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FEATURE ARTICLE

Transition metal-catalysed addition reactions of H–heteroatom and inter-heteroatom bonds to carbon–carbon unsaturated linkages *via* oxidative additions

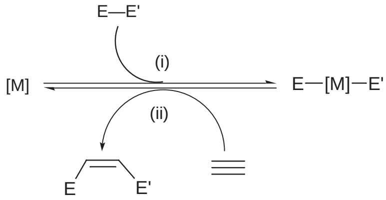
Li-Biao Han and Masato Tanaka*

National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305-8565, Japan.
E-mail: mtanaka@ccmail.nimc.go.jp

Oxidative addition of inter-heteroatom bonds comprising B, Si, Ge, Sn, P, S, Se and Te with late transition metal complexes readily takes place at room temperature and triggers a variety of catalytic additions of the bonds to carbon–carbon unsaturated linkages. The new catalytic reactions are regio- and stereoselective and provide high yield syntheses of synthetically versatile heteroatom compounds.

Introduction

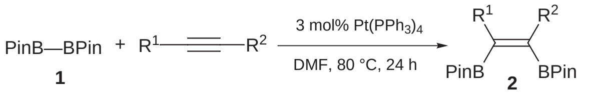
Transition metal complex catalysis in heteroatom chemistry is experiencing vigorous growth these days. This is partly because heteroatom-to-carbon bonds can be very reactive and versatile intermediates in synthetic organic chemistry. In addition, heteroatom compounds can exhibit biological activity. Furthermore heteroatom compounds, inclusive of polymeric ones, are useful as such or as precursors in various applications such as ceramics, heat-resistant materials, semiconductors and electroluminescent materials. Although metal complex-catalysed substitution reaction with heteroatom nucleophiles such as palladium-catalysed amination of organic halides[1] has been fairly well studied, metal complex-catalysed addition reactions of H–heteroatom and inter-heteroatom bonds (H–E, E–E′; E, E′ = heteroatom) to carbon–carbon unsaturated bonds have not been extensively explored until recently. The newly developed addition reactions generally give the products selectively in high yields under mild reaction conditions and hence are particularly attractive from the synthetic point of view. Although mechanistic details may vary depending on the heteroatom compounds used, most of the additions are overall envisioned to proceed *via* a simple sequence of events comprising (i) oxidative addition of an inter-heteroatom bond (E–E′) to a transition metal complex, (ii) insertion of an alkene or alkyne, and reductive elimination (Scheme 1). Exceptional reactions in this category that have been rather well studied include those of group 14 element compounds such as Si–H, Sn–H, Si–Si, Si–Sn, Si–CN and some of them are exploited in industry.[2] Transition metal-catalysed additions of B–H bonds, which provide a possibility to control regio-, stereo- and chemoselectivity in the hydroboration processes, have also been well studied.[3] This article focuses on the recent progress in the transition metal-catalysed additions of groups 13, 15 and 16 (B, N, P, S and Se) heteroatom compounds that are considered to proceed *via* a mechanism similar to Scheme 1. Since additions of group 14 element compounds and the catalysed hydroborations have been subjects of numerous review articles, they will not be discussed here.

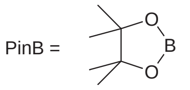


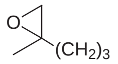
Scheme 1

Metal-catalysed additions of B–E bonds (E = B, Si, Sn, S)

In 1993, Miyaura and Suzuki reported addition reactions of diborons with alkynes (Scheme 2).[4] The addition of bis(pinacolato)diboron **1** to alkynes proceeds efficiently in the presence of a catalytic amount of $Pt(PPh_3)_4$ to afford the *cis*-bis(boryl)alk-





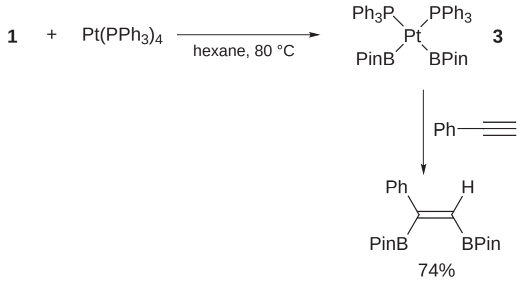
R^1	R^2	% yield of **2**
n-C_8H_{17}	H	86
Cy	H	78
Pr	Pr	86
Ph	Ph	79
Ph	H	79
$CH_2{=}CH(CH_2)_4$	H	85
$Cl(CH_2)_3$	H	83
$NC(CH_2)_3$	H	79
	H	87
$MeOC(O)(CH_2)_4$	H	89

Scheme 2

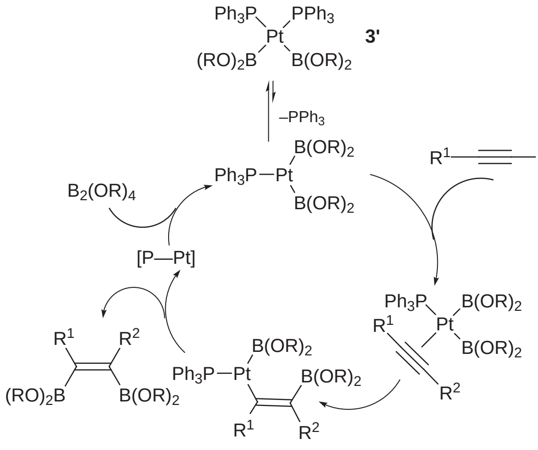
Li-Biao Han was born in Shandong, China in 1965. He finished his university education at Osaka University in 1988 and received his PhD in 1993 under the supervision of Professor N. Sonoda. After several years postdoctoral research experience, he joined the National Institute of Materials and Chemical Research in 1997.

