31   | 0.31   | 0.42   |
| 7     | Ni–C2   | 0.39   | 0.31   | 0.31   | 0.39   |

*Geometry optimizations of [(p-tolL1)Ni(HC≡CPh)] (p-tol4-Ph), [(p-tolL2)Ni(HC≡CPh)] (p-tol5-Ph), and [(PhL3)Ni(HC≡CPh)] (Ph6-Ph) were performed at a B3LYP/6-31g(d,p) level of theory. WBIs were calculated by NBO analysis at a B3LYP/def2TZVP level of theory from the optimized geometries. Hydrogen atoms have been omitted for clarity.

Scheme 4. Ligand Exchange Reaction between the Benzophenone Imine from Ph4-L1 and Different Kinds of Substrates and Coligands
Table 3. Catalytic Comparison for the Cyclotrimerization of Phenylacetylene (8), Methyl Propiolate (9), and Methyl Propargyl Ether (10), Using Catalysts $p^{\text{tol}}$L1 to Ph3, and the Ph$^6$L4 System$^\text{a}$

| entry | substrate (-R1) | catalyst | yield 1,2,4- (a) [%] | yield 1,3,5- (b) [%] | yield COTs (c) [%] | ratio a/b/c |
|-------|-----------------|----------|----------------------|----------------------|------------------|------------|
| 1     | Phenyl acetylene, 8 (-Ph) | $p^{\text{tol}}$L1 | 68.9 | 3.2 | 0 | 97:3:0 |
|       |                  | $p^{\text{tol}}$L2 | 3.1 | 1.9 | 0 | 62:38:0 |
|       |                  | $p^{\text{tol}}$L3 | 2.8 | 0.2 | 0 | 94:6:0 |
|       |                  | $p^{\text{tol}}$L4 + Ni(cod)$_2$ | 4.6 | 1.9 | 0 | 70:30:0 |
| 2     | Methyl propiolate, 9 (-CO:Me) | $p^{\text{tol}}$L1 | 90.2 | 6.3 | 2.5 | 91:7:2 |
|       |                  | $p^{\text{tol}}$L2 | 24.5 | 2.1 | 7.5 | 72:6:22 |
|       |                  | $p^{\text{tol}}$L3 | 65.0 | 12.3 | 6.5 | 77:15:8 |
|       |                  | $p^{\text{tol}}$L4 + Ni(cod)$_2$ | 14.0 | 3.0 | 32 | 29:6:65 |
| 3     | Methyl propargyl ether, 10 (-CH$_2$OMe) | $p^{\text{tol}}$L1 | 71.6 | 6.9 | 0 | 90:10:0 |
|       |                  | $p^{\text{tol}}$L2 | <1 | <1 | 0 | b |
|       |                  | $p^{\text{tol}}$L3 | <1 | <1 | 0 | b |
|       |                  | $p^{\text{tol}}$L4 + Ni(cod)$_2$ | <1 | <1 | 0 | b |

“Similar results were obtained when the active catalysts were generated in situ using $p^{\text{tol}}$L1 to Ph3, 1 equiv of Ni(cod)$_2$, and the corresponding terminal alkyn (Supporting Information; Table S4). Yields and ratios were averaged over two runs (Supporting Information; Tables S2 and S3). Yields are isolated yields. Ratios were determined by $^1$H NMR.$^\text{a}$For systems $p^{\text{tol}}$L2, Ph3, and $p^{\text{tol}}$L4, only trace amounts of products 10a and 10b were detected in which an accurate determination of the ratio between the two regio-isomers was not possible.

Ph$^6$-Ph. The smaller Ni–C1 and Ni–C2 WBIs (Table 2, entries 6 and 7) of 0.31 in $p^{\text{tol}}$L5-Ph corroborate a weaker orbital interaction between the HC≡CPh ligand and the Ni-center in the triphosphine complex $p^{\text{tol}}$5-Ph compared to $p^{\text{tol}}$4-Ph (WBIs of 0.43 and 0.39) and Ph$^6$-Ph (WBIs of 0.42 and 0.39).

In summary, we showed in this section that ligands $p^{\text{tol}}$L1–Ph3 all form Ni(0)–alkyne complexes with phenylacetylene. The triphosphine $p^{\text{tol}}$L2 binds in a tridentate mode in $p^{\text{tol}}$5-Ph, resulting in unusually weak activation of the alkyne, while $p^{\text{tol}}$L3 acts as a bidentate ligand in the tricoordinate $p^{\text{tol}}$6-Ph, in which a strong Ni–alkyne interaction causes a high rotation barrier around the Ni–alkyne axis. The hemilabile ligand $p^{\text{tol}}$L1 is able to sample both binding modes: it binds as a bidentate ligand in $p^{\text{tol}}$4-Ph, resulting in a similar geometry as that of $p^{\text{tol}}$6-Ph, but the observed low rotation barrier around the Ni–alkyne axis is indicative of the ability of $p^{\text{tol}}$L1 to transiently adopt a tridentate mode.

Ligand Exchange Reactions on ($p^{\text{tol}}$L1)Ni(BP1). Having observed that the ketone moiety decodes into binding of an alkyn to the ($p^{\text{tol}}$L1)Ni fragment, we sought to probe the generality of this hemilabile behavior. NMR-tube experiments showed that the BP1 coligand can be reversibly exchanged with several types of ligands, such as benzonitrile ($K_{eq} \approx 2.7 \times 10^{-3}$; $\Delta G_{298.15} \approx 3.5$ kcal/mol), styrene ($K_{eq} \approx 1.5 \times 10^{-3}$; $\Delta G_{298.15} \approx 2.4$ kcal/mol), and diphenylacetylene ($K_{eq} \approx 6.1 \times 10^{-3}$; $\Delta G_{298.15} \approx 3.1$ kcal/mol), as depicted in Scheme 4 (see Supporting Information for more details). The proposed mode of coordination of the benzonitrile ligand in $p^{\text{tol}}$5-PhCN on DFT calculations, which predict the $\eta^1$-(CN) binding to be 9.4 kcal/mol energetically less stable than the $\eta^1$-(N) coordination mode (Supporting Information; Table S11). With triphenylphosphine, the exchange is irreversible. In every case, with the exception of diphenylacetylene, $^{13}$C NMR demonstrates that the ketone moiety is still bound to nickel (no peaks between 190 and 210 ppm). The coordinated ketone appears at 120.4 ppm (dt, $J_{CH} = 13.8$ Hz, $J_{C,H} = 4.4$ Hz) for the PPh$_3$ complex $p^{\text{tol}}$7-C$_{6}$H$_5$Ph and shows two chemically different methyl groups from the para-tolyl substituents at 1.99 ppm (s, 6H) and 1.96 ppm (s, 6H) in $^1$H NMR and at 21.2 and 21.1 ppm, respectively, in $^{13}$C NMR.

