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Reactions of phenylacetylene with nickel POCOP-pincer hydride complexes resulting in different outcomes from their palladium analogues

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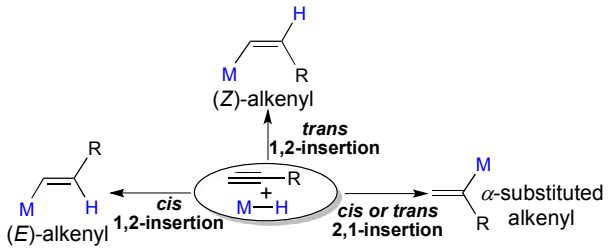
Nickel POCOP-pincer hydride complexes [2,6-$(R_2PO)_2C_6H_3$]NiH (R = ^{i}Pr, **4a**; R = ^{c}Pe = cyclopentyl, **4b**) react with phenylacetylene to generate [2,6-$(R_2PO)_2C_6H_3$]NiC(Ph)=CH_2 (**5a-b**) as the major product and (*E*)-[2,6-$(R_2PO)_2C_6H_3$]NiCH=CHPh (**6a-b**) as the minor product. The 2,1-insertion is more favorable than the 1,2-insertion and both pathways involve *cis* addition of Ni–H across the C≡C bond. Unlike the palladium case, alkynyl complexes [2,6-$(R_2PO)_2C_6H_3$]NiC≡CPh (**7a-b**) and H_2 are not produced in the nickel system. The more bulky hydride complex [2,6-(^{t}$Bu_2PO)_2C_6H_3$]NiH (**4c**) shows no reactivity towards phenylacetylene. Catalytic hydrogenation of phenylacetylene with **4a-b** takes place at an elevated temperature (70-100 ^{o}C) and proves to be heterogeneous. The structures of **5b**, **6a**, **7a** and **7b** have been studied by X-ray crystallography.

Introduction

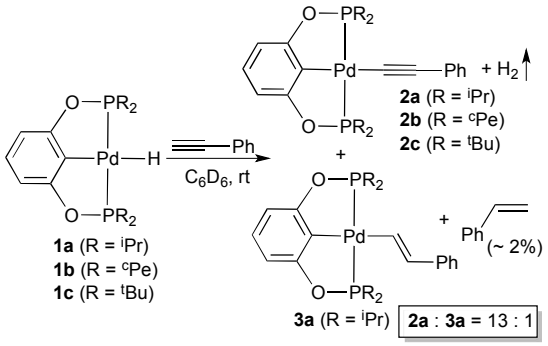
The reaction between an alkyne and a transition metal hydride is fundamentally important, and, in many catalytic processes (e.g., hydrogenation, hydrosilylation, hydroboration and oligomerization of alkynes), is the key step that determines the efficiency, regioselectivity and stereoselectivity of the overall catalytic transformation.[1] Understanding the factors governing the rate and reactivity pattern of metal hydrides towards alkynes is paramount to the rational design of more efficient and selective catalysts. The prototypical outcome of the reaction of a metal hydride with an alkyne involves *cis* addition of M–H across the C≡C bond.[2] *Trans* addition is also possible, though far less common than the *cis* addition, and typically requires at least one electron-withdrawing substituent such as CF_3 and CO_2Me.[2c,3] In some cases, the *cis*- and *trans*-addition products can interconvert depending on the reaction conditions.[4] When a terminal alkyne is employed (Scheme 1), three different types of insertion products can be expected.



Scheme 1

While the importance of utilizing earth abundant metals for homogeneous catalysis is emphasized in this themed issue, it would be particularly useful if the reactivity differences between precious metals and the more abundant first-row metals were well understood. As far as the reactions of metal hydrides with alkynes are concerned, very few reports have specifically examined how first-row metals behave differently from (or similar to) their heavy congeners. Bianchini and co-workers have shown that the reaction of (PP_3)RhH (PP_3 = $P(CH_2CH_2PPh_2)_3$) with 10 equiv of phenylacetylene at room temperature generates (PP_3)RhC≡CPh and styrene in ~40% yield after 24 h.[5] In contrast, (PP_3)CoH does not show any reactivity under the same reaction conditions.[6] The 1 : 1 reaction between (PP_3)RhH and ethyl propiolate affords the 2,1-insertion product (PP_3)RhC(CO_2Et)=CH_2 exclusively,[5] whereas a similar reaction with (PP_3)CoH gives a mixture of the unreacted (PP_3)CoH, (PP_3)CoC(CO_2Et)=CH_2 and (PP_3)CoC≡CCO_2Et in a 2 : 1 : 1 ratio.[6]

We have recently reported the reactions of phenylacetylene with palladium hydride complexes bearing a bis(phosphinite)-based pincer ligand, which is better known as a POCOP-pincer ligand.[7] When the phosphorus substituents are isopropyl groups, palladium alkynyl complex **2a** and (*E*)-alkenyl complex **3a** are formed in a 13 : 1 ratio (Scheme 2). Replacing the isopropyl groups with cyclopentyl or *tert*-butyl groups results in the alkynyl complex **2b** or **2c** as the only new palladium species. In any case, both H_2 and styrene can be detected. A palladium hydride containing a bis(phosphine)-based pincer (or PCP-pincer) ligand also reacts with phenylacetylene to give an alkynyl complex and styrene.[8]



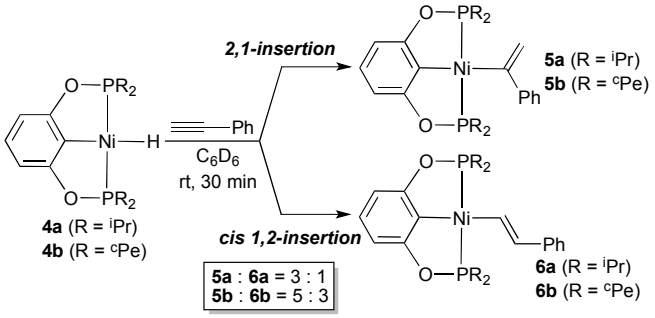
Scheme 2

In this paper, we will describe the reactions of phenylacetylene with the analogous nickel hydride complexes, which lead to insertion products rather than the alkynyl complexes and the elimination of H_2. We will also compare the catalytic performance of the nickel complexes with the palladium analogues in the hydrogenation of phenylacetylene.

