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Facile Regio- and Stereoselective Hydrometalation of Alkynes with a Combination of Carboxylic Acids and Group 10 Transition Metal Complexes: Selective Hydrogenation of Alkynes with Formic Acid

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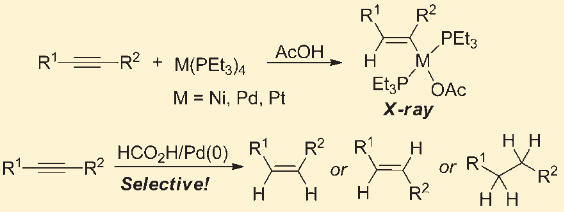
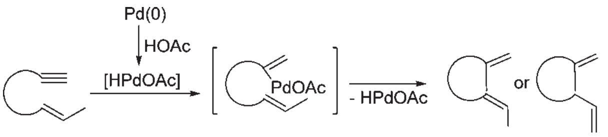
Supporting Information



ABSTRACT: A facile, highly stereo- and regioselective hydrometalation of alkynes generating alkenylmetal complex is disclosed for the first time from a reaction of alkyne, carboxylic acid, and a zerovalent group 10 transition metal complex $M(PEt_3)_4$ (M = Ni, Pd, Pt). A mechanistic study showed that the hydrometalation does not proceed via the reaction of alkyne with a hydridometal generated by the protonation of a carboxylic acid with $Pt(PEt_3)_4$, but proceeds via a reaction of an alkyne coordinate metal complex with the acid. This finding clarifies the long proposed reaction mechanism that operates via the generation of an alkenylpalladium intermediate and subsequent transformation of this complex in a variety of reactions catalyzed by a combination of Brϕnsted acid and Pd(0) complex. This finding also leads to the disclosure of an unprecedented reduction of alkynes with formic acid that can selectively produce *cis*-, *trans*-alkenes and alkanes by slightly tuning the conditions.

INTRODUCTION

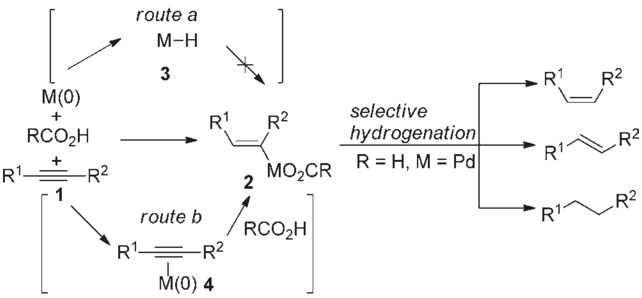
The combination of a palladium(0) complex with acetic acid, discovered by Trost,[1] is an efficient catalyst for various transformations of alkynes such as cyclization of enynes,[1,2] hydrocarbonylation,[3] hydroarylation,[4] and isomerization of alkynes.[1] However, mechanistic aspects were not clear. For example, although an alkenylpalladium intermediate generated by hydropalladation of the triple bond was proposed as the key intermediate in these catalytic reactions, a direct proof of its participation has never been obtained (eq 1).[1]



(1)

In this paper, we report the first isolation of an alkenylpalladium **2**, generated via a facile hydropalladation of the triple bond, from a reaction of an alkyne, carboxylic acid, and a zerovalent palladium complex. This isolation of **2** provides the first clear answer to the long proposed reaction mechanism involving a catalyst of a Brϕnsted acid and a palladium(0) complex.[1,5] A systematic investigation on the reactions of group 10 transition metal(0) complexes $M(PEt_3)_4$ (M = Ni, Pd, Pt) with alkynes in the presence of carboxylic acids further reveals that this facile hydrometalation reaction of alkynes with carboxylic acids affording the corresponding alkenylmetal complexes is a general phenomenon for group 10 transition metal(0) complexes. Moreover, it clearly shows that this hydrometalation (M = Pt) proceeds via a reaction of an alkyne coordinate metal (0) complex **4** with the acid (route b) rather than via the commonly accepted reaction of an alkyne with a hydridometal **3** generated via the protonation[6] (or oxidative addition)[6a−c,7] of carboxylic acid with $M(PEt_3)_4$ (route a) (Scheme 1).[1,8−10]

Scheme 1



A further study using formic acid as the substrate also successfully leads to the disclosure of an unprecedented palladium catalyzed controllable hydrogenation of alkynes with formic acid that can selectively produce one hydrogenated

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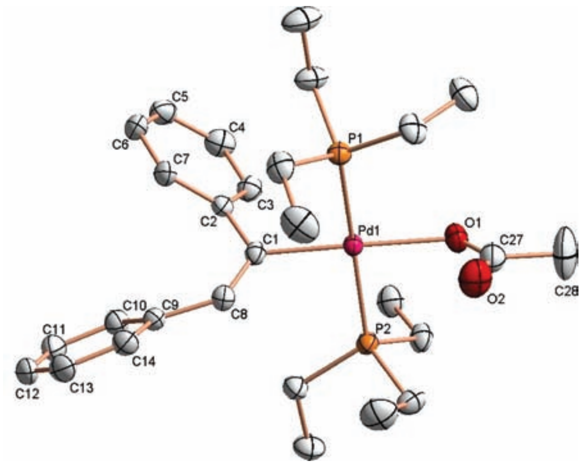


Figure 1. ORTEP drawing of alkenylpalladium **2a**. Hydrogen atoms are omitted for clarity; ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): C1−Pd1 = 2.014(1), C1−C8 = 1.346(2), Pd1−O1 = 2.120(1), Pd1−P1 = 2.3245(5), Pd1−P2 = 2.3219(5), C8−C1−Pd1 = 121.0(1), C1−Pd1−P1 = 88.49(4), C1−Pd1−P2 = 91.66(4), O1−Pd1−P1 = 95.79(3).

product from the three possible, *cis*-, *trans*-alkenes and alkanes, respectively (Scheme 1).