Unfortunately for the PhCN complex $p^{\text{tol}}$7-PhCN and for the styrene complex $p^{\text{tol}}$7-C$_2$H$_5$Ph, the carbon resonance of the bound ketone could not be assigned, as the weak signal is covered by those of the substrate and the starting complex $p^{\text{tol}}$1. However, for all of these complexes, $^1$H NMR shows that the two methyl groups from the para-tolyl substituents on the phosphine are not equivalent ($\delta_H = 2.04$ and 2.03 for $p^{\text{tol}}$7-C$_2$H$_5$Ph), which is also indicative of the pincer-type binding mode of $p^{\text{tol}}$L1 to nickel, with the central ketone moiety bound, as observed with $p^{\text{tol}}$1 and $p^{\text{tol}}$7-Ph$_3$, and in opposition to $p^{\text{tol}}$4-Ph. With the diphenylacetylenic complex $p^{\text{tol}}$7-C$_2$H$_5$Ph, the absence of interaction of the ketone is demonstrated by the presence of a triplet at 198.3 ppm ($J_{C,H} = 4.7$ Hz and with all four C–H being chemically equivalent ($\delta_H = 1.95$; $\delta_C = 21.2$), similar to the closely related terminal alkyne complex $p^{\text{tol}}$4-CH$_2$OMe. The difference in coordination between olefin and alkyne complexes is consistent with alkynes being stronger π-acceptors than olefins and illustrates the ability of the diphenylphosphine ketone framework to adapt its binding mode to the electronic properties of a substrate.

Catalytic Comparison. Having shown that the hemilabile diphenylphosphine-ketone ligand $p^{\text{tol}}$L1 is able to adapt its coordination mode to a substrate bound to Ni(0), we turn to its performance as a supporting ligand in the cyclotrimetrization of alkynes. We compare hemilabile $p^{\text{tol}}$L1 with the strong tridentate $p^{\text{tol}}$L2 and the bidentate Ph$_3$ to delineate specific effects of the hemilabile behavior. In addition, the smaller bite-angle rac-BINAP (Ph$_4$L4) system was also tested.
Terminal alkyne substrate with diverse electronic properties were selected for comparison: first, phenylacetylene (8), as a standard aryl-substituted substrate; second, methyl propiolate (9), as electron poor alkyne and since its additional oligomerization into cyclooctatetraene (COT) regio-isomers is commonly observed;59 and finally, methyl propargyl ether (10) as an electron rich substrate. The catalytic outcome of the reaction of these alkynes with 0.5 mol % of isolated BPI-catalysts \( \text{p-tol}^{-1} \), \( \text{p-tol}^{-2} \), and \( \text{PhL}^{-3} \) and in situ generated \( \text{PhL}^{-4} \) catalyst at room temperature was analyzed. The organic products were separated from the reaction mixture as a mixture of 1,2,4- (a) and 1,3,5- (b) substituted arenes, in addition to cyclo-tetramerization products (when applicable), COTs (c), in which their relative ratio was determined by \(^1\text{H} \) NMR, as described in Table 3. To exclude a particular role of the BPI or cod ligands, the active catalysts were also generated in situ by mixing \( \text{p-tol}^{-1} \text{L}^{-1} - \text{PhL}^{-3} \) with 1 equiv of Ni(cod)_2 and 200 equiv of the corresponding alkyne. The reactions display similar activity as the values reported in Table 3 (Supporting Information; Table S4) and form the same resting states (respectively, \( \text{p-tol}^{-4}, \text{p-tol}^{-5} - \text{R}^{-1}, \text{p-tol}^{-6} - \text{R}^{-1} \) under these conditions.

Mixing phenylacetylene (8) with 0.5 mol % of \( \text{p-tol}^{-1} \) in toluene at room temperature for 16 h yields 86.9% of 1,2,4-triphenylbenzene (8a) and 3.2% of 1,3,5-triphenylbenzene (8b), in an isomeric ratio of 97:3. Under the same conditions, the complexes \( \text{p-tol}^{-2} \) and \( \text{PhL}^{-3} \) and the \( \text{PhL}^{-4} \text{Ni} \) system afforded only low yields of 8a: 3.1%, 2.8%, and 4.6%, respectively. In addition, a lower regioselectivity toward the 1,2,4 isomers of 62:38 and 70:30 compared to the 1,3,5 isomer was observed with \( \text{p-tol}^{-2} \) and \( \text{PhL}^{-4} + \text{Ni(cod)}_2 \) respectively. With the more electron poor alkyne methyl propiolate (9), the reaction catalyzed by \( \text{p-tol}^{-1} \) led to nearly exclusive cyclotrimeration with the formation of the 1,2,4-isomer 9a in a ratio of 91:7 compared to its 1,3,5 analogue 9b and with a yield of 90.2%. Only small amounts of the cyclotrimers, tetramethyl-cyclooctatetraene-tetracarboxylates (9c) are observed, in a ratio of 2:98 compared to the trimerization products. In contrast, the yields obtained for 9a with the other catalysts in the series range from 14.0% to 65.0%. More importantly, catalysts \( \text{p-tol}^{-2} \), \( \text{PhL}^{-3} \), and the \( \text{PhL}^{-4} \) system display lower selectivity. The tridentate triphosphine catalyst \( \text{p-tol}^{-2} \) exhibits a regioselectivity of 92:8 (1,2,4-/1,3,5-isomer) and produces cyclo-trimerization products in a 22:78 ratio compared to the cyclooctatetraene-tetracarboxylates (9c) are observed, in a ratio of 2:98 compared to the trimerization products. In contrast, the yields obtained for 9a with the other catalysts in the series range from 14.0% to 65.0%. More importantly, catalysts \( \text{p-tol}^{-2} \), \( \text{PhL}^{-3} \), and the \( \text{PhL}^{-4} \) system display lower selectivity. The tridentate triphosphine catalyst \( \text{p-tol}^{-2} \) exhibits a regioselectivity of 92:8 (1,2,4-/1,3,5-isomer) and produces cyclo-tetramerization products. The bidentate systems \( \text{PhL}^{-3} \) and \( \text{PhL}^{-4} \) are also less selective and lead to the formation of 9a in 84:16 and 82:18, respectively, compared to 1,3,5-benzene product 9b. The bidentate catalyst \( \text{PhL}^{-3} \) displays good chemoselectivity (92:8) toward cyclo-trimerization, whereas the other diphosphine system \( \text{PhL}^{-4} \) appears to even favor cyclo-octatetraene-tetracarboxylate products 9c (35:65). Finally, methyl propargyl ether (10), bearing an electron rich substituent was also tested and afforded lower yields than 8 and 9. With the ketone-based catalyst \( \text{p-tol}^{-1} \), 10 is converted into 1,2,4-tris(methoxymethyl)-benzene (10a) in a yield of 71.6%, and the regioselectivity toward 10a remains high (90:10). Under the same conditions, the other complexes showed poor activity (less than 1% total yield). Overall, for the three examined substrates, catalyst \( \text{p-tol}^{-1} \), bearing the hemilabile diphosphine benzophenone ligand \( \text{p-tol}^{-1} \), was shown to be more active and more selective toward the formation of the 1,2,4-trisubstituted benzene product.