Masato Tanaka is the Director of the Department of Organic Chemistry of the National Institute of Materials and Chemical Research. He is also an Adjunct Professor of the Department of Industrial Chemistry, Science University of Tokyo. He received his PhD from Kyoto University in 1974 for his work on carbonylation and was a research associate with Professor Howard Alper at the University of Ottawa in 1977–1978. He won several awards, including the Progress Award in Synthetic Organic Chemistry (1986), a Commendation by the Minister of State for Science and Technology (1987), the Divisional Award of the Chemical Society of Japan (1994), and the Wilhelm Manchot Research Professorship (Pinguin Foundation, Germany, 1998).

enes **2** in high yields. In this diboration both terminal and internal alkynes are reactive as substrates. The reaction is accelerated in polar solvents such as DMF and MeCN, but also proceeds in non-polar solvents like hexane to give the products in good yields. $Pt(CO)_2(PPh_3)_2$ also exhibits high activity, but others such as $Pd(PPh_3)_4$ and $RhCl(PPh_3)_3$ that are efficient catalysts for hydroboration[3] are ineffective. Mechanistic studies by these authors and others have disclosed that oxidative addition of the B–B bond to the Pt complex is a key reaction that triggers the catalysis.[4–6] Indeed, $Pt(PPh_3)_4$ reacts with **1** to give a *cis* complex **3**, which reacts with an alkyne (but not with alkene) to afford the adduct (Scheme 3). Since a detailed study on the reaction of *cis*-$Pt(BCat)_2(PPh_3)_2$ (Cat = $C_6H_4O_2$) with alkynes revealed that the addition reaction was strongly retarded by an addition of a free phosphine to the reaction mixture, dissociation of a phosphine ligand from **3′** generating three coordinate species is believed to precede the insertion of an alkyne (Scheme 4).

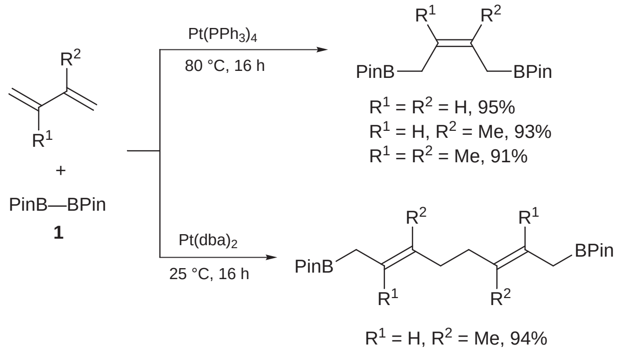


Scheme 3



Scheme 4

1,3-Dienes also react bis(pinacolato)diboron **1** in the presence of $Pt(PPh_3)_4$ to form *Z*-1,4-adducts in high yields with excellent selectivities (Scheme 5).[7] Interestingly, when a phosphine-free platinum complex, $Pt(dba)_2$, is employed as catalyst, a 1:2 adduct of the diboron to the diene is obtained.

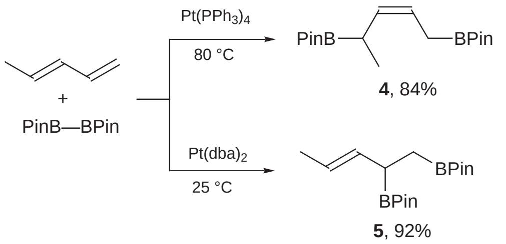


$R^1 = R^2 = H$, 95%
$R^1 = H$, $R^2 = Me$, 93%
$R^1 = R^2 = Me$, 91%

$R^1 = H$, $R^2 = Me$, 94%

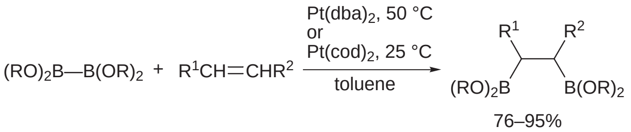
Scheme 5

Regioselectivity in the reaction of penta-1,3-diene varies depending on the platinum complex catalyst being phosphine-ligated or phosphine-free. Thus, 1,4-addition to penta-1,3-diene takes place with $Pt(PPh_3)_4$ to form **4**, whereas the same reaction with $Pt(dba)_2$ selectively affords the 1,2-addition product **5** (Scheme 6).



Scheme 6

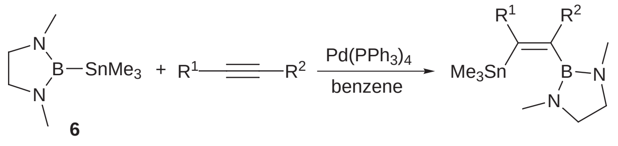
In contrast to the facile additions to alkynes, $Pt(PPh_3)_4$ does not catalyse the additions of diborons to alkenes. In 1995, Baker and co-workers briefly described that a phosphine–gold(I) complex was able to catalyse the addition of a diboron to styrenes to give desired 1,2-diboronate esters.[8] Very recently, phosphine-free platinum complexes such as $Pt(cod)_2$ and $Pt(dba)_2$ have been found to efficiently catalyse the diborations of terminal alkenes and strained cyclic alkenes to afford the addition products in high yields (Scheme 7).[9]



$(RO)_2B$ = PinB or CatB
Alkenes: ethylene, hex-1-ene, styrene, 4-methoxystyrene,
6-chlorohex-1-ene, cyclopentene, norbornene *etc.*

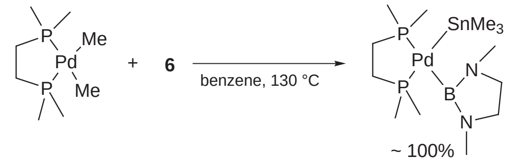
Scheme 7

Palladium- or platinum-catalysed additions of other B–heteroatom bonds are also rapidly emerging. We have found a highly stereo- and regio-selective Pd-catalysed addition of a B–Sn reagent to alkynes, which represents the first addition reaction of a bond comprising groups 13 and 14 elements to unsaturated carbon linkages (Scheme 8).[10] The addition of **6** to terminal alkynes takes place rapidly even at room temperature to afford *cis*-adducts in high yields, although the presence of an N–B bond in the starting diboron reagent retarded the diborations of alkynes.[4] Both terminal and internal alkynes are reactive substrates. The reactions of terminal alkynes end up with the boryl group selectively attached to the terminal carbons. Mechanistic studies have substantiated that oxidative addition of the B–Sn bond of **6** to the palladium centre is involved in the catalytic cycle. In one case such an adduct was isolated and was fully characterized (Scheme 9) and the adduct proved to exhibit a high activity when employed as catalyst. Diynes also readily react with **6**; highly regio- and stereo-selective borylstannylative carbocyclization takes place to