Results and discussion

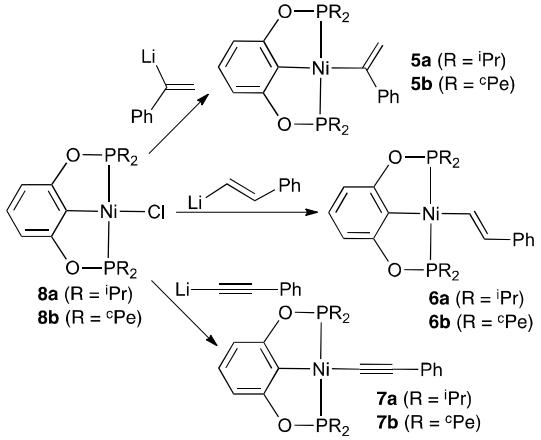
Reactions of nickel hydrides with phenylacetylene

The 1 : 1 reaction of nickel hydride **4a** with phenylacetylene in C_6D_6 was studied by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy (Scheme 3). At room temperature, **4a** (δ_P = 206.6 ppm) was consumed within 30 min and replaced by two new nickel species **5a** and **6a** (δ_P = 185.6 and 189.4 ppm) in a 3 : 1 ratio. Unlike the reaction of phenylacetylene with the palladium hydride **1a**, there was neither H_2 nor styrene detected by ^1H NMR. Instead, two broad resonances (5.35 and 6.32 ppm, $\Delta\nu_{1/2}$ = 23.7 Hz) with equal intensities emerged from the vinylic region, suggesting that the PhC≡CH triple bond had been reduced. The reaction of **4b** (δ_P = 199.7 ppm) with phenylacetylene was similar to **4a**; it went to completion within 30 min and generated two new pincer complexes **5b** and **6b** (δ_P = 179.5 and 180.5 ppm) in a 5 : 3 ratio. The ^1H NMR spectrum of the reaction was more informative due to somewhat sharper peaks. In addition to the vinylic resonances found at 5.40 and 6.39 ppm, a doublet was observed at 7.82 ppm with a relatively large coupling constant of 18.4 Hz. Based on the chemical shifts and coupling constant, it was hypothesized that the major species for the NiH/PhC≡CH reaction was a 2,1-insertion product and the minor one was an (*E*)-alkenyl complex as a result of *cis* 1,2-addition. The lack of H_2 evolution implied that for the nickel system, the alkynyl complex was probably not formed. Monitoring the reaction of phenylacetylene with **4c** by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, however, did not show any new species even when the reaction was carried out for 24 h. The increased steric crowding caused by the bulky ^{t}Bu groups explains the inactivity of **4c** because phenylacetylene is not able to approach close enough to the Ni–H bond for the reaction to occur.



Scheme 3

To confirm the proposed structures, independent syntheses of the alkenyl and alkynyl complexes were pursued (Scheme 4). The α-substituted alkenyl complexes **5a** and **5b** were readily prepared from the reactions of α-lithiostyrene (generated *in situ* from α-bromostyrene and ^{n}BuLi) with nickel POCOP-pincer chloride complexes **8a** and **8b**, respectively. The $^{31}P\{^1H\}$ NMR spectrum of **5a** in C_6D_6 matches the resonance at 185.6 ppm described above. The vinylic region of the ^1H NMR spectrum shows the resonances with the anticipated chemical shifts of 5.35 and 6.33 ppm; however, for the purified product, these resonances are much better resolved as two doublet of triplets. The small coupling constants ($^2J_{H\text{-}H}$ = 3.2 Hz and $^4J_{P\text{-}H}$ = 2.8 Hz) are consistent with each vinylic resonance being coupled by its geminal hydrogen and the pincer phosphorus atoms *via* a long-range coupling. The NMR data of **5b** also support that the α-substituted alkenyl complex is the major product for the reaction between **4b** and PhC≡CH.



Scheme 4

The (*E*)-alkenyl complexes **6a** and **6b** were prepared in a similar fashion from the corresponding nickel chloride complex and (*E*)-β-lithiostyrene, which is available from regiospecific lithiation of (*E*)-β-iodostyrene.[9] The $^{31}P\{^1H\}$ NMR spectrum of the pure product in C_6D_6 has one resonance (189.4 ppm for **6a** and 180.5 ppm for **6b**), and the chemical shift value confirms that *cis*-1,2-insertion is the pathway leading to the minor species (Scheme 3). In agreement with the *E* configuration, the ^1H NMR spectrum displays a large coupling constant (18.8 Hz for **6a**, 18.4 Hz for **6b**) that is characteristic of the *trans* vinylic hydrogens.

To rule out the possibility that an alkynyl complex formed but coincided with one of the ^{31}P resonances, **7a** and **7b** were independently synthesized from the nickel pincer chloride complexes and PhC≡CLi (generated from the lithiation of

PhC≡CH with ^{n}BuLi). The $^{31}P\{^{1}H\}$ and ^{1}H NMR show peaks that are absent from the reactions of nickel hydrides with phenylacetylene, thus confirming that the alkynyl complexes are not involved.

Structures of the alkenyl and alkynyl complexes

The structure of **5b** was more unambiguously established by X-ray crystallography. As expected, nickel is added to the more substituted end of the C=C bond (Fig. 1). While the Ni–C_{ipso} and Ni–P bond lengths of **5b** are comparable to those reported in the literature for nickel POCOP-pincer complexes,[10-12] the Ni–C(27) bond of 2.023(4) Å is noticeably longer. Zargarian and co-workers have shown that for PCP-pincer complexes of the type [(^{i}Pr$_2$PCH$_2$CH$_2$)$_2$CH]NiR (R = Me, Ph and C≡CMe), the Ni–R bond length follows the order of Ni–C_{sp3} > Ni–C_{sp2} > Ni–C_{sp}.[13] Consistent with this trend, the Ni–C(Ph)=CH_2 bond of **5b** is significantly longer than the Ni–C_{sp} bond of the alkynyl complex **7b** [1.874(3) Å] (*vide infra*) and nickel alkynyl and cyano complexes [1.87-1.94 Å] bearing a different POCOP-pincer ligand.[11e,g,j] It is, however, still longer than the Ni–C_{sp2} bond of the alkenyl complex **6a** [1.924(4) Å] (*vide infra*) and [(^{i}Pr$_2$PCH$_2$CH$_2$)$_2$CH]Ni–Ph [1.9440(20) Å],[13] as well as the Ni–C_{sp3} bond of nickel trifluoromethyl complexes [1.93-1.94 Å] supported by a POCOP- or PCP-pincer ligand.[11k,l] Only Zargarian's [(^{i}Pr$_2$PCH$_2$CH$_2$)$_2$CH]Ni–Me [2.0160(20) Å][13] and our [2,6-(^{i}Pr$_2$PO)$_2$C$_6$H$_3$]Ni–CH_2CN [2.0123(19) Å][12g] have a similarly long Ni–C bond distance. This suggests that the metal-carbon bond length is not solely decided by the hybridization of the carbon. The elongation of the Ni–C bond in **5b** likely stems from the steric clash between the pincer periphery and the phenyl ring. To further minimize the unfavorable steric interactions, the phenyl group adopts a conformation that is almost perpendicular to the pincer backbone; the dihedral angle between the two aromatic rings is measured to be 89.2(1)°. The phenyl group also orientates itself towards one side of the pincer arms and the C=CH_2 plane is rotated out of the phenyl plane by 33.1(2)° to avoid the steric repulsion from the *ortho* hydrogens. Even though the phenyl group is situated in close proximity to the nickel center, the closest H…Ni distances [H30…Ni = 3.00 Å; H28B…Ni = 2.87 Å] and the corresponding C–H…Ni angles [C30–H30…Ni = 105°; C28–H28B…Ni = 80°] fall outside of the ranges for agostic and anagostic interactions.[14] The chemical shifts of the phenyl and vinyl groups appear in the normal region for aromatic and vinylic hydrogens, further arguing against the possibility of having any Ni–H–C interaction.