**Additional Substrates.** In addition to the substrates described in Table 3, catalyst \( \text{p-tol}^{-1} \) was applied to the cyclo-trimerization of terminal alkynes 11a to 13a with high

| Entry | Substrate (-R') | Product | Yield [%] | Ratio 1,2,4-:1,3,5-trimer | Ratio trimer:COTs |
|-------|-----------------|---------|-----------|--------------------------|------------------|
| 1[a]  | \( \text{-CO}_2\text{Et} \) | 11      | 90        | 93.7:1                   | 98:2             |
| 2[b]  | \( \text{-p-F-C}_2\text{H}_5 \) | 12      | 93        | 95.5:1                   | 100:0            |
| 3[b]  | \( \text{-p-OMe-C}_2\text{H}_5 \) | 13      | 65        | 95.5:1                   | 100:0            |

*a*Reaction temperature = room temperature. *b*Reaction temperature = 50 °C. *c*Reported yields are isolated yield for the 1,2,4-trisubstituted benzene isomer. Isomeric ratios between the 1,2,4 and 1,3,5 isomer and between the trimers and tetramers were determined by \(^1\text{H} \) NMR. Yields and ratios were averaged over two runs (Supporting Information; Table S5). Catalytic method A was applied (see experimental part).
selectivity for 1,2,4-substituted benzenes and in good isolated yields (>65%, Table 4). Ethyl propiolate (11) (entry 1) affords triethylbenzene-1,2,4-tricarboxylate (11a) at room temperature. At 50 °C, 4-ethynylanisole (13) produces the desired 1,2,4-cyclotrimerization product in a lower yield than the weakly electron-withdrawing analogue 1-ethyl-4-fluorobenzene (12), supporting a preference for electron-withdrawing substrate (entries 2 and 3). The preference for electron poor alkynes is commonly observed in Ni-catalyzed cyclotrimerization of terminal alkynes. A catalyst loading of 0.05 mol % mediated the cyclotrimerization of ethyl propiolate (11) into triethylbenzene-1,2,4-tricarboxylate (11a) in 87% isolated yield, reaching a TON of 1740 after 16 h.

Mechanistic Considerations. The comparison study between \( P^{\text{tol1}} \) and the other Ni-systems \( (P^{\text{tol2}}, \text{Ph}_{3}, \text{and PhL}_{4}) \) strongly suggests that the hemilabile \( \pi \)-acceptor moiety contributes to the high catalytic performance. In this section, the role of the ketone fragment in the improved catalytic performance of \( P^{\text{tol1}} \) is studied and supported by computational modeling of some targeted compounds. To address the question, an overview of the general mechanism in metal-catalyzed [2 + 2 + 2] alkyny cyclotrimerization is discussed first (Scheme 5), followed by differences in reactivity among the three catalysts tested in the comparison study.

Scheme 5 shows a commonly proposed mechanism for the cyclotrimerization of acetylene catalyzed by transition metals. For base metals, most mechanistic studies have been carried out using cobalt complexes as catalysts. From the acetylene metal complex \( \text{14-C}\text{H}_2 \), the association of a second molecule of acetylene generates complex \( \text{14-}(\text{C}\text{H}_2)_2 \), which requires an open coordination site in \( \text{14-C}\text{H}_2 \). Next, the oxidative coupling of the two coordinated alkyne fragments from \( \text{14-}(\text{C}\text{H}_2)_2 \) gives rise to the key metallacyclopentadiene intermediate. This step is generally thought to be rate determining. The metallacyclopentadiene intermediate can be best described as one of two resonance structures, 14-MCP or 14-MCP′, depending on the nature of metal complex used. For example Saâ et al. calculated that CpRuCl \( (\text{Cp} = \text{cyclopentadiene}) \)-catalyzed alkyne cyclotrimerization proceeds via 14-MCP′, while the cobalt system CpCo proceeds via 14-MCP. Late transition metals tend to favor the concerted-oxidative cyclization between two alkynes and the low-valent metal center. However, a stepwise zwitterionic diradical pathway, involving the formation of a \( \sigma(\text{C}–\text{C}) \) bond and one \( \text{Ni}–\text{C} \) bond cannot be excluded. When acetylene is substituted, the formation of the substituted metallacyclopentadiene is of importance as different 14-MCP regio-isomers can be generated. The substituted 14-MCP will thus dictate the overall selectivity toward the product formation of the 1,2,4- or 1,3,5-trisubstituted benzene regio-isomer (more precisely the transition state TS1 between the bisalkyne and metallacyclopentadiene intermediate). In the last step (insertion of the third alkyne), different mechanisms have been proposed. The insertion of a third alkyne could either proceed via a Diels–Alder type [4 + 2] cycloaddition, in which the metal does not participate in the bond formation (Scheme 5 pathway a), or with the assistance of the metal, prior to the new C–C bond formation (Scheme 5 pathway b). Metallanorbornadiene \( (14-[4 + 2]) \) is frequently presented as an unstable species and immediately collapses to arene, forming a metal–arene adduct. As regards pathway b, the coordination of the third alkyne is followed by either migratory insertion (metallacycloheptatriene 14-I) or \( [2 + 2] \) cycloaddition (cycloadduct 14-[2 + 2]). These complexes can also be formed in a concerted way, without involving the direct formation of an acetylene metallacyclopentadiene complex 14-AMCP, but still with participation of the metal center. It has also been suggested that an additional pathway could occur via an intermolecular \( [4 + 2] \) cycloaddition forming the \( \eta^4 \)-bound intermediate, 14-[4 + 2]. Pathway a is likely to happen for strong donor ligands or solvents. The insertion of a fourth alkyne (especially if the intermediate formed is 14-I) leads to formation of COT side products. Eventually, the formation of the benzene product happens by either reductive elimination or ligand exchange of benzene with a molecule of acetylene (cycloadduct 14-[2 + 2]) rearranges itself prior to the reductive elimination).