Transition-metal catalyzed hydrogenation of alkynes to alkenes and alkanes is one of the most important reactions in organic chemistry.[11] It is particularly relevant for the synthesis of biologically important molecules such as natural products, pharmaceuticals, and fragrance chemicals, since many of these molecules incorporate carbon−carbon double bonds with defined *Z* or *E* configurations.[12] This transformation has been accomplished by using hydrogen gas in the presence of either a heterogeneous catalyst[13] such as Raney Ni, Lindlar catalyst, Pd/C, or a homogeneous catalyst[14] of Rh, Ru, or Ir complexes. However, this method often suffers from the lack of chemo- and stereoselectivity arising from the *cis*/*trans* interconversion of the alkenes and the over-reduction of the resulted alkenes to alkanes. Low tolerance with functionalities such as carbonyl, formyl, nitro groups, and C−X bonds (X = O, N, Cl, etc.) due to the competitive hydrogenolysis also narrows its generality. Instead of hydrogen gas, alkynes could also be hydrogenated by using ammonium formate in the presence of a palladium catalyst.[15] Heck first explored the Pd/C catalyzed heterogeneous transfer hydrogenation of a few alkynes using ammonium formate in 1970s[15a,b] and Sato described the hydrogenation of aliphatic alkynes to alkenes using a palladium(0) complex catalyst.[15c] Very recently, Elsevier reported the highly selective hydrogenation of alkynes by employing a Pd(0) N-heterocyclic carbene complex[15d] and studied its mechanism in detail.[15e] However, ammonium formate, rather than the simple formic acid, was employed in these reactions which took place via a different mechanism (vide infra). In addition, only *cis*-alkenes were produced selectively from these reactions.

RESULTS AND DISCUSSION

Facile Hydropalladation of Alkynes with Acetic Acid and Pd(PEt$_3$)$_4$. When acetic acid (0.5 mmol) was added to a solution of Pd(PEt$_3$)$_4$ (0.1 mmol) and diphenylacetylene **1a** (0.1 mmol) in C$_6$D$_6$ (0.5 mL) at room temperature, the color of the solution immediately turned from brown to colorless (eq 2). As followed by ^{1}H NMR and ^{31}P NMR spectroscopies, the starting materials **1a** and Pd(PEt$_3$)$_4$ were consumed after 20 h at room temperature, while a characteristic alkenyl proton signal was clearly observed at 6.70 ppm, indicative of the formation of an alkenylpalladium species. Removal of the volatiles in vacuo afforded **2a** as a white solid, which was recrystallized from toluene−hexane at −30 °C to give crystals suitable for X-ray analysis. The ORTEP drawing as depicted in Figure 1 unambiguously reveals the *trans* geometry of the carbon−carbon double bond as well as the *trans* geometry on Pd, showing that this hydropalladation of the triple bond is highly stereoselective. The Pd atom in **2a** adopts a square-planar coordination geometry which is ligated by two PEt$_3$ in a *trans* manner. The five atoms Pd1, C1, C2, C8, and C9 are not coplanar. C1, C2, C8, and C9 adopt a dihedral angle of 10.6(3)°, while the dihedral angle of Pd1, C1, C8, and C9 is 170.7(1)°. Interestingly, although complex **2a** is stable in the presence of an extra PEt$_3$, the isolated pure **2a** gradually isomerizes to **2a′** bearing *cis* geometry on the carbon−carbon double bond (% conversion of **2a** to **2a′**: 25 °C, 14 d, 17%; 60 °C, 2 h, 20%).[16]

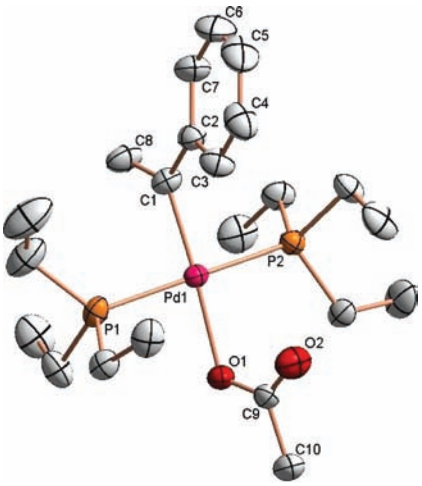
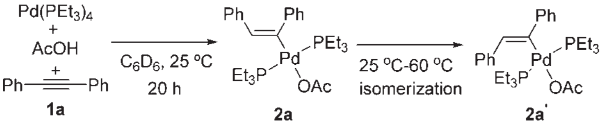


Figure 2. ORTEP drawing of alkenylpalladium **2b**. Hydrogen atoms are omitted for clarity; ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): C1−Pd1 = 2.008(3), C1−C8 = 1.3339(6), Pd1−O1 = 2.122(2), Pd1−P1 = 2.3197(9), Pd1−P2 = 2.3299(8), C8−C1−Pd1 = 121.4(3), C1−Pd1−P1 = 92.3(1), C1−Pd1−P2 = 88.4(1), O1−Pd1−P1 = 85.24(7).