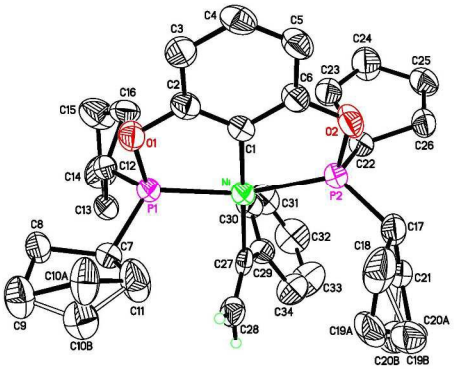


Fig. 1 ORTEP drawing of [2,6-(^{c}Pe$_2$PO)$_2$C$_6$H$_3$]NiC(Ph)=CH_2 (**5b**) at the 50 % probability level. Selected bond lengths (Å) and angles (°): Ni–C(1) 1.909(4), Ni–C(27) 2.023(4), Ni–P(1) 2.1393(11), Ni–P(2) 2.1446(11), C(27)–C(28) 1.267(6), C(27)–C(29) 1.453(6), P(1)–Ni–P(2) 163.80(5), C(1)–Ni–C(27) 175.77(16).

The X-ray structure of **6a** (Fig. 2) confirms the geometry of the C=C bond for the minor product. As in the case of the analogous palladium complex **3a**,[7] the phenyl group in **6a** is coplanar with the CH=CH plane and perpendicular to the pincer aromatic ring. Interestingly, the C(27)–C(28) bond is shorter for **6a** [1.276(6) Å] than **3a** [1.329(5) Å], perhaps due to more π-back donation from palladium. This bond length is, however, almost identical to that of **5b** [1.267(6) Å] even though the Ni–C(27) bond in the latter is longer by 0.10 Å. The elongation of the Ni–C bond is primarily offset by the shortening of the C–Ph bond [1.453(6) Å vs. 1.494(5) Å in **6a**], which in turn explains why the C=CH_2 plane is not coplanar with the phenyl ring.

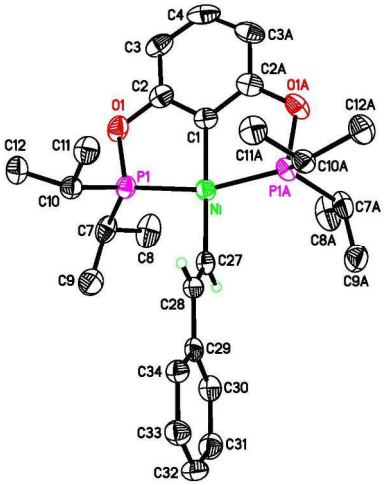


Fig. 2 ORTEP drawing of (*E*)-[2,6-(^{i}Pr$_2$PO)$_2$C$_6$H$_3$]NiCH=CHPh (**6a**) at the 50 % probability level. Selected bond lengths (Å) and angles (°): Ni–C(1) 1.903(4), Ni–C(27) 1.924(4), Ni–P(1) and Ni–P(1A) 2.1270(8), C(27)–C(28) 1.276(6), C(28)–C(29) 1.494(5), P(1)–Ni–P(1A) 164.40(5), C(1)–Ni–C(27) 179.55(18).

Complexes **7a** and **7b** crystallize readily from pentane or methanol, providing a good opportunity for crystallography study. Unlike the solid-state structures of the alkenyl complexes, the phenyl ring in the alkynyl complexes is not perpendicular to the pincer aromatic backbone (Figs 3 and 4), presumably because the phenyl ring is further extended out from the pincer core so that its rotation is not restricted. In fact, the dihedral angle between the two aromatic rings is scattered between 0° and 90° for nickel and palladium POCOP-pincer phenylacetylide complexes (Table 1). On the other hand, the C≡C bond length is consistently measured within the narrow range of 1.198-1.214 Å regardless of the metal and pincer ligand used. The C≡C stretching frequency of **7a** (2089 cm^{-1}) or **7b** (2082 cm^{-1}) is substantially lower than that of [2,6-(Ph_2PO)$_2$C$_6$H$_3$]NiC≡CPh (2105 cm^{-1}),[11g] which can be explained by less π-back donation from nickel when supported by the less-donating phenyl-substituted POCOP-pincer ligand. Using this electronic argument to rationalize the difference between **7a** and **7b** is however challenging, as the opposite trend of ν(C≡C) was observed in the palladium case (Table 1). Given the fact that *tert*-butyl-substituted phosphines are more basic than other alkyl-substituted phosphines,[15] one might have anticipated that among the palladium series, **2c** should have the

lowest wavenumber for the C≡C stretch. On the contrary, the C≡C stretching frequency of **2c** is higher than that of **2b** and **2a** by 5 cm^{-1} and 15 cm^{-1}, respectively. It is possible that the phosphorus donor ability in **2c** is compromised by slightly longer Pd–P bonds. In other words, steric effects may also play an important role in determining the strength of the C≡C bond. The electrochemistry study of nickel PCP-pincer complexes also shows that $[(^{i}Pr_2PCH_2CH_2)_2CH]NiBr$ bears a more electron-rich metal center than $[(^{t}Bu_2PCH_2CH_2)_2CH]NiBr$.[13]

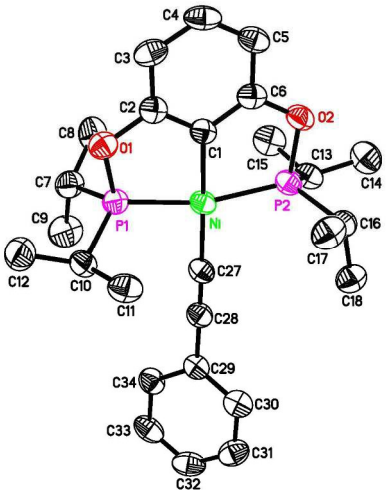


Fig. 3 ORTEP drawing of $[2,6\text{-}(^{i}Pr_2PO)_2C_6H_3]NiC{\equiv}CPh$ (**7a**) at the 50 % probability level. Selected bond lengths (Å) and angles (°): Ni–C(1) 1.895(4), Ni–C(27) 1.871(5), Ni–P(1) 2.1226(14), Ni–P(2) 2.1309(14), C(27)–C(28) 1.198(6), P(1)–Ni–P(2) 164.85(6), C(1)–Ni–C(27) 176.2(2).