In this overall picture, several effects of the hemilabile \( \pi \)-acceptor ketone moiety ion complex \( P^{\text{tol1}} \) can be envisioned. First, the hemilabile interaction of the ketone unit can be
thought to facilitate the alkyne uptake, especially in comparison with the tridentate phosphine system $p$-tol2. In situ NMR spectroscopy experiments with the three complexes $p$-tol1, $p$-tol2, and $p$-tol3 showed that the corresponding monoalkyne complexes $p$-tol4-R1-$p$-tol6-R1 are the resting states of the catalyst in all cases. For the ketone catalyst $p$-tol1 and the bidentate catalysts $p$-tol2, these resting states ($p$-tol4-R1 and $p$-tol6-R1) are 16 VE species that can readily accept an incoming alkyne molecule, while the corresponding triphosphine complex $p$-tol5-R1 is saturated (18 VE). Most probably, coordination of a second equivalent of alkyne to $p$-tol5-R1 requires decoordination of one of the phosphorus atoms, which is likely to raise the overall reaction barrier and result in lower activity under the same conditions (Supporting Information; Scheme S4). The unique feature of the ketone unit is that the tricoordinate alkyne complex can be accessed directly from the tetracoordinate precursor $p$-tol1. A similar process can be thought to happen at the end of the catalytic cycle: the ketone may accelerate product release by transient coordination to Ni(0), which would explain the lower propensity of $p$-tol1 to form cyclooctatetraenes.

Second, the interaction of the ketone with the nickel center could help to stabilize transient intermediates, such as the key metallacyclopentadiene 14-MCP species. In order to assess structural differences between the metallacyclopentadiene supported by the different ligands, $p$-tol1, $p$-tol2, and $p$-tol3, we made use of geometry optimization by DFT calculation at a B3LYP/6-31g(d,p) level of theory using acetylene as a model substrate.

Unsurprisingly, the ketone moiety is not bound in the bisalkyne diphosphine benzophenone complex $p$-tol15-(C2H2)$_2$. However, geometry optimization of the metallacyclopentadiene intermediate formed by oxidative coupling reveals a pentacoordinate geometry in which the ketone is bound to the metal ($p$-tol16-MCP, Scheme 6), suggesting hemilabile behavior of $p$-tol1 in the key oxidative coupling step. Respective Ni–O and Ni–C distances of 1.93 and 1.99 Å, as well as an elongated C–O bond (1.35 Å), indicate a strong interaction with the metal center. In addition, a P1–Ni–P2 angle of 171° results in an approximate trigonal-bipyramidal geometry with apical P atoms. The fact that the C=O unit binds side-on to a formal Ni(II) center can be surprising at first sight in view of its low propensity to bind to divalent metal halides.24,25 This can be understood by a synergistic interaction between a strongly σ-donating bidentate hydrocarbonyl ligand and the strongly π-accepting ketone ligand in the equatorial plane of the trigonal bipyramid.

For comparison, the geometry of the metallacycles supported by the triphosphine $p$-tol2 and the diphosphine ether $p$-tol3 ligands were also optimized (Figure 7). The triphosphine-supported [(tol15)-Ni(C$_{10}$H$_{12}$)] ($p$-tol17-MCP) adopts a similar trigonal bipyramidal geometry to $p$-tol16-MCP. This binding mode may contribute to explain the differences in reactivity with the rac-BINAP system, for which this mode is inaccessible. In contrast, [(tol15)-Ni(C$_{10}$H$_{12}$)] ($p$-tol18-MCP) exhibits a distorted square planar geometry, in which the Ph3L3 is bound in bidentate manner (N–O = 3.20 Å; WBI(Ni–O) < 0.01). Hence, the metallacycle in $p$-tol18-MCP is not stabilized by its central ether donor group, which may partly explain the lower regioselectivity of $p$-tol3 is toward the 1,2,4-trisubstituted arene cyclotrimerization product. Furthermore, no significant modifications of the P1–O–P2 bite angle from phenylacetylene analogue $p$-tol6-Ph are visible.

At this point, we showed that the hemilabile character of the ketone ligand $p$-tol1 contributes to higher activity and selectivity in the cyclotrimerization of terminal alkynes. The combination of the two effects presented in this section, that is, decoordination and coordination of the C=O unit to assist the substrate uptake and stabilize the key metallacyclopentadiene intermediate, can explain its superior performance. Exchanging the C=O moiety in complex $p$-tol1 with a stronger donor atom, like a phosphine group (P–Ph) or with a bidentate ligand (O as central atom) decreases either the activity or the selectivity of the overall process.

Therefore, based on the computational and experimental observations obtained from this study, a simplified catalytic cycle is proposed for the cyclotrimerization of terminal alkynes catalyzed by the nickel diphosphine benzophenone system (Scheme 7). The resting state, $p$-tol4-R1, can be generated by ligand exchange from $p$-tol1 or in situ from the ligand and Ni(cod)$_2$. The in situ system and $p$-tol1 operate at similar rates of product formation under the same tested conditions (similar percentage of isolated yields), showing that the dissociation of the coligand (cod vs BPI) and competitive binding with the metal center does not affect the final yields, as long as $p$-tol4-R1 can be formed. At this step, the ketone is not bound, which facilitates coordination of the second alkyne to generate Ni-bisalkyne $p$-tol15-(C$_{2}$HR)$_2$. The next step (3) involves the C–C oxidative coupling, which is coupled to coordination of the ketone to nickel in $p$-tol1 for a new turnover (4). Throughout the reaction coordinate, the ligand can adapt its geometry by the labile interaction of C=O to Ni and stabilize intermediates.