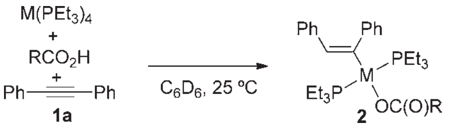


(2)

It is worth noting that complex **2a** is the first example of an alkenylpalladium complex generated via the direct hydropalladation of an alkyne with a carboxylic acid. This finding provides the first clear answer to the long proposed reaction mechanism involving a catalyst of a Brϕnsted acid and a palladium(0) complex.[1]

Remarkably, the hydropalladation of alkynes also took place highly regioselectively. Under similar reaction conditions, when a terminal alkyne, phenylacetylene (**1b**), was used as the substrate, the exclusive formation of the Markovnikov-type complex **2b** with palladium bonding to the internal carbon of the double

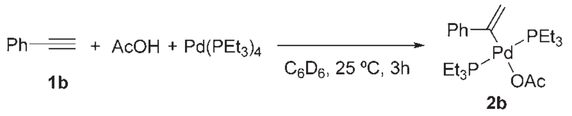
Table 1. Facile Hydrometalation of Diphenylacetylene with $M(PEt_3)_4$ (M = Ni, Pd, Pt)[a]



$M(PEt_3)_4$	RCO_2H	isolated yield of **2**
$Ni(PEt_3)_4$	AcOH	**2c**, 70% (X-ray)[b]
$Pd(PEt_3)_4$	AcOH	**2a**, 85% (X-ray)
	CF_3CO_2H	**2d**, 84%
	$PhCO_2H$	**2e**, 90%
$Pt(PEt_3)_4$	AcOH	**2f**, 76% (X-ray)[c]

[a] Reaction conditions: RCO_2H was added to an equimolar mixture of $M(PEt_3)_4$ and diphenylacetylene **1a** in C_6D_6 at room temperature. Complex **2** was isolated by recrystallization from hexane−toluene at −30 °C. [b] Conducted in the absence of solvent. [c] See Supporting Information for X-ray data.

bond was observed (eq 3). **2b** was isolated as a white solid in 80% yield and its structure was also unambiguously confirmed by an X-ray crystallographic analysis (Figure 2).



(3)

Selective Hydrometalation of Alkynes with a Combination of Carboxylic Acids and Group 10 Transition Metal (0) Complexes $M(PEt_3)_4$ (M = Ni, Pd, Pt): A General Phenomenon. As shown in Table 1, a systematic study on the reactions of group 10 transition metal (0) complexes with alkynes in the presence of carboxylic acids was carried out, which revealed that this hydrometalation of alkynes with carboxylic acids was a rather general reaction for group 10 transition metal (0) complexes $M(PEt_3)_4$ (M = Ni, Pd, Pt) (Table 1). Thus, in addition to acetic acid, under similar reaction conditions described for eq 2, $Pd(PEt_3)_4$ also readily reacted with benzoylic acid and the strong trifluoroacetic acid at room temperature to produce the corresponding alkenylpalladium complexes in high yields. The corresponding platinum (0) complex $Pt(PEt_3)_4$ was found as reactive as $Pd(PEt_3)_4$ in the reaction with diphenylacetylene and acetic acid to give the corresponding alkenylplatinum complex **2f** at room temperature in high yields. Compared to its palladium and platinum counterparts that are stable at room temperature, alkenylnickel complex **2c** decomposes at room temperature in solution which prevents its isolation from the mixture. Fortunately, we found that, in the absence of a solvent, the reaction of $Ni(PEt_3)_4$ with diphenylacetylene and acetic acid also proceeded readily from which complex **2c** gradually precipitated out as red solids (Figure 3). Noted that, in addition to that of complex **2a**, the structures of complexes **2c** and **2f** were also unambiguously determined by X-ray analysis.

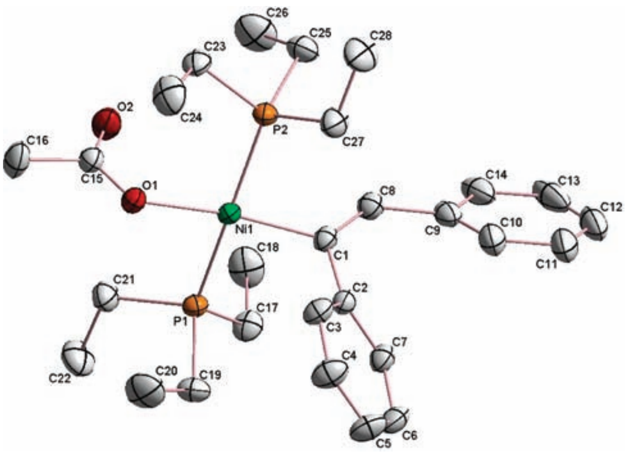
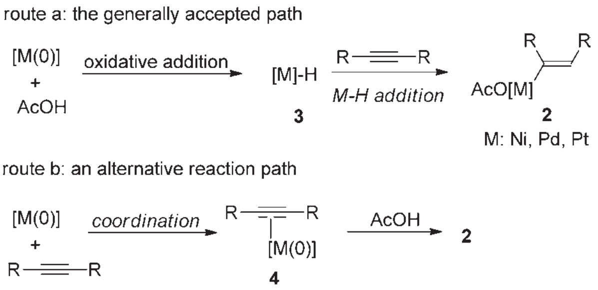
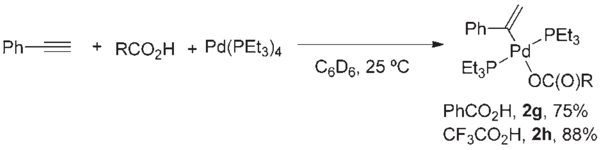


Figure 3. ORTEP drawing of alkenylnickel **2c**. Hydrogen atoms are omitted for clarity; ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): C1−Ni1 = 1.906(1), C1−C8 = 1.350(2), Ni1−O1 = 1.9203(8), Ni1−P1 = 2.2286(4), Ni1−P2 = 2.2250(4), C8−C1−Ni1 = 125.23(9), C1−Ni1−P1 = 90.40(3), C1−Ni1−P2 = 88.67(3), O1−Ni1−P1 = 89.38(3).