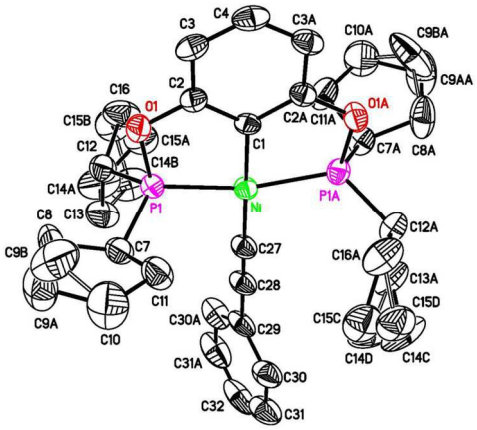


Fig. 4 ORTEP drawing of $[2,6\text{-}(^{c}Pe_2PO)_2C_6H_3]NiC{\equiv}CPh$ (**7b**) at the 50 % probability level. Selected bond lengths (Å) and angles (°): Ni–C(1) 1.889(3), Ni–C(27) 1.874(3), Ni–P(1) and Ni–P(1A) 2.1374(6), C(27)–C(28) 1.213(5), P(1)–Ni–P(1A) 164.42(4), C(1)–Ni–C(27) 180.0.

Table 1 IR and X-ray data for nickel and palladium POCOP-pincer phenylacetylide complexes

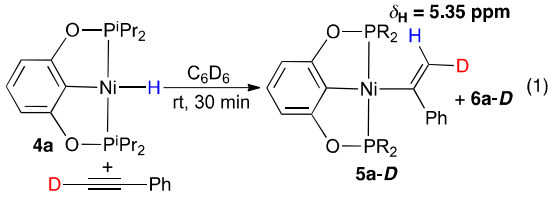
complex	dihedral angle (°)[d]	C≡C (Å)	M–P (Å)	ν(C≡C) (cm^{-1})
$[2,6\text{-}(^{i}Pr_2PO)_2C_6H_3]NiC{\equiv}CPh$ (**7a**)	42.3(2)	1.198(6)	2.1226(14), 2.1309(14)	2089
$[2,6\text{-}(^{c}Pe_2PO)_2C_6H_3]NiC{\equiv}CPh$ (**7b**)	63.6(1)	1.213(5)	2.1374(6)	2082
$[2,6\text{-}(Ph_2PO)_2C_6H_3]NiC{\equiv}CPh$[a]	16.39, 29.02	1.204(2)	2.1343(4), 2.1283(4)	2105
$[2,6\text{-}(^{i}Pr_2PO)_2C_6H_3]PdC{\equiv}CPh$ (**2a**)	85.66	1.214(3)	2.2597(7), 2.2614(7)	2085
$[2,6\text{-}(^{c}Pe_2PO)_2C_6H_3]PdC{\equiv}CPh$ (**2b**)[b]	N/A	N/A	N/A	2095
$[2,6\text{-}(^{t}Bu_2PO)_2C_6H_3]PdC{\equiv}CPh$ (**2c**)[b,c]	18.66	1.213(6)	2.2720(10), 2.2745(11)	2100
	21.40	1.211(5)	2.2753(10), 2.2802(10)	
	8.81	1.210(6)	2.2664(10), 2.2750(10)	

[a]Reported in ref. 11g. [b]Reported in ref. 7. [c]Three sets of data are listed because three independent molecules of **2c** crystallize in the lattice. [d]Dihedral angle between the phenyl ring and the pincer aromatic backbone.

The mechanism for the insertion reactions

The preference of 2,1- over 1,2-insertion of phenylacetylene was unexpected. From the steric point of view, the α-substituted alkenyl complexes **5a-b** should be less favored than the (*E*)-alkenyl complexes **6a-b**, as inferred by the crystal structures. Regioselective 2,1-insertion of phenylacetylene has been reported for other metal hydrides,[2i,16] although the origin for the regioselectivity is not fully understood. Huggins and Bergman have proposed that sterics control the regioselectivity for the insertion of unsymmetrical alkynes into $(acac)(PPh_3)Ni–CH_3$, in which case nickel is added to the sterically more demanding side of the triple bond.[17] One could argue that for the current system, the transition state for 2,1-insertion could be stabilized by π,π-stacking between the aromatic rings of phenylacetylene and the pincer backbone. However, for the reaction between **4a** (or **4b**) and an *aliphatic* alkyne such as 1-hexyne, the major product remains to be the α-substituted alkenyl complex.

Another possible explanation involves hydrogen atom (H•) transfer from metal to phenylacetylene,[18] resulting in selective formation of a radical on the more substituted carbon (H_2C=CPh•). Combining this radical with the metalloradical would yield an α-substituted alkenyl complex. If this mechanism is operating, the reaction of a metal hydride with PhC≡CD should lead to 50% of D for the vinylic hydrogens because the vinyl radical H(D)C=CPh• is linear.[19] The reaction of **4a** and PhC≡CD, however, showed that for the resulting **5a**, the hydrogen *trans* to the nickel was all D (eq 1). The product ratio for the **4a**/PhC≡CH reaction was also unaffected by the radical inhibitor TEMPO. The insertion of phenylacetylene into **4a** or **4b** most likely proceeds *via* a concerted addition of Ni–H across the triple bond, which is primarily controlled by electronic effects.



The reason why phenylacetylene does not prefer the insertion into the palladium-hydrogen bond remains unclear. Perhaps with a more electron rich metal, the oxidative addition of C_{sp}–H bond of phenylacetylene becomes more favorable, and the subsequent reductive elimination of H_2 generates the observed palladium alkynyl complexes.