**CONCLUSIONS**

In conclusion, we have reported here the synthesis and characterization of Ni(0) complexes, incorporating a diphosphine ketone ($p$-tol1), triphosphine ($p$-tol2), and diphosphine ether ($p$-tol3) ligand, in which the binding mode of the stabilizing imine or alkyne coligand can change according to the structural and electronic characteristics of the supporting ligand. The characterization of [(tol15)-Ni(HC=CPH)] ($p$-tol18-Ph) provides a rare example of weak activation of alkynes by nickel complexes, attributed to its...
unique coordination geometry. We show in this study that \([p\text{-tol}L1] \text{Ni(BPI)}\) \((p\text{-tol}1)\) is an effective catalyst in the \([2 + 2 + 2]\) cyclotrimerization of terminal alkynes. In contrast, related \(\text{Ni}(0)\) complexes \([p\text{-tol}L2] \text{Ni(BPI)}\) \((p\text{-tol}2)\) and \([\text{PhL3}] \text{Ni(BPI)}\) \((\text{Ph3})\) are less active or less selective toward the 1,2,4-trisubstituted benzene cyclotrimerization product under similar conditions. We attribute the enhanced reactivity of \(p\text{-tol}1\) to the hemilabile character of its diphosphine benzophenone ligand. In situ NMR spectroscopy and DFT calculations suggest that C═O hemilability may facilitate substrate uptake and assist the key oxidative coupling step. A more detailed mechanistic study of the reaction and applications of diphosphine-ketone ligands to other catalytic processes are actively investigated in our laboratories.

**EXPERIMENTAL SECTION**

**Chemicals and Reagents.** Unless otherwise noted, all reactions were carried out under an inert \(\text{N}_2(\text{g})\) atmosphere, using standard Schlenk line or glovebox techniques, and stirred magnetically. Silica gel \(\text{P}_{60}\) (SiliCycle) was used for column chromatography. Analytical thin layer chromatography was performed using SiliCycle 60 \(\text{F}_{254}\) silica gel (precoated sheets, 0.20 mm thick) from Merck KGaA (Darmstadt, Germany). Deuterated solvents were purchased from Cambridge Isotope Laboratory Incorporation (Cambridge, USA) and were degassed by standard freeze–thaw–pump procedure and subsequently stored over molecular sieves. Common solvents were purified using a MBRAUN MB SPS-80 purification system or by standard distillation techniques or both. They were degassed by bubbling \(\text{N}_2(\text{g})\) through the liquid for at least
30 min and then stored over molecular sieves. Non-halogenated solvents were tested with a standard purple solution of sodium benzenephone ketyl in tetrahydrofuran to confirm effective oxygen and moisture removal. Other solvents were checked for water content by the Karl Fischer titration or by 1H NMR. Liquid chemicals were first degassed by standard freeze–pump–thaw procedures or purged with N2(g) and then stored over molecular sieves prior to use. Phosphorus-containing compounds were checked for oxidation by 31P NMR before use. O-(Bromophenyl)-diphenylphosphine, 2,3,47 o-(bromophenyl)-di-p-tolylyphosphine, 2,5 2,2'-bis-(diphenylphosphino)benzophene (PbL1), 25 and 2,2'-bis(di-p-tolylyphosphino)benzophene (Pb2L1) 25 were synthesized according to reported procedures. All other reagents and starting materials were purchased from commercial sources and used without further purification, except when specified.

**Physical Methods.** The 1H, 13C, 31P, and 19F NMR (400, 100, 161, and 400 MHz, respectively) spectra were recorded at 297 K on an Agilent MRF 400 spectrometer. All chemical shifts are reported in the standard δ notation of parts per million, referenced to residual peak of the solvent, as determined relative to Me6Si (δ = 0 ppm).66 Variable-temperature (VT) NMR were recorded in d-toluene from −85 °C to room temperature. Infrared spectra were recorded using a PerkinElmer Spectrum Two FT-IR spectrometer. For orbital (nBO) calculation, the NBO6 program, 26 up to the NLMO quasi Newton number 3) method. For NBO (natural bond orbital) calculation, the NBO6 program,68 up to the NLMO method. The transition states search was performed without any symmetry restraints and are either minima or transition states. Frequency analyses were performed on all calculations. The transition states search was performed using the QST3 (synchronous transit-guided quasi Newton number 3) method. For NBO (natural bond orbital) calculation, the NBO6 program, 50 up to the NLMO (natural localized molecular orbital) basis set, was used at B3LYP/def2TZVP level of theory from the optimized geometry. Pictures derived from DFT calculations have been generated using the GaussView software. The B3LYP functional was chosen as it has been shown to be accurate for geometry optimization of related metal compounds 69 including closely related PbL1–metal systems.24,25

**Synthetic Methods. Ligand: Bis(2-di-p-tolylyphosphino) Phenylphosphine (Pb2L2).** Adapted from the procedure by Koshevoy et al. 24 To a suspension of (o-bromophenyl)di-p-tolylyphosphine (0.01 g, 16.6 mmol) in dried and degassed THF (76 mL), a hexane solution of n-ButLi (1.6 M, 8.50 mL, 13.5 mmol) was added dropwise within 10 min at −78 °C under a N2 atmosphere. The reaction mixture was stirred at −78 °C for 1 h, and PbPhCl2 (0.92 mL, 6.77 mmol) was added dropwise. The mixture was stirred at this temperature for one additional hour and then allowed to slowly warm up to room temperature. The solution was stirred at room temperature for three more hours and then quenched with MeOH (30 mL). The volatiles were removed in vacuo, and the yellow amorphous residue was washed with MeOH (5 × 15 mL) to afford Pb2L2 as a white solid, which was dried overnight under vacuum (3.52 g, 5.10 mmol, 76%). 1H NMR (400 MHz, C6D6, 25 °C): δH 7.40–7.33 (ArH, m, 6H), 7.33–7.25 (ArH, m, 6H), 7.19–7.16 (ArH, m, 2H), 7.01–6.94 (ArH, m, 5H), 6.93–6.87 (ArH, m, 6H), 6.84 (ArH, d, JHH = 7.9 Hz, 4H), 2.03 (CH3, s, 6H), 2.01 (CH3, s, 6H). 31P NMR (161 MHz, C6D6, 25 °C): δP −14.8 (p-tolyl, 2P) −16.9 (PhP, 1P) [AB system, δAB = 155 Hz]. 13C NMR (100 MHz, C6D6, 25 °C): δC 145.6–144.8 (m, 138.4–138.1 (m), 138.0 (d, JCP = 12.7 Hz), 135.2–134.9 (m), 134.7 (t, JCP = 4.4 Hz), 134.6–134.3 (m), 129.6, 129.4 (t, JCP = 3.3 Hz), 129.1, 128.9, 128.2, 129.9, 21.2 (CH3), 21.2 (CH3). ATR-IR: ν [cm−1] = 3043, 1494, 1439, 1184, 1090, 806, 752, 504. HRMS (ESI, CH3CN, AgNO3): m/z calcd for [M + Ag]+ 793.1472; found 793.1605.