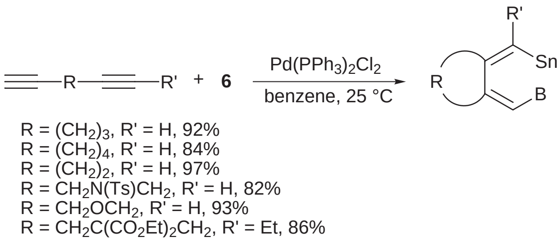
R^1 = n-C_6H_{13}, R^2 = H, 83%
R^1 = Ph, R^2 = H, 73%
$R^1 = R^2$ = Ph, 78%

Scheme 8



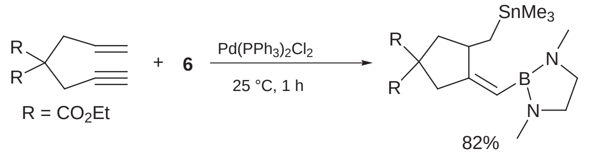
Scheme 9

afford good yields of 1-(borylmethylidene)-2-(stannylmethylidene)cycloalkanes (Scheme 10).[11] Simple addition products to the triple bonds are not found in the reaction mixture. It is surprising that even a very strained four-membered ring can be selectively formed nearly quantitatively starting with a hexa-1,5-diyne as substrate. An enyne compound also undergoes the borylstannylative carbocyclization (Scheme 11). These carbocyclization reactions are very regioselective; the boryl group is selectively introduced to the more reactive unsaturated linkage, *i.e.* the terminal C≡C rather than internal one in the unsymmetrical diyne system and the C≡C rather than the C=C in the enyne system. On the basis of these experiments, the triple bond insertion to the Pd–B bond (in preference to the Pd–Sn bond) is believed to follow the oxidative addition of **6** in the catalytic cycle. The reaction of 1,3-dienes requires narrower tuning of the nature of the ligand. Triphenylphosphine–palladium complexes that were active in the reactions of alkynes, diynes, and enyne compounds are not so efficient with dienes. 4-Ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane [$P(OCH_2)_3CEt$ = etpo] proved to be the ligand of choice, the use of which results in more than 80% yields of 1,4-adducts (Scheme 12).[12]

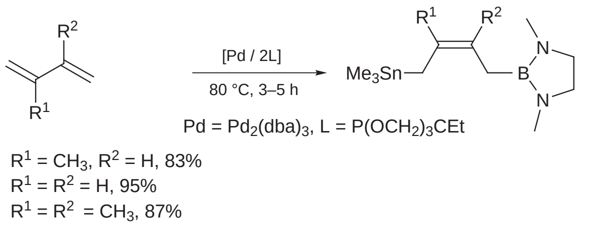


R = $(CH_2)_3$, R' = H, 92%
R = $(CH_2)_4$, R' = H, 84%
R = $(CH_2)_2$, R' = H, 97%
R = $CH_2N(Ts)CH_2$, R' = H, 82%
R = CH_2OCH_2, R' = H, 93%
R = $CH_2C(CO_2Et)_2CH_2$, R' = Et, 86%

Scheme 10



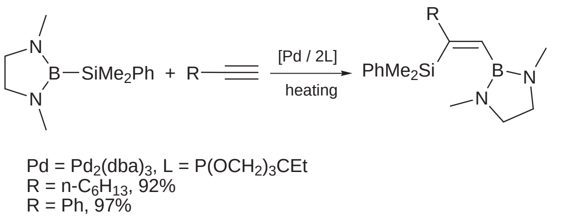
Scheme 11



$R^1 = CH_3$, R^2 = H, 83%
$R^1 = R^2$ = H, 95%
$R^1 = R^2 = CH_3$, 87%

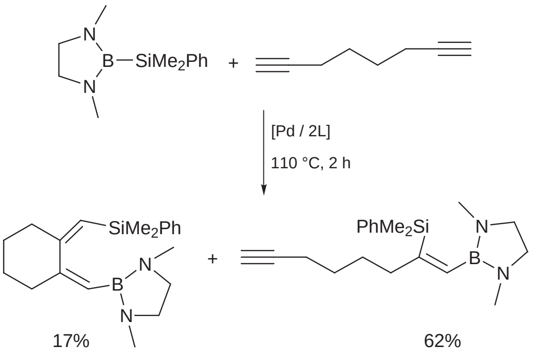
Scheme 12

In contrast to the B–Sn additions to alkynes, analogous B–Si additions are not straightforward and do not proceed efficiently under similar conditions. The $Pd_2(dba)_3$/etpo catalyst system is again the catalyst of choice but heating (typically 110 °C) is required for the reaction to take place (Scheme 13). The $Pd_2(dba)_3/PMe_3$ system, which was among the better catalysts for the additions of disilanes or digermanes,[13] also exhibits respectable performance.[14] Both the regio- and stereo-selectivities of the B–Si addition to terminal alkynes are similar to those found in the B–Sn addition to give the *cis* adduct with the boryl group bound to the terminal carbon predominantly. Unlike the borylstannylative carbocyclization in which the cyclization products were exclusively produced, the reaction of octa-1,7-diyne with the silylborane is not selective but gives a mixture of a cyclization product and a simple addition product (Scheme 14) when catalysed by the $Pd_2(dba)_3$/etpo catalyst system. The palladium(0)–*tert*-alkyl isocyanide catalyst systems, which were efficient for the addition of Si–Si bonds,[15] are also active catalysts for the addition of another B–Si reagent to alkynes to produce similar *cis*-addition products (Scheme 15).[16]