Catalytic hydrogenation of phenylacetylene

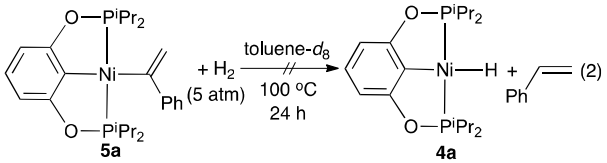
In our previous study,[7] palladium complexes **2a-c** (or **1a-c**) were shown to catalyze room temperature hydrogenation of phenylacetylene to styrene under 1 atm of H_2 pressure. In contrast, nickel complexes **4a** and **4b** showed practically no catalytic activity at room temperature even under a much higher H_2 pressure (entries 1 and 2, Table 2). Raising the temperature to 70 °C resulted in up to 3 catalytic turnovers, and **4a** exhibited better activity than **4b** (entries 3 and 4). Using the high-boiling toluene as the solvent allowed the temperature to be raised further to 100 °C without significant pressure build up. Under this condition (p_{H2} = 5 atm) for 24 h, 67% of phenylacetylene was converted to styrene and 31% was reduced fully to ethylbenzene (entry 5). Apparently, the hydrogenation process is pressure dependent; under 2 atm of H_2 pressure with 10 mol% catalyst, only 10% of phenylacetylene was hydrogenated to styrene after 24 h (entry 6). The catalytic reaction with **4b** was less effective than that with **4a**, and produced a lesser amount of styrene when lowering the H_2 pressure (entry 8) or the temperature (entry 9).

Table 2 Nickel-catalyzed hydrogenation of phenylacetylene[a]

entry	catalyst	catalyst loading	solvent	temperature	H_2 pressure	conversion[b]
1	**4a**	5 mol%	THF	22 °C	5 atm	< 1%
2	**4b**	5 mol%	THF	22 °C	5 atm	< 1%
3	**4a**	5 mol%	THF	70 °C	5 atm	15%
4	**4b**	5 mol%	THF	70 °C	5 atm	1%
5	**4a**	5 mol%	toluene	100 °C	5 atm	67% (31%)
6	**4a**	10 mol%	toluene	100 °C	2 atm	10% (1%)
7	**4b**	5 mol%	toluene	100 °C	5 atm	9%
8	**4b**	5 mol%	toluene	100 °C	4 atm	4%
9	**4b**	5 mol%	toluene	80 °C	5 atm	3%

[a]Reaction conditions: phenylacetylene (0.5 or 1.0 mmol) and nickel catalyst (50 μmol) in 0.60 mL of solvent for 24 h. [b]The conversion of phenylacetylene to styrene was determined by NMR; the conversion to ethylbenzene is listed in parenthesis.

Our previous mechanistic investigation on the palladium system confirms that the hydrogenation of alkynes is catalyzed by palladium particles rather than a molecular catalyst.[7] The release of particles from the palladium pincer complexes is made possible by oxidative addition of H_2 to the Pd(II) species followed by reductive elimination of the pincer ligand. Such a process is expected to be more difficult for Ni(II), which is likely the reason why **4a** and **4b** are inactive at room temperature. Nevertheless, both compounds catalyze the hydrogenation of phenylacetylene at elevated temperatures, probably *via* a completely different decomposition pathway from metal complexes to particles. An attempt to hydrogenate **5a** did not yield **4a** and styrene (eq 2), suggesting that oxidative addition of H_2 followed by reductive elimination of styrene is not a viable pathway. During the catalytic hydrogenation reaction, darkening of the solution was noted. Consistent with a heterogeneous mechanism, adding elemental mercury (200 equiv with respect to PhC≡CH) to the reaction in entry 5 poisoned the catalyst, resulting in <5% of phenylacetylene converted to styrene.



Conclusions

Through this study, we have shown distinctively different reactivity of nickel from palladium for the reaction between a POCOP-pincer hydride complex and phenylacetylene. The nickel system generates (*E*)-alkenyl and *α*-substituted complexes through *cis* 1,2- and 2,1-insertion, with the latter being the major pathway. In contrast, the palladium system yields an alkynyl complex and H_2 with little or no insertion products. We have attributed these differences to the tendency of palladium to undergo oxidative addition of the C_{sp}–H bond of phenylacetylene to a M(II) center, which, following reductive elimination of H_2, gives the alkynyl complex. Similarly, oxidative addition of H_2 to a Pd(II) pincer complex is more facile, creating a unique pathway for the formation of palladium particles that can catalyze

heterogeneous hydrogenation of phenylacetylene. Nickel-catalyzed hydrogenation is possible and also heterogeneous, but the reaction conditions are harsher, requiring higher temperature to decompose the metal complexes to particles. Our future direction will be focused on the assessment of M–H and M–C bond strengths for a better understanding of nickel vs. palladium in reduction reactions.

Experimental

Materials and methods

Unless otherwise mentioned, all the organometallic compounds were prepared and handled under an argon atmosphere using standard glovebox and Schlenk techniques. Dry and oxygen-free solvents for carrying out syntheses (pentane, THF and toluene) were collected from an Innovative Technology solvent purification system. Acetonitrile, anhydrous methanol (packed in a Sure/Seal™ bottle), PhC≡CD and α-bromostyrene (95% purity) were used as received without purification. Phenylacetylene was freshly distilled prior to the stoichiometric reduction and catalytic hydrogenation studies; however, for the synthesis of alkynyl complexes, it was used as received without purification. Benzene-d_6 was distilled from Na and benzophenone under an argon atmosphere. (*E*)-β-iodostyrene,[9] **4a**,[12a] **4b**,[12d] [2,6-(^{t}Bu$_2$PO)$_2$C$_6$H$_3$]NiH (**4c**),[12a] **8a**[11b] and **8b**[12d] were prepared as described in the literature.