**Nickel Complexes.** [(PbL1)Ni(BP)] (Pb1). Ni(cod), (249 mg, 0.91 mmol), PbL1 (502 mg, 0.91 mmol), and benzophenone imine (181 mg, 0.92 mmol) were dissolved in dried degassed toluene (10 mL) under an inert atmosphere. The reaction mixture was stirred at room temperature for 20 min. Dried and degassed hexane (5 mL) was added to the resulting black solution, causing the precipitation of a black solid. The precipitate was collected by filtration, washed with hexane (3 × 4 mL), and dried under vacuum to afford Pb1 as a black powder (597 mg, 0.76 mmol, 83%). Single crystals suitable for X-ray diffraction and elemental analysis were obtained by slow exchange of hexane into a concentrated THF solution of Pb1.

1H NMR (400 MHz, C6D6, 25 °C): δH 7.90 (ArH, d, JHH = 7.2 Hz, 2H), 7.83 (ArH, d, JHH = 7.6 Hz, 2H), 7.75–7.70 (ArH, m, 4H), 7.23–7.19 (ArH, m, 2H). ATR-IR: ν [cm−1] = 3069, 2963, 1650, 1579, 1560, 1541, 1491, 1402, (t, JCP = 17.0 Hz), 138.7, 138.6 (t, JCP = 11.2 Hz), 136.4 (t, JCP = 13.7 Hz), 129.9 (t, JCP = 7.7 Hz), 132.6, 131.8 (t, JCP = 6.6 Hz), 129.62 (t, JCP = 4.0 Hz), 128.9–126.7 (m) 125.8, 125.5 (t, JCP = 8.1 Hz), 117.2 (C≡O, t, JCP = 7.6 Hz). ATR-IR: ν [cm−1] = 3163, 3050, 1583, 1404, 1432, 1478, 1432, 1303, 1294, 1091, 912, 778, 739, 692, 515. UV–vis (toluene): λmax [nm] 365, 574. Elemental analysis, Anal. Calcd for C45H36NiClO2P: C, 76.37; H, 5.56; N, 1.68. Found: C, 76.33; H, 5.58; N, 1.52. The crystal structure contains channels along the c-axis, which are filled with disordered hexane molecules (Supporting Information; Figure S110).

[(PbL1)Ni(BP)] (Pb2). Ni(cod), (108 mg, 0.39 mmol), Pb2L1 (238 mg, 0.39 mmol), and benzophenone imine (71 mg, 0.39 mmol) were dissolved in dried degassed toluene (10 mL) under inert atmosphere. The reaction mixture was stirred at room temperature for 20 min. The solvent was evaporated, and the crude mixture was subsequently dissolved in dried and degassed THF (5 mL). Dried and degassed hexane (5 mL) was added to the resulting black solution, causing the precipitation of a black solid. The precipitate was filtered, washed with...
hexane (3 × 4 mL), and dried under vacuum to afford p-tol1 as a black powder (221 mg, 0.31 mmol, 79%). Single crystals for elemental analysis were obtained by slow exchange of hexane into a concentrated toluene solution of p-tol1. 1H NMR (400 MHz, CDCl3, 25 °C): δ 10.01 (NH, s, 1H), 7.98 (ArH, d, JCH = 7.4 Hz, 2H), 7.88 (ArH, dd, JCH = 7.7, JH,P = 1.3, 2H), 7.66 (ArH, dt, JH,P = 7.9, JH,H = 4.6, 4H), 7.30–7.25 (ArH, m, 2H), 7.05 (ArH, dt, JH,H = 7.9 Hz, JH,P = 4.4 Hz), 6.97–6.88 (ArH, m, 6H), 6.86–6.73 (ArH, m, 14H), 2.11 (CH3, s, 6H), 2.09 (CH2, s, 6H). 31P NMR (161 MHz, CDCl3, 25 °C): Δδ 15.5 (s, 2P). 

In situ Generation of [p-tol1]Ni(H(CC═CR)] (p-tol1-R). Under an inert atmosphere, 1 equiv of [p-tol1]Ni(BP1) (p-tol1) was mixed with 1 equiv of a terminal alkylene and dissolved in dried degassed CDCl3 (0.6 mL). The solution was transferred into a Young-type NMR tube, and the mixture was analyzed. 31P and 1H NMR show the appearance of one new single species, [p-tol1]Ni(H(CC═CR)] (p-tol1-R), in addition to the partial release of BP1. High in situ yield was obtained with methyl propargyl ether (R = CH2OMe) as alkylene reactant, leading to the formation of [p-tol1]Ni(H(CC═CHOMe)] (p-tol1-4-CHOMe). The solution contains a mixture of p-tol1-4-CHOMe, p-tol1, BP1, and methyl propargyl ether. 1H NMR (400 MHz, CDCl3, 25 °C): δH 10.01 (p-tol1, NH, s, 1H), 9.82 (BP1, NH, br. s, 1H). 8.03 (p-tol1, ArH, d, JH,H = 7.4 Hz, 2H), 7.92 (p-tol1, ArH, dd, JH,P = 7.7, JH,H = 1.3, 2H), 7.70 (p-tol1, ArH, dt, JH,H = 7.9, JH,P = 4.6, 4H), 7.54 (p-tol1-4-CHOMe, p-tol1-ArH, td, JH,H = 8.0 Hz, JH,P = 7.2 Hz, 8H), 7.35–7.29 (p-tol1, ArH, m, 2H), 7.10 (p-tol1, ArH, dt, JH,H = 7.9 Hz, JH,P = 4.4 Hz), 7.02–6.92 (p-tol1, ArH, m, 6H), 6.91–6.76 (p-tol1, ArH, m, 14H), 6.74 (p-tol1-4-CHOMe, ArH, t, JH,H = 1.6 Hz, 2H), 6.66 (p-tol1-4-CHOMe, ArH, td, JH,H = 7.6 Hz, JH,P = 1.6 Hz, 2H), 3.32 (p-tol1-4-CHOMe, OCH3, s, 3H), 3.03 (HCCOCH3OMe, OCH3, s, 3H), 2.10 (p-tol1, CH2, s, 6H), 1.96 (HCCOCH3OMe, CH2, d, JH,H = 1.6 Hz, 2H), 1.67 (HCCOCH3OMe, CH2, d, JH,H = 1.6 Hz, 2H), 1.19 (HCCOCH3OMe, CH2, d, JH,H = 1.6 Hz, 2H), 1.19 (HCCOCH3OMe, CH2, d, JH,H = 1.6 Hz, 2H), 1.91 (p-tol1, CH2, s, 6H). 31P NMR (161 MHz, CDCl3, 25 °C): δ 33.3 (p-tol1-4-CHOMe, s, 2P), 15.5 (p-tol1, s, 2P).