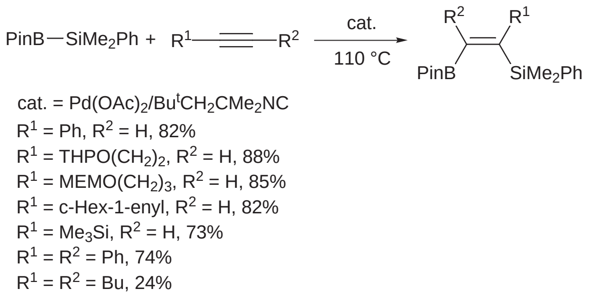


Pd = $Pd_2(dba)_3$, L = $P(OCH_2)_3CEt$
R = n-C_6H_{13}, 92%
R = Ph, 97%

Scheme 13



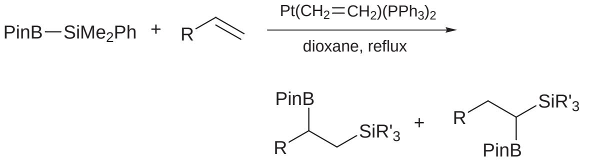
Scheme 14



cat. = $Pd(OAc)_2/Bu^tCH_2CMe_2NC$
R^1 = Ph, R^2 = H, 82%
R^1 = $THPO(CH_2)_2$, R^2 = H, 88%
R^1 = $MEMO(CH_2)_3$, R^2 = H, 85%
R^1 = c-Hex-1-enyl, R^2 = H, 82%
R^1 = Me_3Si, R^2 = H, 73%
$R^1 = R^2$ = Ph, 74%
$R^1 = R^2$ = Bu, 24%

Scheme 15

Successful addition of the Si–B reagent to alkenes has been achieved by using platinum complex catalysts (Scheme 16).[17] Thus, refluxing a mixture of the silylborane and 1-alkenes in dioxane in the presence of $Pt(CH_2{=}CH_2)(PPh_3)_2$ affords the adducts **7** with the boryl group bonded to the internal carbon of the double bond; note that the regioselectivity is the reverse of that found in addition reactions of terminal alkynes. Besides **7**, significant amounts of 1-boryl-1-silylalkanes **8** are also formed in the reactions of 1-alkenes.[18] Interestingly, the palladium(0)–*tert*-alkyl isocyanide complexes and $Pd(PPh_3)_4$, both of which are efficient in the Si–B and Sn–B additions to alkynes, respectively, do not show catalytic activity towards the addition to alkenes.

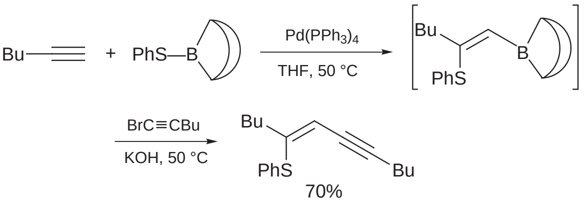


7 8

R = n-C_6H_{13}, 53% (87:13)
R = $AcO(CH_2)_2$, 46% (84:16)
R = $MeC(O)(CH_2)_2$, 46% (85:15)
R = Ph, 51% (> 99:1)
R = 4-$MeOC_6H_4$, 53% (> 99:1)
R = 4-$CF_3C_6H_4$, 46% (> 99:1)
R = H, 73% (> 99:1)

Scheme 16

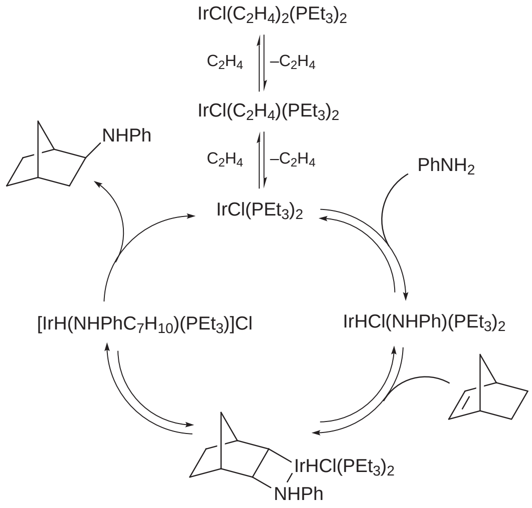
The palladium-catalysed addition of B–S bonds to terminal alkynes is another example of metal catalysed B–heteroatom bond additions.[19] The reaction takes place in THF to afford the adduct in high yields and selectively with the boryl group bound to the terminal carbons, as for the B–Si and B–Sn additions. Isolation of the adducts is hampered by the very high susceptibility of the C–B bond to cleavage, but the product generated *in situ* can be used for further manipulations, *e.g*. the Suzuki–Miyaura coupling reaction, without isolation (Scheme 17). A catalytic cycle starting with the oxidative addition of the B–S bond to Pd has been proposed for this reaction, but the mechanistic detail remains to be clarified.



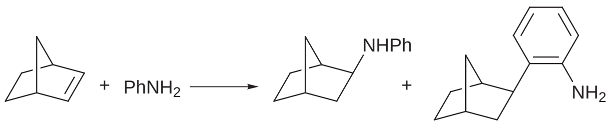
Scheme 17

Metal-catalysed additions of N–H, P–H and P–Se bonds

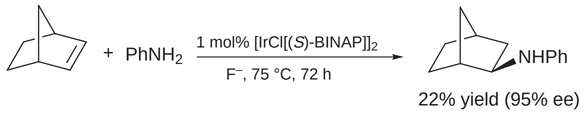
Compared to other heteroatom compounds, only a few metal-catalysed additions of group 15 element compounds are known. Although catalytic additions of N–H bonds to unsaturated bonds are highly attractive from the practical viewpoint,[20] only limited success has been achieved.[21] Milstein and co-workers have demonstrated that aniline oxidatively adds cleanly to an electron-rich Ir^I complex, $[Ir(PEt_3)_2(C_2H_4)Cl]$, to produce an Ir^{III} anilido hydrido complex. Despite its low catalytic efficiency, the Ir^{III} anilido hydrido complex undergoes insertion of norbornene leading to a new complex containing a chelating aminoalkyl ligand, from which the addition product is formed through reductive elimination (Scheme 18).[22] A catalytic system generated from $[RhCl(PEt_3)_2]_2$ and LiNHPh in aniline has also been used for hydroamination of norbornene, in which a rhodium anilido complex is probably involved as key catalytic species. Another adduct arising from addition of an *ortho* C–H bond of aniline to norbornene is also formed in addition to the desired hydroamination product (Scheme 19).[23] Recently, asymmetric hydroamination of norbornene with aniline was reported by use of an Ir^I–binap catalyst system, albeit in low chemical yields.[24] An addition of fluoride ion to the reaction mixture enhances the catalytic activity to give 22% chemical yield and 95% ee of the *exo*-2-(phenylamino)norbornane (Scheme 20). Palladium-catalysed hydroamination of allenes has also appeared recently (Scheme 21).[25] Addition of acetic acid facilitates the reaction, but the detailed reaction mechanism remains to be clarified.