Scheme 2. Reaction Path to Complex 2



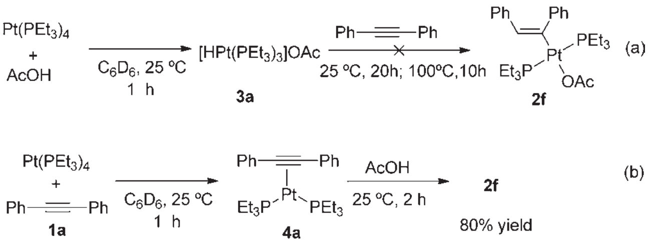
As to the regioselectivity of this hydrometalation, it was shown that, in addition to acetic acid, the reactions of phenylacetylene and $Pd(PEt_3)_4$ with both benzoylic acid and trifluoroacetic acid all could produce highly regioselectively the corresponding alkenylmetal complexes with palladium bonding to the internal carbon of the alkyne (eq 4).



(4)

Hydridometal M−H Formation vs Alkyne Coordination to $M(PEt_3)_4$ (M = Ni, Pd, Pt): The Real Reaction Path to Alkenylmetals 2. Activation of an H-heteroatom bond by the oxidative addition of H-heteroatom bond to a transition metal is known as an essential step for the metal catalyzed addition reactions.[8,17] Because of its similarity to the generally proposed mechanism for transition metal-catalyzed H-heteroatom bond addition reactions to carbon−carbon unsaturated bonds, the oxidative addition of AcOH to Pd(0) generating the hydridopalladium complexes **3** is also commonly accepted as a key reaction for the formation of the alkenylpalladium complex **2**, although there is a lack of experimental evidence.[1,8,9b] Thus, it was thoroughly interpreted that complex **3** reacted with diphenylacetylene via the H−Pd bond *cis*-addition (hydropalladation)

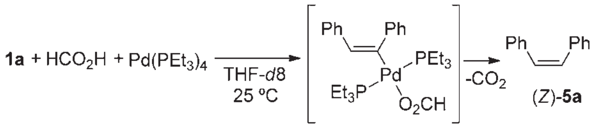
Scheme 3. Reaction Path to Complex 2f



to produce complex **2** (route a, Scheme 2).[1,8] Although this mechanism (route a) can explain the experiment's results observed so far,[1] as described below, it is probably not the true reaction path. The real reaction path seems to be route b, via first a coordination of an alkyne with palladium generating an alkyne complex **4** which then reacts with acetic acid to produce complex **2**.

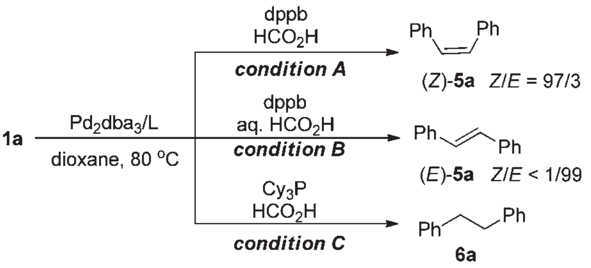
This phenomenon was accidently found during the preparation of complex **2f** by changing the addition sequence of the substrates. Thus, it was found that while the addition of acetic acid to a mixture of $Pt(PEt_3)_4$ and diphenylacetylene could produce the alkenyl complex **2f** readily at room temperature, the addition of diphenylacetylene to a mixture of $Pt(PEt_3)_4$ and acetic acid could not produce **2f** even at an elevated temperature (60−100 °C). Separate experiments showed that protonation of $Pt(PEt_3)_4$ by AcOH took place readily to produce a hydridoplatinum complex **3a** quantitatively after 1 h.[9,18] However, no reaction took place between complex **3a** and diphenylacetylene at room temperature for 20 h or under an elevated temperature (60−100 °C) for another 10 h. On the other hand, an alkyne coordinated complex **4a** was also readily generated by mixing $Pt(PEt_3)_4$ with diphenylacetylene.[19] This complex **4a** reacted readily at room temperature with acetic acid to produce the alkenylplatinum complex **2f** in 80% yield (Scheme 3).[10] Therefore, the experiments shown in Scheme 3 could exclude the possibility for route a as a possible path to **2f**, indicating that route b is the true reaction path for its formation.[20]

Selective Hydrogenation of Alkynes with Formic Acid. For a similar reaction shown in eq 2 by using formic acid as the substrate, the corresponding alkenylpalladium complex could not be isolated, probably because of the easy decomposition of the resulted complex.[21] Thus, when acetic acid was replaced by formic acid, the reaction of **1a** with $Pd(PEt_3)_4$ did not produce the corresponding alkenylpalladium complex, but remarkably afforded a reduction product, *cis*-stilbene ((*Z*)-**5a**) in 97% yield exclusively (eq 5).[21]



(5)

On the basis of this observation, catalytic hydrogenation of alkynes with formic acid was subsequently investigated. This leads to the successful disclosure of an unprecedented controllable hydrogenation process of alkynes with simple formic acid that can selectively produce either *cis*-, *trans*-alkenes or alkanes, by slightly tuning the reaction conditions (eq 6).[22]

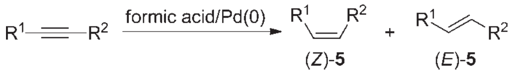


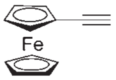
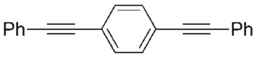
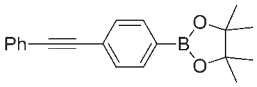
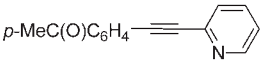
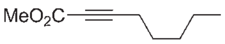
(6)