13C NMR was acquired in order to locate the resonances from the carbonyl and methyl groups of the ligand of p-tol1-4-CHOMe. 13C NMR (100 MHz, CDCl3, 25 °C): δC 203.1 (C=O, t, JCC = 4.7 Hz), 22.2 (HCC, d, JCH = 2.3 Hz). Barely visible.
In Situ Generation of \[\text{CPh}\] for Analytical Comparison with \[\text{CPh}\]. Under inert atmosphere, Ni(cod)\(_2\) (7.6 mg, 0.028 mmol), Ph\(_3\)CPh (15.6 mg, 0.029 mmol), and diphenylacetylene (5.0 mg, 0.028 mmol) were combined together and diluted in C\(_6\)D\(_6\) (0.6 mL) at room temperature, a suspension of \[\text{Ni} \equiv \text{CPh}\] was formed. The same procedure as for the synthesis of \[\text{PhCPh}\] was followed, using Ni(cod)\(_2\) (292 mg, 1.06 mmol), Ph\(_3\)CPh (567 mg, 1.05 mmol), and phenylacetylene (108 mg, 1.06 mmol) were mixed together and dissolved in dried degassed toluene (7 mL). The reaction mixture was subsequently stirred at room temperature for 20 min. Precipitation of a yellow solid was observed after adding dried degassed hexane (10 mL) and leaving the solution to stand overnight. The resulting solid was filtered, washed with hexanes (5 × 5 mL), and dried under vacuum to afford \[\text{PhCPh}\] as a yellow powder (387 mg, 0.55 mmol, 53%).

**Synthesis of Deuterated Analogue of \[\text{PhCPh}\]**. The same experimental procedure as for the synthesis of \[\text{PhCPh}\] was followed, using Ni(cod)\(_2\) (50 mg, 0.18 mmol), Ph\(_3\)CPh (99 mg, 0.18 mmol), and diphenylacetylene (19 mg, 0.18 mmol) as starting materials. \[\text{NtDC(Ph)CPh}\] was isolated as a yellow powder (60 mg, 0.08 mmol, 48%).  

**Synthesis of Deuterated Analogue of \[\text{PhCPh}\]**. Under inert atmosphere and at room temperature, a suspension of \[\text{NtDC(Ph)CPh}\] was formed. The same procedure as for the synthesis of \[\text{PhCPh}\] was followed, using Ni(cod)\(_2\) (30 mg, 0.10 mmol), Ph\(_3\)CPh (70 mg, 0.10 mmol), and phenylacetylene (11 mg, 0.10 mmol). \[\text{NtDC(Ph)CPh}\] was isolated as a red solid in a 74% yield (63 mg, 0.07 mmol). 

**Alternative Synthesis of \[\text{CPh}\]**. Under inert atmosphere, Ni(cod)\(_2\) (80 mg, 0.29 mmol), Ph\(_3\)CPh (200 mg, 0.29 mmol), and phenylacetylene (32 mg, 0.31 mmol) were mixed together and dissolved in dried degassed toluene (5 mL). The reaction mixture was subsequently stirred at room temperature for 1 h. Precipitation of a red solid was observed after adding dried degassed hexane (10 mL) and leaving the solution to stand overnight in the freezer at −35 °C. The resulting solid was filtered, washed with cold hexane (5 × 5 mL), and dried under vacuum to afford \[\text{CPh}\] as a red powder (169 mg, 0.20 mmol, 70%).

**Synthesis of Deuterated Analogue of \[\text{CPh}\]**. The same procedure as for the synthesis of \[\text{CPh}\] was followed, using Ni(cod)\(_2\) (30 mg, 0.10 mmol), Ph\(_3\)CPh (70 mg, 0.10 mmol), and phenylacetylene (11 mg, 0.10 mmol). \[\text{NtDC(Ph)CPh}\] was isolated as a red solid in a 74% yield (63 mg, 0.07 mmol). \[\text{NtDC(Ph)CPh}\] can also be generated from reaction of \[\text{PhCPh}\] with d-phenylacetylene in a 1:1 stoichiometry. 1H NMR (400 MHz, C\(_6\)D\(_6\), 25 °C): δ\(_H\) 7.94–7.87 (ArH, m, 4H), 7.46–7.40 (ArH, m, 4H), 7.30 (ArH, dd, J\(_{HH}\) = 6.8 Hz, J\(_{HP}\) = 1.4 Hz, 2H), 7.05–6.80 (ArH and \(\equiv\)CH, m, 18H), 6.75 (ArH, ddd, J\(_{HH}\) = 7.6 Hz, J\(_{HP}\) = 4.4 Hz, J\(_{PH}\) = 1.2 Hz, 1H), 6.66–6.56 (ArH, m, 3H), 6.39 (ArH, ddd, J\(_{HH}\) = 7.2 Hz, J\(_{HP}\) = 4.4 Hz, J\(_{PH}\) = 1.2 Hz, 1H), 6.32 (ArH, t, J\(_{HH}\) = 7.6 Hz, J\(_{PH}\) = 1.0 Hz, 1H), 1.3P NMR (161 MHz, C\(_6\)D\(_6\), 25 °C): δ\(_C\) 29.2 (d, J\(_{CP}\) = 22.5 Hz, 1P), 27.3 (d, J\(_{CP}\) = 22.5 Hz, 1P). 13C NMR (100 MHz, C\(_6\)D\(_6\), 25 °C): δ\(_C\) 29.2 (d, J\(_{CP}\) = 22.5 Hz, 1P), 27.3 (d, J\(_{CP}\) = 22.5 Hz, 1P).
temperature, turning the solution red. The mixture was transferred into a Young-type NMR tube and measured after 30 min of reaction. NMR analysis showed full conversion of the starting reagents and the release of cod, in addition to the single generation of a new species, \( [\text{PhL}3\text{Ni(PhC}=\text{CPh})] \).

1H NMR (400 MHz, CD_{3}D_{6}, 25 °C): \( \delta_H = 7.71\) to 7.61 (m, 8H), 7.18–7.13 (m, 4H), 6.97–7.02 (m, 6H), 6.86–6.90 (m, 6H), 6.73–6.60 (m, 4H), 6.55 (dd, \( J_{HF} = 0.76 \) Hz, 2H), 2.28 (t, \( J_{CF} = 5.0 \) Hz), 1.58 (t, \( J_{CF} = 9.0 \) Hz), 1.29, 1.27 (s, 6H, 2H), 2.03 (p, \( J_{CP} = 3.0 \) Hz).

1P NMR (161 MHz, CD_{3}D_{6}, 25 °C): \( \delta_P = 28.1 \) (s, 2P).