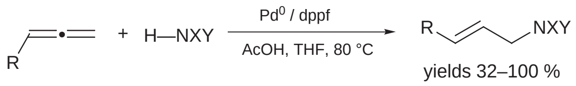
Scheme 18



Scheme 19



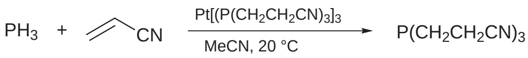
Scheme 20



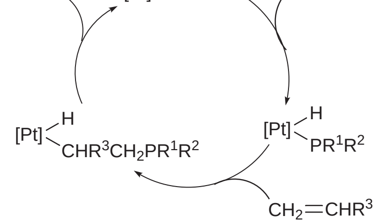
X = Y = CH_2CO_2Et, CH_2Ph, Ph
X = β-Naphthyl, Y = Ph
R = Ph, *p*-MeC_6H_4, *p*-$CF_3C_6H_4$, $Ph(CH_2)_2$, n-Octyl, *p*-$F_3COC_6H_4$

Scheme 21

Transition metal-catalysed additions of phosphorus compounds *via* oxidative addition are still very rare. Pringle and coworkers have reported that PH_3 reacts with acrylonitrile in the presence of $Pt[P(CH_2CH_2CN)]_3$ to give $P(CH_2CH_2CN)_3$ (Scheme 22).[26] The reaction has been proposed to proceed *via* oxidative addition of the P–H bond to platinum. A recent mechanistic study has confirmed this idea, showing furthermore that the reaction is likely proceed through insertion of acrylonitrile into the Pt–P (but not Pt–H) bond, followed by a C–H reductive elimination (Scheme 23).[27]

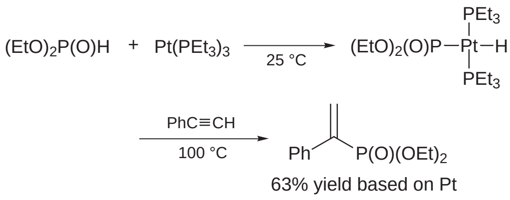


Scheme 22



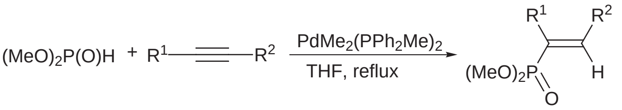
Scheme 23

We also have found that oxidative addition of the H–P bonds of hydrogen phosphonates $[(RO)_2P(O)H]$ with Pt^0 complexes readily takes place to afford the corresponding hydrido(phosphoryl) complex quantitatively. Heating the complex with phenylacetylene formed a vinylphosphonate (Scheme 24).[28]



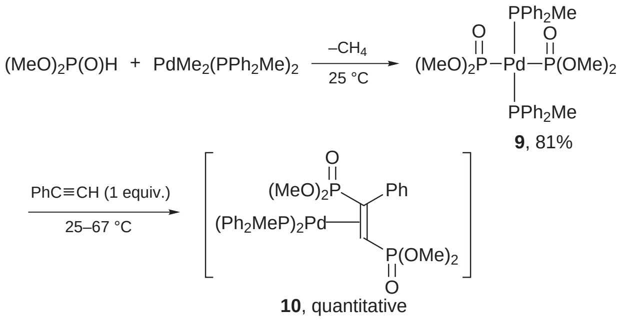
Scheme 24

Accordingly, catalytic addition of hydrogen phosphonates to alkynes readily proceeds when palladium complexes are used as catalysts (hydrophosphorylation). Markovnikov adducts are normally formed in high yields and with high selectivities (Scheme 25). When oct-4-yne was employed as substrate, only the *cis*-adduct was selectively obtained. Among the complexes screened, $Pd(CH_2{=}CH_2)(PPh_3)_2$ and $PdMe_2(PPh_2Me)_2$ show highest activity. The frequently employed $Pd(PPh_3)_4$ also catalyses the addition, albeit slowly. Pd^{II} complexes such as $PdCl_2$, $Pd(OAc)_2$, $PdCl_2(PPh_3)_2$ and $PdCl_2(PhCN)_2$ are totally ineffective, presumably because of the difficulty of these precursor complexes being reduced to Pd^0 active species. When $PdMe_2(PPh_2Me)_2$ is used as precursor, Pd^0 species **10** is readily formed through the sequence shown in Scheme 26,[29] and the species **10** does catalyse the addition of $(MeO)_2P(O)H$ to phenylacetylene efficiently.



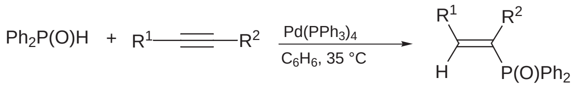
R^1 = n-C_6H_{13}, R^2 = H, 95%
R^1 = Ph, R^2 = H, 93%
R^1 = 4-MeC_6H_4, R^2 = H, 90%
R^1 = $NC(CH_2)_3$, R^2 = H, 94%
R^1 = cyclohex-1-en-1-yl, R^2 = H, 89%
R^1 = Me_3Si, R^2 = 41%
R^1 = R^2 = Pr, 82%