Thus, a preliminary examination on the reaction of **1a** with formic acid (2 equiv) in dioxane at 80 °C catalyzed by $Pd(PPh_3)_4$ (5 mol %) showed that hydrogenation proceeded readily to give the partially reduced *cis* and *trans* mixture of stilbene quantitatively after 5 h (*Z*/*E* = 87/13). An extensive screening[23] on the optimization of the reaction conditions successfully revealed that the selectivity to (*Z*)-**5a** could be significantly improved when dppb (dppb = 1,4-bis(diphenylphosphino)butane) was used as the ligand. Thus, when **1a** (0.2 mmol) and formic acid (0.4 mmol) were heated in dioxane at 80 °C for 15 h in the presence of 1 mol % of Pd_2dba_3 and 4 mol % of dppb, (*Z*)-**5a** was obtained in 97% yield with a *Z*/*E* ratio up to 98/2 as confirmed by GC (***condition A***). Worth noting is that the ratio of dppb to Pd_2dba_3 (Pd/P = 1/4) is also crucial for the high stereoselectivity. With a decreasing amount of dppb (Pd/P = 1:2), the stereoselectivity became low (*Z*/*E*: 72/28 for 5 h, 11/89 for 20 h).[24] Surprisingly, when a similar reaction was conducted using 25% aqueous formic acid, a dramatic reversal of the stereoselectivity was achieved to afford (*E*)-**5a** exclusively. For example, under similar reaction conditions, **1a** (0.2 mmol) and 25% aqueous formic acid (0.6 mmol) in dioxane were heated at 80 °C for 10 h in the presence of 1 mol % Pd_2dba_3 and 2 mol % dppb (***condition B***) to produce (*E*)-**5a** exclusively in 92% isolated yield. Although the exact mechanism was not clear, this unexpected finding undoubtedly allowed a direct conversion of alkynes to alkenes with *E*-configuration. More surprisingly, a complete hydrogenation of **1a** to the saturated hydrocarbon 1,2-diphenylethane (**7a**) could also be selectively achieved when tricyclohexylphosphine (Cy_3P) was used as the ligand. Thus, **1a** (0.2 mmol) and formic acid (0.6 mmol) mixed in dioxane were heated at 80 °C for 3 h in the presence of palladium catalyst (1 mol % Pd_2dba_3, 4 mol % Cy_3P) (***condition C***) to produce **6a** exclusively in 96% yield.

The results complied in Table 2 show that a variety of alkynes, both terminal and internal, were readily reduced to the corresponding alkenes in high yields with high chemo- and stereoselectivity. Worth noting particularly is that the reaction features a wide tolerance to a variety of functional groups which could be hardly achieved by hydrogenation reactions with hydrogen gas. As illustrated in entries 3−8 and 12−15, a lot of valuable functionalities such as carbonyl, formyl, chloro,[25] and even nitro groups were all tolerable under the present conditions. Noteworthy, benzyloxyl group that can be easily hydrogenolyzed also survived as exemplified by the reaction of 1-(benzyloxy)-3-ethynylbenzene (entry 8). The reaction of 3-ethynylaniline with formic acid, however, is slightly complicated since formylation of the amino group occurred to some extent to produce a mixture of products. These side reactions could be suppressed by adding 2.5 equiv of Et_3N to facilitate the formation of **5f** (entry 5). When 3-ethynylphenol was employed, the reaction proceeded

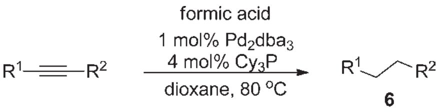
Table 2. Pd(0)-Catalyzed Selective Hydrogenation of Alkynes to Alkenes with Formic Acid[a]



entry	alkyne **1**	**5**, yield[b] (%), (Z/E)[c]
1	R—≡ R = $CH_3(CH_2)_{12}$	**5b**, 95[d]
2	Ph	**5c**, 90[d]
3	*m*-$HCOC_6H_4$	**5d**, 85[d]
4	*p*-$NO_2C_6H_4$	**5e**, 93
5[e]	*m*-$NH_2C_6H_4$	**5f**, 90
6	*p*-$CH_3C(O)NHC_6H_4$	**5g**, 96
7	*m*-HOC_6H_4	**5h**, 91
8	*m*-$BnOC_6H_4$	**5i**, 89
9		**5j**, 91
10	*n*-C_6H_{13}—≡—Ph	(Z)-**5k**, 93 (95/5)
11		(E)-**5k**, 95 (27/73)[f]
12	*p*-ClC_6H_4—≡—Ph	(Z)-**5l** 91 (99/1)
13		(E)-**5l**, 90 (<1/99)
14	*p*-$MeC(O)C_6H_4$—≡—Ph	(Z)-**5m**, 95 (99/1)
15		(E)-**5m**, 91 (<1/99)
16		(Z,Z)-**5n**, 98 (97/3)[f]
17		(E,E)-**5n**, 85 (<1/99)[g]
18		(Z)-**5o**, 96 (98/2)
19		(E)-**5o**, 95 (<1/99)
20		(Z)-**5p**, 89 (95/5)
21		(E)-**5p**, 94 (<1/99)
22	EtO_2C—≡—Ph	(Z)-**5q**, 90 (98/2)[h]
23		(E)-**5q**, 95 (1/99)
24		(Z)-**5r**, 90 (>99/1)[h]
25		(E)-**5r**, 93 (<1/99)
26	*n*-C_7H_{15}—≡—C_7H_{15}-*n*	**5s**, 95 (61/39)
27		**5s,** 88 (31/69)
28	*t*-Bu—≡—Ph	**5t**, 55 (91/8)[i]
29		**5t**, 83 (70/30)[j]
30	TMS—≡—Ph	complicated[k]

[a] Conditions for entries 1–9: 1 mol % $Pd(Ph_3P)_4$, HCO_2H (2 equiv), 80 °C, 3 h. Conditions for entries 10–29: unless otherwise noted *condition A* for (Z)-alkenes and *condition B* for (E)-alkenes. [b] Isolated yields unless otherwise noted. [c] Determined by ^1H NMR unless otherwise noted. [d] GC yields. [e] A total of 2.5 equiv of Et_3N was added. [f] Determined by GC. Four equivalents of HCO_2H was used. [g] Conditions: 6 equiv of 25% aqueous formic acid, 48 h. [h] Conditions: 3 h. [i] Determined by GC. 44% starting alkyne remained. [j] Determined by GC. 17% starting alkyne remained [k] C–Si cleavage took place under these conditions giving a mixture of styrene, Z/E-trimethyl(styryl)silane and ethylbenzene. Condition A: 12% styrene, 10% Z/E-trimethyl(styryl)silane (Z/E = 30/70), 14% ethylbenzene; Condition B: 20% styrene, 21% Z/E-trimethyl(styryl)silane (Z/E = 0/100), 59% ethylbenzene.