Synthesis of [2,6-(^{i}Pr$_2$PO)$_2$C$_6$H$_3$]NiCPh=CH$_2$ (5a). At –78 °C under an argon atmosphere, a 2.5 M solution of ^{n}BuLi in hexanes (485 μL, 1.21 mmol) was added slowly to a solution of α-bromostyrene (175 μL, 1.35 mmol) in pentane (10 mL). The reaction mixture was warmed to 22 °C and stirred at this temperature for 15 min. The resulting colorless suspension was transferred *via* a cannula to a cold (–78 ˚C) solution of **8a** (295 mg, 0.68 mmol) in THF (10 mL). The orange colored reaction mixture was stirred at 22 °C for 3 h, after which the volatiles were removed under vacuum. Extraction of the orange residue with toluene (10 mL × 3) followed by filtration through a short plug of Celite gave a yellow solution. Removal of the solvent under vacuum yielded a light orange oil. The pure product was obtained as yellow crystals from a concentrated solution in acetonitrile or methanol kept at –30 ˚C (55 mg, 16 % yield). ^{1}H NMR (400 MHz, C$_6$D$_6$, δ): 1.07-1.15 (m, CH_3, 24H), 2.05-2.10 (m, PCH, 4H), 5.35 (dt, J_{H-H} = 3.2 Hz, J_{P-H} = 2.8 Hz, CPh=CH_2, 1H), 6.32 (dt, J_{H-H} = 3.2 Hz, J_{P-H} = 2.8 Hz, CPh=CH_2, 1H), 6.75 (d, J_{H-H} = 8.0 Hz, ArH, 2H), 6.99 (t, J_{H-H} = 8.0 Hz, ArH, 1H), 7.07 (t, J_{H-H} = 7.6 Hz, ArH, 1H), 7.22 (t, J_{H-H} = 7.6 Hz, ArH, 2H), 7.72 (d, J_{H-H} = 7.6 Hz, ArH, 2H). ^{13}C{^{1}H} NMR (101 MHz, C$_6$D$_6$, δ): 16.5 (s, *C*H$_3$), 17.4 (t, J_{P-C} = 3.0 Hz, *C*H$_3$), 27.6 (t, J_{P-C} = 11.6 Hz, *C*H), 104.6 (t, J_{P-C} = 6.1 Hz, Ar*C*), 119.1 (t, J_{P-C} = 5.1 Hz, C=*C*H$_2$), 125.6 (s, Ar*C*), 129.2 (s, Ar*C*), 137.3 (t, J_{P-C} = 9.1 Hz, Ar*C*), 152.3 (s, Ar*C*), 165.8 (t, J_{P-C} = 22.2 Hz, *C*=CH$_2$), 168.1 (t, J_{P-C} = 10.1 Hz, Ar*C*); other resonances were obscured by the solvent resonances. ^{31}P{^{1}H} NMR (162 MHz, C$_6$D$_6$, δ): 185.6 (s). Anal. Calcd for C$_{26}$H$_{38}$O$_2$P$_2$Ni: C, 62.06; H, 7.61. Found C, 61.91; H, 7.73.

Synthesis of [2,6-(^{c}Pe$_2$PO)$_2$C$_6$H$_3$]NiCPh=CH$_2$ (5b). This compound was prepared in 31 % yield using a procedure similar to that used for **5a**. X-ray quality crystals were obtained from an acetonitrile solution that was kept at –5 °C. ^{1}H NMR (400 MHz, C$_6$D$_6$, δ): 1.27-1.37 (m, CH_2, 8H), 1.47-1.51 (m, CH_2, 4H), 1.60-1.65 (m, CH_2, 4H), 1.75-1.88 (m, CH_2, 12H), 2.01-2.07 (m, CH_2, 4H), 2.22-2.29 (m, PCH, 4H), 5.40 (d, J_{H-H} = 3.6 Hz, CPh=CH_2, 1H), 6.39 (d, J_{H-H} = 3.6 Hz, CPh=CH_2, 1H), 6.80 (d, J_{H-H} = 8.0 Hz, ArH, 2H), 7.02-7.08 (m, ArH, 2H), 7.15-7.20 (m, ArH, 2H), 7.77 (d, J_{H-H} = 7.6 Hz, ArH, 2H). ^{13}C{^{1}H} NMR (101 MHz, C$_6$D$_6$, δ): 26.3 (t, J_{P-C} = 4.0 Hz, *C*H$_2$), 26.7 (t, J_{P-C} = 4.0 Hz, *C*H$_2$), 28.2 (t, J_{P-C} = 3.0 Hz, *C*H$_2$), 28.5 (s, *C*H$_2$), 39.2 (t, J_{P-C} = 12.6 Hz, *C*H), 104.7 (t, J_{P-C} = 5.6 Hz, Ar*C*), 118.2 (t, J_{P-C} = 5.6 Hz, C=*C*H$_2$), 125.6 (s, Ar*C*), 128.4 (s, Ar*C*), 128.6 (s, Ar*C*), 129.1 (s, Ar*C*), 151.7 (s, Ar*C*), 167.2 (t, J_{P-C} = 22.2 Hz, *C*=CH$_2$), 168.0 (t, J_{P-C} = 10.1 Hz, Ar*C*); one resonance was obscured by the solvent resonances. ^{31}P{^{1}H} NMR (162 MHz, C$_6$D$_6$, δ): 179.5 (s). Anal. Calcd for C$_{34}$H$_{46}$O$_2$P$_2$Ni: C, 67.23; H, 7.63. Found: C, 67.03; H, 7.44.

Synthesis of (*E*)-[2,6-(^{i}Pr$_2$PO)$_2$C$_6$H$_3$]NiCH=CHPh (6a). At –78 °C under an argon atmosphere, a 2.5 M solution of ^{n}BuLi in hexanes (184 μL, 0.46 mmol) was added slowly to a solution of *E*-iodostyrene (100 mg, 0.43 mmol) in pentane (10 mL). The reaction mixture was warmed to 22 °C and stirred at this temperature for 15 min. The resulting colorless suspension was transferred *via* a cannula to a cold (–78 ˚C) solution of **8a** (100 mg, 0.23 mmol) in THF (10 mL). The orange colored reaction mixture was stirred at 22 °C for 45 min, after which the volatiles were removed under vacuum. Extraction of the yellow residue with toluene (10 mL × 3) followed by filtration through a short plug of Celite gave a yellow solution. Removal of the solvent under vacuum yielded the product as a yellow powder (46 mg, 40% yield). X-ray quality crystals were obtained from a methanol solution that was kept at –5 °C. ^{1}H NMR (400 MHz, C$_6$D$_6$, δ): 1.09-1.18 (m, CH_3, 24H), 2.07-2.14 (m, PCH, 4H), 6.78 (d, J_{H-H} = 8.0 Hz, ArH, 2H), 6.95-7.07 (m, NiCH=CHPh + ArH, 3H), 7.28 (t, J_{H-H} = 7.6 Hz, ArH, 2H), 7.45 (d, J_{H-H} = 7.6 Hz, ArH, 2H), 7.75 (d, J_{H-H} = 18.8 Hz, NiCH=CHPh, 1H). ^{13}C{^{1}H} NMR (101 MHz, C$_6$D$_6$, δ): 17.0 (s, *C*H$_3$), 17.7 (s, *C*H$_3$), 27.8 (t, J_{P-C} = 12.1 Hz, *C*H), 105.0 (t, J_{P-C} = 6.1 Hz, Ar*C*), 128.8 (s, Ar*C*), 129.2 (s, Ar*C*), 138.1 (t, J_{P-C} = 6.1 Hz, Ar*C*), 142.0 (s, Ar*C*), 152.4 (t, J_{P-C} = 24.8 Hz, *C*H=CHPh), 168.4 (t, J_{P-C} = 10.1 Hz, Ar*C*); other resonances were obscured by the solvent resonances. ^{31}P{^{1}H} NMR (162 MHz, C$_6$D$_6$, δ): 189.4 (s). Anal. Calcd for C$_{26}$H$_{38}$O$_2$P$_2$Ni: C, 62.06; H, 7.61. Found: C, 62.33; H, 7.57.