Scheme 25



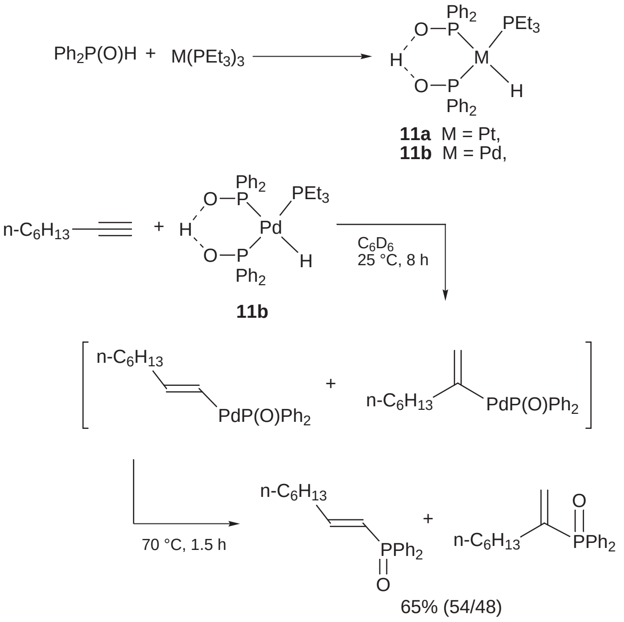
Scheme 26

Unlike the reaction of alkynes with hydrogen phosphonates, the reactions with $Ph_2P(O)H$ in the presence of $Pd(PPh_3)_4$ catalyst proceeds under very mild conditions (hydrophosphinylation) and selectively forms *anti*-Markovnikov products through *cis*-addition (Scheme 27).[30] The P–H bond of $Ph_2P(O)H$ also undergoes oxidative addition with Pd^0 and Pt^0 complexes to afford *cis*-$MH[P(O)Ph_2][PPh_2(OH)](PEt_3)$ (M = Pd, Pt) (Scheme 28).[30,31] Although platinum complex **11a** does not react with oct-1-yne upon heating, **11b** does react in benzene at room temperature to afford two regioisomeric alkenylpalladium species. Heating the reaction mixture at 70 °C affords the corresponding alkenylphosphine oxides. This result indicates that the catalysis proceeds through insertion of an alkyne into the Pd–H bond (hydropalladation) followed by reductive elimination of the alkenyl and phosphinyl ligands forming the product, which differs from the platinum-catalysed addition of PH_3 to acrylonitrile (*vide supra*).[27]



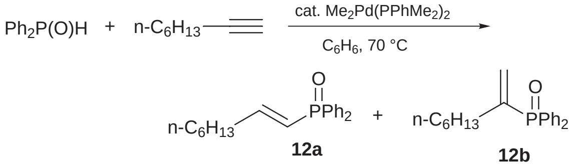
R^1 = n-C_6H_{13}, R^2 = H, 81%
R^1 = Ph, R^2 = H, 79%
R^1 = 4-MeC_6H_4, R^2 = H, 83%
R^1 = $NC(CH_2)_3$, R^2 = H, 73%
R^1 = $HO(CH_2)_2$, R^2 = H, 86%
R^1 = R^2 = H, 51%
R^1 = R^2 = Pr, 61%
R^1 = R^2 = Ph, 85%

Scheme 27



Scheme 28

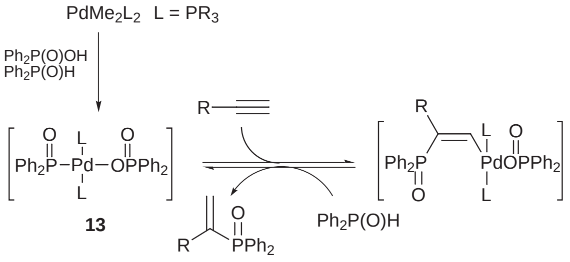
Very interestingly, the regioselectivity of the hydrophosphinylation of alkynes can be easily switched by addition of only one drop of $Ph_2P(O)OH$ to the reaction mixture (Scheme 29).[32]



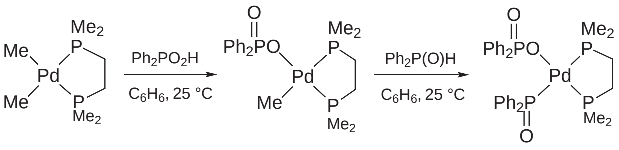
mol% $Ph_2P(O)OH$ added	% yield of **12** (**a**/**b**)
0	75 (88/12)
1	92 (21/79)
5	99 (5/95)
10	96 (4/96)

Scheme 29

Thus, when an equimolar mixture of $Ph_2P(O)H$ and oct-1-yne in C_6D_6 was heated at 70 °C for 2 h in the presence of a catalytic quantity (5% relative to the substrate) of *cis*-$Me_2Pd(PPhMe_2)_2$, isomeric **12b** and **12a** were formed in 75% total yield with a ratio of 12:88. However, another reaction run in the presence of only 1 mol% (relative to the substrate) of $Ph_2P(O)OH$ under otherwise identical conditions resulted in 92% total yield and a **12b**/**12a** ratio of 79:21. The regioselectivity for **12b** was further improved with an increase in the quantity of $Ph_2P(O)OH$ to achieve nearly quantitative formation of the adducts in a ratio of 95:5 in the presence of 5 mol% $Ph_2P(O)OH$. Besides the phosphinic acid, dibutyl phosphate and phosphoric acid work as well to give **12b** as the major product. However, the reversal is not observed with HMPA, acetic acid or benzoic acid. To explain the reversal we propose another reaction mechanism, in which a new palladium species **13** plays a key catalytic role (Scheme 30). Complex **13′** was indeed generated and isolated when $PdMe_2(PR_3)_2$ was treated with $Ph_2P(O)H$ and $Ph_2P(O)OH$ (Scheme 31). In addition, species **13′**, when used as catalyst in the addition reaction of $Ph_2P(O)H$ to oct-1-yne, exhibited essentially the same activity and regioselectivity as the combination of $PdMe_2(dmpe)_2$ [dmpe = 1,2-bis(dimethylphosphino)ethane] and $Ph_2P(O)OH$.



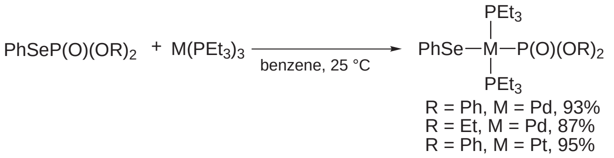
Scheme 30



13' 93%

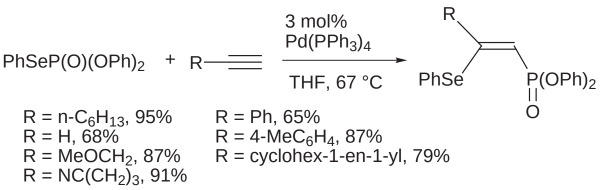
Scheme 31

Besides P–H bonds, oxidative additions of other P–heteroatom bonds also proceed and catalytic addition reactions can be designed. For instance, a selenophosphate readily reacts with Pd^0 and Pt^0 complexes to generate seleno(phosphoryl)metal(II) species (Scheme 32). *cis*-Additions of the selenophosphate to terminal alkynes also readily proceed to afford the adducts regio- and stereo-selectively with the phosphoryl group bound to the terminal carbons (Scheme 33).[33]