Table 3. Pd(0)-Catalyzed Selective Hydrogenation of Alkynes to Alkanes with Formic Acid[a]

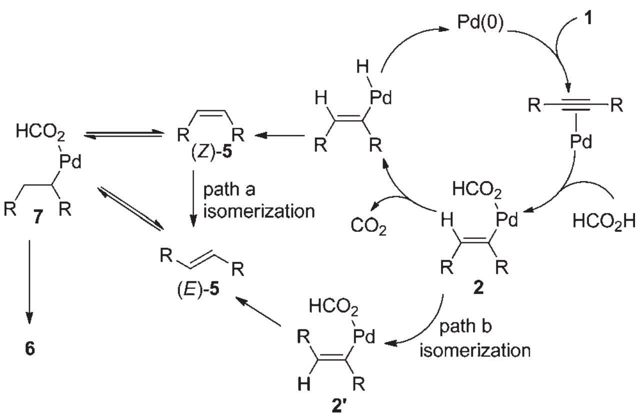


entry	alkyne **1**	**6**, yield (%)[b]
1	R^1, R^2 = H, $CH_3(CH_2)_{12}$	**6b**, 95[c]
2	R^1,R^2 = H, Ph	**6c**, 99[c]
3	R^1,R^2 = H, *p*-$HCOC_6H_4$	**6d**, 90[d]
4	R^1, R^2 = H, *p*-$CH_3C(O)NHC_6H_4$	**6e**, 94
5	R^1, R^2 = H, *m*-HOC_6H_4	**6f**, 93
6	R^1, R^2 = H, *m*-$BnOC_6H_4$	**6g**, 95
7	R^1, R^2 = *p*-$MeCOC_6H_4$, *p*-MeC_6H_4	**6h**, 95
8	R^1, R^2 = Ph, *p*-$BpinC_6H_4$	**6i**, 95
9	R^1, R^2 = Ph, *n*-C_6H_{13}	**6j**, 96
10	R^1, R^2 = Ph, CO_2Et	**6k**, 99
11	R^1 = R^2 = *n*-C_7H_{15}	**6l**,90
12	R^1, R^2 = *n*-C_5H_{13}, CO_2Me	**6m**, 91
13	R^1, R^2 = $PhCCC_6H_4$, Ph	**6n**, 90[e]
14	R^1, R^2 = H, *p*-$NO_2C_6H_4$	**6o**, 85[f]
15	R^1, R^2 = Ph, *p*-ClC_6H_4	**6p**, 29[c]
16	R^1, R^2 = *t*-Bu, Ph	**6q**, 43[g]

[a] Conditions: 1 mol % $Pd_2(dba)_3$, 4 mol % Cy_3P, aq. HCO_2H (3 equiv), 80 °C, 3–5 h. [b] Isolated yields unless otherwise noted. [c] GC yield. [d] GC yield; 4% yield of (4-ethylphenyl)methanol was also detected. [e] Conditions; 6.0 equiv aq HCO_2H. [f] Seven percent yield of 4-ethylaniline was formed. [g] Determined by GC. Fifty-seven percent (E)-**5t** was formed.

smoothly to give **5h** in 91% yield without formylation of the hydroxyl group (entry 7). The expected product **5g** was also obtained in high yield when N-(4-ethynylphenyl)acetamide was used, and the possible transformylation was not observed (entry 6). In addition, boronic ester group was also compatible with the current Pd-catalyzed hydrogenation (entries 18 and 19). High chemo- and stereoselectivity were achieved for hydrogenation of internal alkynes under the catalysis of Pd_2dba_3 and dppb to selectively produce both (Z) (***condition A***) and (E)-alkenes (***condition B***). Thus, by using condition A, a combination of 1 mol % of Pd_2dba_3 and 4 mol % of dppb efficiently catalyzed the reaction of 1-chloro-4-(phenylethynyl) benzene with formic acid to afford (Z)-**5l** in 91% yield with a Z/E ratio up to 99/1 (entry 12). On the other hand, the use of 25% aqueous formic acid with 1 mol % of Pd_2dba_3 and 2 mol % of dppb (***condition B***) produced (E)-**5l** in high yield selectively (entry 13).[25] It should be mentioned that 4-acetylphenyl(phenyl)acetylene, which showed low chemoselectivity in Elsevier̀s system producing a mixture of (Z)-**5m** and over-reduced product in a ratio of 69:31,[15d] was also successfully reduced to (Z)-**5m** and (E)-**5m**, respectively, with excellent stereoselectivity (entries 14 and 15). The expected products (Z)-**5p** and (E)-**5p** were also obtained stereoselectively in high yields from a substrate bearing a pyridinyl group 1-(4-(pyridin-2-ylethynyl)phenyl)ethanone, implying that the reactions could be used for the synthesis of C_2-tethered heterocyclic compounds (entries 20 and 21). Although sluggishly due to steric bulkiness, the reaction of *tert*-butylphenylacetylene with formic acid also took place under conditions A and B to produce **5t** in 55% and 83% yield, respectively, whereas phenyl(trimethylsilyl)ethyne could not produce the corresponding silylalkenyl products satisfactorily (entry 30). Finally, carboxylate

Scheme 4

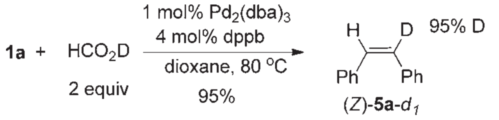


alkynes ethyl 3-phenylpropiolate and methyl oct-3-ynoate were also proved to be good substrates for the current transformation (entries 22−25). However, an aliphatic-aromatic internal alkyne hex-1-ynylbenzene (entries 11) gave 73% selectivity of the *trans* isomer under condition B. The *Z*/*E* selectivities for an aliphatic-aliphatic internal alkyne 8-hexadecyne (entries 26 and 27) were not very high either.