Synthesis of (*E*)-[2,6-(^{c}Pe$_2$PO)$_2$C$_6$H$_3$]NiCH=CHPh (6b). This compound was prepared in 17 % yield using a procedure similar to that used for **6a**. ^{1}H NMR (400 MHz, C$_6$D$_6$, δ): 1.36-1.40 (m, CH_2, 8H), 1.52-1.75 (m, CH_2, 16H), 1.85-1.98 (m, CH_2, 4H), 2.00-2.12 (m, CH_2, 4H), 2.32-2.38 (m, PCH, 4H), 6.79 (d, J_{H-H} = 8.0 Hz, ArH, 2H), 6.85 (dt, J_{H-H} = 18.8 Hz, J_{P-H} = 3.2 Hz, NiCH=CHPh, 1H), 7.00 (t, J_{H-H} = 8.0 Hz, ArH, 2H), 7.27 (t, J_{H-H} = 8.0 Hz, ArH, 2H), 7.47 (d, J_{H-H} = 8.0 Hz, ArH, 2H), 7.83 (dt, J_{H-H} = 18.8 Hz, J_{P-H} = 2.8 Hz, NiCH=CHPh, 1H). ^{13}C{^{1}H} NMR (101 MHz, C$_6$D$_6$, δ): 26.9 (t, J_{P-C} = 4.5 Hz, *C*H$_2$), 27.0 (t, J_{P-C} = 3.0 Hz, *C*H$_2$), 28.0 (t, J_{P-C} = 3.5 Hz, *C*H$_2$), 28.7 (s, *C*H$_2$), 38.5 (t, J_{P-C} = 13.1 Hz, *C*H), 105.0 (t, J_{P-C} = 6.0 Hz, Ar*C*), 124.6 (s, Ar*C*), 124.7 (s, CH=*C*HPh), 128.7 (s, Ar*C*), 128.9 (s, Ar*C*), 129.2 (s, Ar*C*), 137.6 (t, J_{P-C} = 5.5 Hz, Ar*C*), 154.5 (t, J_{P-C} = 24.7 Hz, *C*H=CHPh), 168.3 (t, J_{P-C} = 10.1 Hz, Ar*C*); one

resonance was obscured by the solvent resonances. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 26.7 (t, J_{P-C} = 4.0 Hz, *C*H_2), 26.9 (t, J_{P-C} = 3.5 Hz, *C*H_2), 27.7 (t, J_{P-C} = 3.0 Hz, *C*H_2), 28.6 (s, *C*H_2), 38.3 (t, J_{P-C} = 13.1 Hz, *C*H), 104.3 (t, J_{P-C} = 6.1 Hz, Ar*C*), 124.0 (s, CH=*C*HPh), 124.3 (s, Ar*C*), 128.3 (s, Ar*C*), 128.5 (s, Ar*C*), 129.3 (s, Ar*C*), 136.6 (t, J_{P-C} = 5.0 Hz, Ar*C*), 141.5 (s, Ar*C*), 154.9 (t, J_{P-C} = 25.8 Hz, *C*H=CHPh), 167.6 (t, J_{P-C} = 10.5 Hz, Ar*C*). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, δ): 180.5 (s). Anal. Calcd for $C_{34}H_{46}O_2P_2Ni$: C, 67.23; H, 7.63. Found: C, 66.74; H, 7.70.

Synthesis of [2,6-(^{i}Pr$_2$PO)$_2$C$_6$H$_3$]NiC≡CPh (7a). At –78 °C under an argon atmosphere, a 2.5 M solution of ^{n}BuLi in hexanes (276 μL, 0.69 mmol) was added slowly to a solution of phenylacetylene (83 μL, 0.76 mmol) in pentane (10 mL). The reaction mixture was warmed to 22 °C and stirred at this temperature for 15 min. The resulting colorless suspension was transferred *via* a cannula to a cold (–78 °C) solution of **8a** (150 mg, 0.34 mmol) in THF (10 mL). The orange colored reaction mixture was stirred at 22 °C for 3 h, after which the volatiles were removed under vacuum. Extraction of the yellow residue with pentane (10 mL × 3) followed by filtration through a short plug of Celite gave a yellow solution. Removal of the solvent under vacuum yielded the product as a yellow powder (85 mg, 49% yield). X-ray quality crystals were obtained from a methanol solution that was kept at –5 °C. ^1H NMR (400 MHz, C_6D_6, δ): 1.14-1.19 (m, C*H*$_3$, 12H), 1.33-1.39 (m, C*H*$_3$, 12H), 2.26-2.29 (m, PC*H*, 4H), 6.73 (d, J_{H-H} = 8.0 Hz, Ar*H*, 2H), 6.93-6.99 (m, Ar*H*, 2H), 7.13 (t, J_{H-H} = 8.0 Hz, Ar*H*, 2H), 7.54 (d, J_{H-H} = 8.0 Hz, Ar*H*, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, δ): 16.8 (s, *C*H$_3$), 17.7 (t, J_{P-C} = 3.0 Hz, *C*H$_3$), 28.5 (t, J_{P-C} = 12.1 Hz, *C*H), 105.0 (t, J_{P-C} = 6.1 Hz, Ar*H*), 108.2 (t, J_{P-C} = 28.8 Hz, *C*≡CPh), 125.0 (s, Ar*C*), 129.3 (s, Ar*C*), 129.4 (s, Ar*C*), 130.6 (s, Ar*C*), 135.9 (t, J_{P-C} = 20.2 Hz, Ar*C*), 168.8 (t, J_{P-C} = 10.1 Hz, Ar*C*); other resonances were obscured by the solvent resonances. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 17.0 (s, *C*H$_3$), 17.9 (t, J_{P-C} = 3.0 Hz, *C*H$_3$), 28.6 (t, J_{P-C} = 12.1 Hz, *C*H), 104.5 (t, J_{P-C} = 6.6 Hz, Ar*H*), 108.1 (t, J_{P-C} = 28.8 Hz, *C*≡CPh), 125.0 (s, Ar*C*), 126.2 (s, C≡*C*Ph), 127.9 (s, Ar*C*), 128.6 (s, Ar*C*), 128.8 (s, Ar*C*), 130.6 (s, Ar*C*), 135.5 (t, J_{P-C} = 20.2 Hz, Ar*C*), 168.4 (t, J_{P-C} = 10.6 Hz, Ar*C*). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, δ): 195.7. ATR-IR (solid): ν(C≡C) = 2089 cm^{-1}. Anal. Calcd for $C_{26}H_{36}O_2P_2Ni$: C, 62.31; H, 7.24. Found: C, 62.60; H, 7.34.