R = Ph, M = Pd, 93%
R = Et, M = Pd, 87%
R = Ph, M = Pt, 95%

Scheme 32

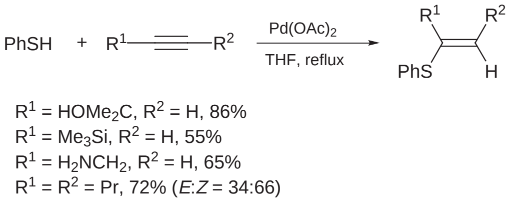


R = n-C_6H_{13}, 95%
R = H, 68%
R = $MeOCH_2$, 87%
R = $NC(CH_2)_3$, 91%
R = Ph, 65%
R = 4-MeC_6H_4, 87%
R = cyclohex-1-en-1-yl, 79%

Scheme 33

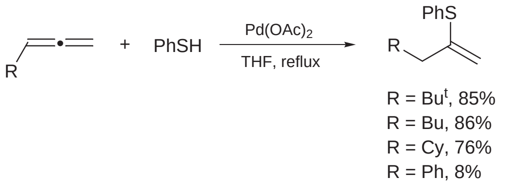
Metal-catalysed additions of chalcogen compounds

Metal-catalysed addition reactions of chalcogen reagents to carbon–carbon unsaturated bonds did not attract much attention until the pioneering work reported by Ogawa, Sonoda and their co-workers.[34] In the presence of $Pd(OAc)_2$, thiophenol and selenophenol react with terminal alkyne to produce Markovnikov *cis*-addition products in good yields with high regioselectivity (Scheme 34).[35] Allenes[36] and conjugated enynes[37] similarly react with PhSH (Schemes 35 and 36). A very interesting thioformylation reaction also proceeds when the addition of PhSH to alkynes was carried out under a CO atmosphere in the presence of a catalytic amount of Rh^I complex (Scheme 37).[38] $Pd(OAc)_2$, which is a good catalyst for the addition of PhSH, does not exert activity towards the thioformylation reaction. The use of $Pd(PPh_3)_4$ and $PdCl_2(PPh_3)_2$ resulted in a rather complicated mixture. On the other hand, addition of chalcogen–chalcogen bonds (S–S and Se–Se) to alkynes is efficiently catalysed by $Pd(PPh_3)_4$ to give predominantly the *cis*-addition products in good yields (Scheme 38).[39] When the reaction is run under a CO atmosphere, the simple addition of the dichalcogenides is suppressed, resulting in a selective carbonylative addition to produce the *Z* products in high yields (Scheme 39). A very interesting variation is the reaction of alkynes bearing an OH group at a proper position (propargylic alcohols, for example); a novel thiolative lactonization takes place to afford the corresponding lactons in good yields (Scheme 40).[40] The metal-catalysed additions of S–S bonds are applicable to other substrates. For example, $(ArS)_2$ undergoes telomerization with isocyanides (C=NAr′) in the



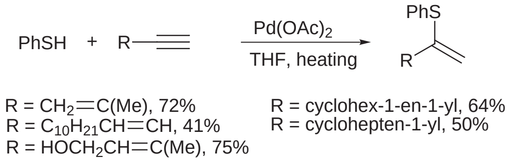
$R^1 = HOMe_2C$, R^2 = H, 86%
$R^1 = Me_3Si$, R^2 = H, 55%
$R^1 = H_2NCH_2$, R^2 = H, 65%
$R^1 = R^2$ = Pr, 72% (*E*:*Z* = 34:66)

Scheme 34



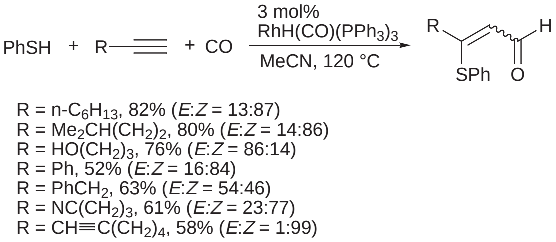
R = Bu^t, 85%
R = Bu, 86%
R = Cy, 76%
R = Ph, 8%

Scheme 35



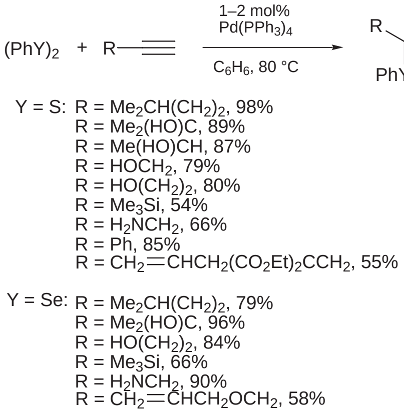
R = $CH_2{=}C(Me)$, 72%
R = $C_{10}H_{21}CH{=}CH$, 41%
R = $HOCH_2CH{=}C(Me)$, 75%
R = cyclohex-1-en-1-yl, 64%
R = cyclohepten-1-yl, 50%

Scheme 36

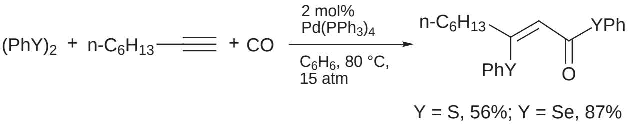


R = n-C_6H_{13}, 82% (*E*:*Z* = 13:87)
R = $Me_2CH(CH_2)_2$, 80% (*E*:*Z* = 14:86)
R = $HO(CH_2)_3$, 76% (*E*:*Z* = 86:14)
R = Ph, 52% (*E*:*Z* = 16:84)
R = $PhCH_2$, 63% (*E*:*Z* = 54:46)
R = $NC(CH_2)_3$, 61% (*E*:*Z* = 23:77)
R = $CH{\equiv}C(CH_2)_4$, 58% (*E*:*Z* = 1:99)