13C NMR (100 MHz, CD_{3}D_{6}, 25 °C): \( \delta_C = 79.2 \) (s, 8H). 31P NMR (161 MHz, CD_{3}D_{6}, 25 °C): \( \delta_P = 28.1 \) (s, 2P). 13C NMR (100 MHz, CD_{3}D_{6}, 25 °C): \( \delta_C = 79.2 \) (s, 8H). 31P NMR (161 MHz, CD_{3}D_{6}, 25 °C): \( \delta_P = 28.1 \) (s, 2P).

In Situ Generation of \( [\text{PhL}1\text{Ni(PhP)}] \) and \( [\text{PhL}1\text{Ni(PhP)}] \) in a Young-type NMR tube, and an NMR spectrum was recorded approximately 15 min after the two reactants have reacted. 31P NMR was recorded with a relaxation time of 21 s. For 1H NMR, the singlet at 10.01 ppm (1H) for \( \text{PhL}1\text{Ni(PhP)} \) and the singlet at 1.95 ppm (12H) for \( \text{PhL}1\text{Ni(PhP)} \) were selected. The solution was transferred to a Young-type NMR tube, and an NMR spectrum was recorded approximately 15 min after the two reactants have reacted.
diphenylacetylene (i.e., 50 equiv and 200 equiv compared to \( p^{tol1} \)). \(^1\)H NMR (400 MHz, \( CD_2\)O, 25 ºC): \( \delta_H \) 10.01 (\( p^{tol1} \), NH, s, 1H), 9.82 (BPI, NH, br, s, 1H), 8.03 (\( p^{tol1} \), ArH, d, \( J_{HH} = 7.4 \) Hz, 2H), 7.92 (2\( p^{tol1} \), ArH, dd, \( J_{HH} = 7.7, J_{HP} = 1.3, 2H \)), 7.70 (2\( p^{tol1} \), ArH, d, \( J_{HH} = 7.9, J_{HP} = 4.6, 4H \)), 7.52 (\( C_2Ph_2 \), PhH, dd, \( J_{HH} = 8.0 \) Hz, \( J_{HP} = 2.4 \) Hz, 2H), 7.35–7.29 (2\( p^{tol1} \), ArH, m, 2H), 7.23 (\( C_2Ph_2 \), PhH, d, \( J_{HH} = 7.2 \) Hz, 2H), 7.10 (\( p^{tol1} \), ArH, dt, \( J_{HH} = 7.9 \) Hz, \( J_{HP} = 4.4 \) Hz), 7.02–6.92 (2\( p^{tol1} \), ArH, m, 6H), 6.91–6.76 (2\( p^{tol1} \), ArH, m, 14H), 6.70 (\( p^{tol7}_CPh_2 \), PhH, d, \( J_{HH} = 8.0 \) Hz, 8H) 2.10 (\( p^{tol1} \), CH\(_2\), s, 6H), 1.95 (\( p^{tol7}_CPh_2 \), CH\(_2\), s, 12H), 1.91 (\( p^{tol1} \), CH\(_2\), s, 6H). \(^{31}\)P NMR (161 MHz, \( C_6D_6 \), 25 ºC): \( \delta_P \) 198.3 (C=O, \( t \), \( J_{CP} = 4.7 \) Hz), 21.2 (CH, 2). 

**Catalysis: General procedure for alkyne cyclotrimerization** (Table 3 and Table 4). **Method A.** In the glovebox, a toluene solution (3 mL) of alkyn was added slowly, within 1 min, to a toluene solution (3 mL) containing 0.5 mol % of the nickel catalyst (Ni-cat. \( p^{tol1} \) to Ni-cat. \( p^{tol4} \)). The solution was stirred at room temperature (substrates 8–11) or 50 ºC (substrates 12 and 13) for 16 h. The solution was then opened to air, and the organic layer was extracted with HCl 1 M (1 × 10 mL) and water (2 × 10 mL). The aqueous layer was washed with Et\(_2\)O (3 × 10 mL), and the organic portions were combined together, dried over MgSO\(_4\), filtered and concentrated under vacuum. The product was extracted with Et\(_2\)O and filtered through a silica plug. The final product was dried in vacuo and analyzed by GC-MS and NMR. The NMR characterization values of the organic catalytic products were compared with literature. The isomeric ratios were calculated and are reported according to \(^1\)H NMR. The reported values (yields and isomeric ratios) presented in Table 3 and Table 4 are the average values over two runs.

**Method B.** In the glovebox, a toluene solution (3 mL) of alkyn was added slowly, within 1 min, to a toluene solution (3 mL) containing 0.5 mol % of the ligand (\( p^{tol1}_L \) to \( p^{tol4}_L \)) and 0.5 mol % of Ni(cod). The solution was stirred at room temperature for 16 h. The solution was then opened to air, and the organic layer was extracted with HCl 1 M (1 × 10 mL) and water (2 × 10 mL). The aqueous layer was washed with Et\(_2\)O (3 × 10 mL), and the organic portions were combined together, dried over MgSO\(_4\), filtered, and concentrated under vacuum. The product was extracted with Et\(_2\)O and filtered through a silica plug. The final product was dried under vacuum and analyzed by GC-MS and NMR. The NMR characterization values of the organic catalytic products were compared with literature. The ratios were calculated and are reported according to \(^1\)H NMR.

**TON Experiment for the Cyclotrimerization of Ethyl Propiolate Catalyzed by \( p^{tol1} \).** In the glovebox, a toluene solution (3 mL) of ethyl propiolate (11, 232 mg, 2.37 mmol) was added slowly, within 1 min, into a toluene solution (3 mL) containing 0.05 mol % of the nickel catalyst \( p^{tol1} \) (1 mg, 1.2 \( \mu \)mol). The solution was stirred at room temperature for 16 h. The solution was then opened to air, and the organic layer was extracted with HCl 1 M (1 × 10 mL) and water (2 × 10 mL). The aqueous layer was washed with Et\(_2\)O (3 × 10 mL), and the organic portions were combined together, dried over MgSO\(_4\), filtered, and concentrated under vacuum. The product was extracted with Et\(_2\)O and filtered through a silica plug. The ratios between 1,2,4- (11a) and 1,3,5- (11b) regioisomers in addition to a minor amount of tetraethyl-cyclooctatetraene-tetracarboxylates (11c) were determined by \(^1\)H NMR in a ratio of 91:7:2. Triethylbenzene-1,2,4-tricarboxylate (11a) was obtained in a yield of 87% (202 mg, 0.69 mmol).

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