Synthesis of [2,6-(^{c}Pe$_2$PO)$_2$C$_6$H$_3$]NiC≡CPh (7b). This compound was prepared in 64 % yield using a procedure similar to that used for **7a**. X-ray quality crystals were obtained from a pentane solution that was kept at –5 °C. ^1H NMR (400 MHz, C_6D_6, δ): 1.38-1.42 (m, C*H*$_2$, 8H), 1.73-1.80 (m, C*H*$_2$, 12H), 1.85-1.95 (m, C*H*$_2$, 4H), 2.04-2.13 (m, C*H*$_2$, 4H), 2.31-2.40 (m, C*H*$_2$, 4H), 2.46-2.55 (m, PC*H*, 4H), 6.75 (d, J_{H-H} = 7.6 Hz, Ar*H*, 2H), 6.92-6.99 (m, Ar*H*, 2H), 7.13 (t, J_{H-H} = 7.6 Hz, Ar*H*, 2H), 7.53 (d, J_{H-H} = 7.6 Hz, Ar*H*, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, δ): 26.7-26.8 (m, two *C*H$_2$ overlapped), 28.0 (t, J_{P-C} = 3.0 Hz, *C*H$_2$), 28.8 (s, *C*H$_2$), 39.6 (t, J_{P-C} = 13.1 Hz, *C*H), 105.1 (t, J_{P-C} = 6.1 Hz, Ar*C*), 110.4 (t, J_{P-C} = 28.3 Hz, *C*≡CPh), 125.0 (s, Ar*C*), 125.8 (s, C≡*C*Ph), 129.5 (s, Ar*C*), 129.6 (s, Ar*C*), 130.5 (s, Ar*C*), 136.1 (t, J_{P-C} = 20.2 Hz, Ar*C*), 168.8 (t, J_{P-C} = 10.1 Hz, Ar*C*); one resonance was obscured by the solvent resonances. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 26.6 (t, J_{P-C} = 5.1 Hz, *C*H$_2$), 27.8 (t, J_{P-C} = 3.0 Hz, *C*H$_2$), 28.6 (s, *C*H$_2$), 39.4 (t, J_{P-C} = 13.1 Hz, *C*H), 104.4 (t, J_{P-C} = 6.1 Hz, Ar*C*), 110.1 (t, J_{P-C} = 28.8 Hz, *C*≡CPh), 124.66 (s, C≡*C*Ph), 124.73 (s, Ar*C*), 127.9 (s, Ar*C*), 128.7 (s, Ar*C*), 128.8 (s, Ar*C*), 130.3 (s, Ar*C*), 135.8 (t, J_{P-C} = 20.2 Hz, Ar*C*), 168.2 (t, J_{P-C} = 10.1 Hz, Ar*C*). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, δ): 186.4 (s). ATR-IR (solid): ν(C≡C) = 2082 cm^{-1}. Anal. Calcd for $C_{34}H_{44}O_2P_2Ni$: C, 67.46; H, 7.33. Found: C, 67.52; H, 7.34.

Procedures for catalytic hydrogenation of phenylacetylene

(a) Hydrogenation in THF: At room temperature under an argon atmosphere, phenylacetylene (0.5 or 1.0 mmol), nickel catalyst **4a** or **4b** (50 μmol) and 0.6 mL of THF were mixed in a Fisher-Porter bottle. The reaction vessel was then exposed to a dihydrogen atmosphere (2 atm), after which the system was flushed with H_2 three times before being placed under the appropriate pressure and temperature. For the reaction at 70 °C, after 24 h, the color of the reaction mixture changed from yellow to red with some particle formation, which were removed by filtration. The solvent was removed under vacuum and the residue was dissolved in $CDCl_3$ for NMR analysis. The conversion of phenylacetylene to styrene was calculated based on NMR integrations. For the reactions catalyzed by **4b**, the resonances of ethylbenzene were overlapped with those of **4b** and therefore, to ensure accuracy, 1,4-dioxane (0.11 mmol) was added as an NMR internal standard. *(b) Hydrogenation in toluene*: The procedure was the same as described above except that the reaction was carried out in toluene-d_8 and analyzed by NMR directly without filtration and removal of the solvent.

X-ray structure determinations

Crystal data collection and refinement parameters can be found in ESI. Intensity data were collected at 150K on a Bruker SMART6000 CCD diffractometer using graphite-monochromated Cu Kα radiation, λ = 1.54178Å. The data frames were processed using the program SAINT. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. The structures were solved by a combination of direct methods in SHELXTL and the difference Fourier technique and refined by full-matrix least-squares procedures. Non-hydrogen atoms were refined with anisotropic displacement parameters. H-atoms were calculated and treated with a riding model. No solvent of crystallization is present in the lattice for any of the structures. Typical disorder was observed for the cyclopentyl rings of **5b** and **7b**; two-component disorder models were applied. The crystal structures for **5b**, **6a**, **7a** and **7b** have been deposited at the Cambridge Crystallographic Data Centre (CCDC) and allocated the deposition numbers CCDC 1043222-1043225.

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Notes and references

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† Electronic supplementary information (ESI) available: CCDC 1043222-1043225 for **5b**, **6a**, **7a** and **7b**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

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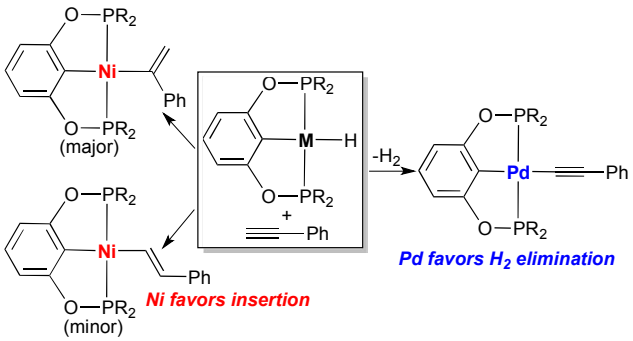

Nickel POCOP-pincer hydride complexes react with phenylacetylene to afford alkenyl complexes whereas the palladium analogs give alkynyl complexes.