As shown in Table 3, a complete reduction of the alkynes to the saturated alkanes was achieved by employing reaction ***condition* C**. The reaction also proceeded with good chemoselectivity. Functionalities such as acyl, carboxylic ester, boronic ester, and acylamino group were all well tolerated. Noteworthy, the C−O bond of benzyl ether, as exemplified in entry 6, also survived after reduction. Although the competitive reductions of formyl and nitro groups were observed when 4-ethynylbenzaldehyde and 4-nitrophenylacetylene were used as substrates, the selectivity to the desired alkanes was also satisfactory (entries 3 and 14). However, this reduction was not satisfactorily applicable to 1-chloro-4-(phenylethynyl)benzene (entry 15) under ***condition* C**, presumably because of the deactivation of the catalyst during the reaction of C−Cl bond with the Pd-PCy_3 catalyst.[26] On the other hand, the reduction of the bulky *tert*-butylphenylacetylene proceeded slowly to produce the corresponding alkane in 43% yield.

Mechanistic Aspects of the Selective Hydrogenation. Mechanism studies on transition-metal catalyzed homogeneous hydrogenation of alkynes with formic acid or formates are rare.[22,27] Puddephatt reported that diruthenium (0) complex decomposes formic acid to CO_2 and hydrogen, which then slowly hydrogenated alkynes.[22a] As for the Pd-catalyzed hydrogenation of alkynes with formates, most of them were explained based on an empirical hypothesis consisting of oxidative addition of the O−H bond, migratory insertion of the hydride into the Pd-alkyne bond, decarboxylation, and reductive elimination.[15d,28] Recently, Elsevier studied the mechanism of the highly selective hydrogenation of alkynes catalyzed by a Pd(0) N-heterocyclic carbene complex using ammonium formate as hydrogen donor in detail.[15e] They proposed a mechanism involving hydrogen transfer from coordinated formate anion to a Pd(0) N-heterocyclic carbene complex and subsequent migratory insertion of hydride to alkyne to form a vinyl palladium (0) anion which undergoes protonolysis to give *cis*-alkenes.

On the basis of our findings, the current reduction of an alkyne to a *cis*-alkene with formic acid can be clearly rationalized to take place via a catalytic cycle involving hydropalladation of the triple bond with formic acid to produce alkenenylpalladium species **2** followed by subsequent decarboxylation and reductive elimination to afford the *cis* products (*Z*)-**5** (Scheme 4). A labeling experiment using *O*-deuterium formic acid produced monodeuterated *cis*-stilbene ((*Z*)-**5a**-d_1) in 95% yield (D incorporation: ca. 95%), clearly indicative of the origin of the hydrogen atoms (eq 7).



(7)

As to the mechanisms for the production of *trans*-alkene, we assume that there are two possible reaction paths for its generation: isomerization of the *cis*-alkene **5** (path a) and isomerization of **2** (path b). A separate experiment showed that path a could take place in the presence of aqueous formic acid and Pd_2dba_3/dppp.[29,30] However, path b should be a major route, especially in case of alkyl internal alkynes, because easy isomerization of **2** to **2′** is clearly evidenced in the absence of an extra phosphine (eq 2) and, more importantly, only a trace amount of other regioisomers of olefins by the double bond shift could be detected from the reactions, a result which could be hardly explained by path a.[8,31] The use of tricyclohexylphosphine which is known to be capable of preventing the β−H elimination in palladium catalyzed reactions[32] can facilitate the reduction of the double bonds of the alkenes via a process of insertion of the H−Pd species to the double bond, decarboxylation, and reductive elimination, therefore, enabling a full hydrogenation of alkynes (Scheme 4). Indeed, under *condition* C, styrene could be converted to ethylbenzene quantitatively.

■ SUMMARY

In conclusion, for the first time, a facile hydrometalation of alkynes with a combination of carboxylic acids and group 10 transition metal complexes $M(PEt_3)_4$ (M = Ni, Pd, Pt) to afford fully characterized alkenylmetals was revealed. This finding provides direct proof for the reaction mechanism involving the combination of carboxylic acid and zerovalent palladium catalyst. On the basis of this finding, an unprecedented controllable hydrogenation of alkynes with formic acid was developed to selectively produce *cis*-, *trans*-alkenes and alkanes by slightly tuning the conditions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. General information, experimental procedures, CIF files of **2a**, **2b**, **2c**, and **2f**, characterization data, copies of ^1H, ^{13}C, and ^{31}P NMR spectra for products. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Further heating at 110 °C for another 70 h produced **2a**′ in 86% yield. The ratio of **2a**′/**2a** remained the same even after further heating for another 10 h, indicating that **2a**′/**2a** reached an equilibrium. As determined by GC, complex **2a** could be reduced to (*Z*)-stilbene by Ph_2SiH_2 (**2a**, 15 mg; Ph_2SiH_2, 10 mg; C_6D_6, 0.5 mL; 25 °C, 20 h, 92% GC yield, $Z/E > 99/1$). In a similar manner, a mixture of **2a**′ and **2a** (**2a**′/**2a** = 81/19 based on ^{31}P NMR) was also converted to the corresponding stilbenes stereospecifically (93% GC yield, $Z/E = 18/82$). These results agree with the Pd/AcOH mediated semihydrogenation of alkynes with silanes (ref 2c). For a similar isomerization of an alkenylpaltinum complex, see: (a) Lorusso, G.; Boccaletti, G.; Di Masi, N. G.; Fanizzi, F. P.; Maresca, L.; Natile, G. *Eur. J. Inorg. Chem.* **2004**, 4751. (b) It was also reported that *trans*-chlorovinylplatinum (II) complex underwent *trans*/*cis* isomerization upon treatment with acids. The rate of isomerization depends on the acid and solvent, see:Bell, R. A.; Chisholm, M. H. *Inorg. Chem.* **1977**, *16*, 698.

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(18) Reaction of $Pt(PEt_3)_4$ with AcOH at room temperature readily gave **4a** quantitatively as estimated from ^{1}H and ^{31}P NMR spectroscopy. Complex **4a** is an oily product which has not been obtained in pure form. However, its structure could be confirmed from its ^{1}H NMR spectroscopy. δ (H−Pt) = −6.27 (dt, J_{H-Pt} = 789.2 Hz, J_{P-H} = 14.8 Hz, 157.2 Hz). For details see Supporting Information.

(19) Han, L.-B.; Ono, Y.; Xu, Q.; Shimada, S. *Bull. Chem. Soc. Jpn.* **2010**, *83*, 1089.

(20) The conclusion shown in Scheme 3 is assumed applicable to $Pd(PEt_3)_4$ too. Under similar reaction conditions, Pd−H species (δ(Pd−H) = −8.3) was also readily confirmed from the reaction of $Pd(PEt_3)_4$ with AcOH. As it is different from that of $Pt(PEt_3)_4$, there is an equilibrium between this Pd−H species and the starting $Pd(PEt_3)_4$ and AcOH (ref 9b). Therefore, as estimated from ^{1}H NMR, ca. 30% yield of the Pd−H was generated after 1 h to reach equilibrium. An attempted isolation of this Pd−H complex by evaporation of the volatiles resulted in the complete disappearance of the Pd−H species, leaving $Pd(PEt_3)_3$ as the sole product. Presumably because of this easy equilibrium, **2a** was also obtained in high yield by adding diphenylacetylene to the mixture of $Pd(PEt_3)_4$ and AcOH. A similar reaction with $PhSO_3H$ could react with $Pd(PEt_3)_4$ to give $HPd(PhSO_3)(PEt_3)_3$ quantitatively. However, this H−Pd complex did not react with diphenylacetylene to produce the corresponding alkenylpalladium complex at all. These observations agree with the conclusion shown in Scheme 3.

(21) For attempted isolation of organopalladium formato complexes, see: (a) Grushin, V. V.; Bensimon, C.; Alper, H. *Organometallics* **1995**, *14*, 3259. (b) Oshima, M.; Shimizu, I.; Yamamoto, A.; Ozawa, F. *Organometallics* **1991**, *10*, 1221. (c) Johansson, R.; Wendt, O. F. *Organometallics* **2007**, *26*, 2426. $Pd(PEt_3)_4$ could catalyze the reduction of **1a** with formic acid to give the corresponding *cis*-stilbene in 60% yield (Z/E = 98/2) ($Pd(PEt_3)_4$, 0.01 mmol; **1a**, 0.2 mmol; formic acid, 0.4 mmol (additional 0.4 mmol was added after 2h); 1,4-dioxane, 0.5 mL, 50 °C, 4h).

(22) Ru-catalyzed reduction of alkynes to alkenes with formic acid, see: (a) Gao, Y.; Jennings, M. C.; Puddephatt, R. J. *Can. J. Chem.* **2001**, *79*, 915. (b) Belger, C.; Neisius, N. M.; Plietker, B. *Chem.—Eur. J.* **2010**, *16*, 12214.

(23) These conditions A, B, and C were finally established after an extensive screening on the reaction conditions (ligands, palladium source, solvents, etc.). For details of these experiments, see Supporting Information.

(24) The Z/E isomerization was significantly retarded under condition A. Thus, even after heating the reaction mixture for a much longer time, no significant change of the Z/E ratio was observed (Z/E: 97/3 for 21 h, 93/7 for 30 h). For details, see Supporting Information.

(25) However, a similar reaction with 1-bromo-4-(phenylethynyl)-benzene did not proceed at all.

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(27) For a mechanism study on heterogeneous hydrogenation with formates, see: (a) Yu, J.; Spender, J. B. *Chem. Commun.* **1998**, 1935. (b) Yu, J.; Spender, J. B. *Chem.—Eur. J.* **1995**, *5*, 2237.

(28) (a) Li, J.; Hua, R.; Liu, T. *J. Org. Chem.* **2010**, *75*, 2966. (b) Brunel, J. M. *Tetrahedron* **2007**, *63*, 3899. (c) Trost, B. M.; Braslau, R. *Tetrahedron Lett.* **1989**, *30*, 4657.

(29) For details of these experiments, see Supporting Information.

(30) (a) Reger, D. L.; Garza, D. G. *Organometallics* **1993**, *12*, 554. (b) Clark, H. C.; Ferguson, G.; Goel, A. B.; Janzen, E. G.; Ruegger, H.; Siew, P. Y.; Wong, C. S. *J. Am. Chem. Soc.* **1986**, *108*, 6961. (c) Shirakawa, E.; Otsuka, H.; Hayashi, T. *Chem. Commun.* **2005**, 5885.

(31) This was supported by the experimental results that *cis*-octene did not isomerize under both conditions A and B.

(32) (a) Netherton, M. R.; Dai, C.; Neuschütz, K.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 10099. (b) Kirchhoff, J. H.; Dai, H.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 1945.