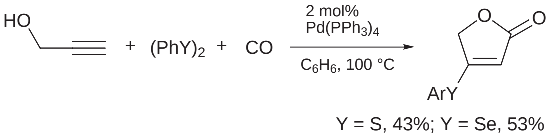
Scheme 37



Scheme 38

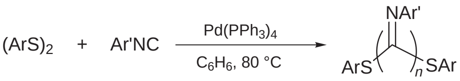


Scheme 39



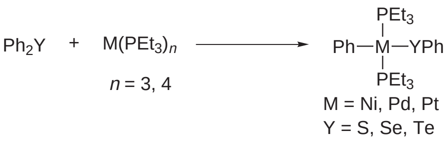
Scheme 40

presence of $Pd(PPh_3)_4$ to furnish novel telomeric products, $(ArS)(C{=}NAr')_n(SAr)$ (Scheme 41).[41]



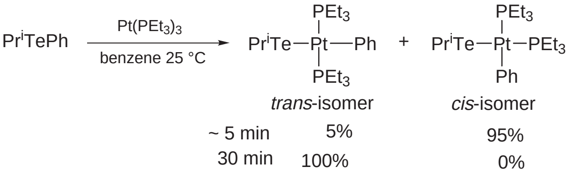
Scheme 41

Oxidative additions of S–H and S–S bonds to transition metal complexes have long been known[42] and are probably involved in the foregoing catalytic reactions. Related C–S bond scissions by metal complexes have also been extensively studied for modeling the hydrodesulfurization (HDS) process. However, similar studies on other chalcogen compounds are rare.[43] A recent systemic study on the reaction of Ph_2Y (Y = S, Se, Te) with group 10 transition metal complexes $M(PEt_3)_n$ (M = Ni, Pd, Pt; n = 3, 4) has revealed the formation of corresponding *trans*-$MPh(YPh)(PEt_3)_2$ complexes in high yields (Scheme 42).[44]



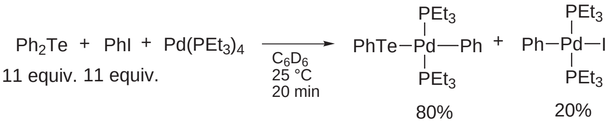
Scheme 42

However, the reaction of $PhTePr^i$ with $Pt(PEt_3)_3$ clearly suggests that *cis*-$PtPh(TePr^i)(PEt_3)_2$ is the initial product, which isomerizes rapidly to the thermodynamically more stable *trans*-form on standing (Scheme 43).



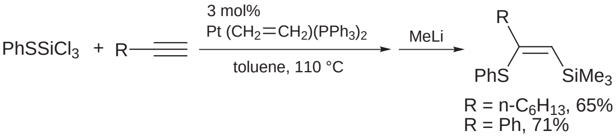
Scheme 43

The ease of the oxidative addition decreases in the order of C–Te > C–Se > C–S, which is the reverse of the order of their bond strengths and has similarity to the trend found with organic halides. The C–Te bond is extremely reactive; its oxidative addition to Pd^0 is even faster than the corresponding iodide (Scheme 44)!



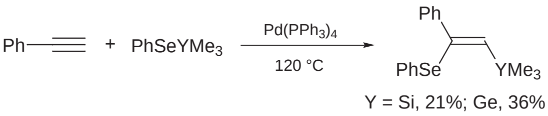
Scheme 44

Oxidative addition of chalcogenides to the palladium and platinum complexes seems quite general. In practice, chalcogenides of Si, Ge and Sn were more reactive in the oxidative addition reaction than their corresponding C–chalcogen bonds.[45] The reactivity trends were S–Si < Se–Si < Te–Si, and Si–Se < (Ge–Se) < Sn–Se, *i.e.* a heavier element bond reacted more readily. Obviously, these results have suggested new clues for the manipulations of chalcogen compounds using transition metal catalysts.[46] For example, we have found the addition of $PhSSiCl_3$ to terminal alkynes is efficiently catalysed by Pt^0 complexes to produce the *Z* adducts in high yields regioselectively with the Si moiety bound to the terminal carbons (Scheme 45).[47]



Scheme 45

Similar to the additions of $PhSeSiMe_3$ and $PhSeGeMe_3$ to phenylacetylene catalysed by $Pd(PPh_3)_4$ (Scheme 46),[34] this reaction is envisioned to proceed *via* oxidative addition of the S–Si bond.

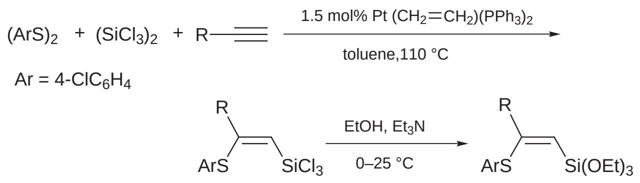


Scheme 46

However, there is no need to prepare starting $PhSSiCl_3$ in advance, since $PhSSiCl_3$ is generated *in situ* from $(PhS)_2$ and $(SiCl_3)_2$. In a new protocol, the same adduct can be obtained regio- and stereo-selectively in good yields, by simply heating a mixture of a disulfide, $(SiCl_3)_2$ and an alkyne in the presence of the platinum catalyst (Scheme 47). Possible byproducts coming from additions of the disulfide and/or disilane are not formed at all.

Conclusion

As described in this article, the simple combination of the classical elemental processes, oxidative addition, insertion of unsaturated compounds and reductive elimination, proves powerful for the design of new catalytic reactions in heteroatom chemistry. We believe homogeneous catalysis will find more opportunities not only in organic synthesis but in organometallic synthesis. Accumulation of knowledge concerning the chemistry of transition metal–heteroatom bonds is a pre-



R = n-C_6H_{13}, 83%
R = $PhCH_2$, 76%
R = Ph, 62%
R = 4-ClC_6H_4, 65%
R = 4-MeC_6H_4, 60%
R = $Cl(CH_2)_3$, 79%
R = $NC(CH_2)_3$, 81%
R = $Bu^tMe_2SiO(CH_2)_4$, 72%
R = $Bu^tCO_2(CH_2)_2$, 87%
R = cyclohex-1-en-1-yl, 51%

Scheme 47

requisite for this goal. Research along the line covering a wider range of elements is being actively pursued in our group.

Acknowledgments

We are indebted to our co-workers whose names appear in the references. Financial support from the Japan Science and Technology Corporation (JST) through the CREST program is gratefully acknowledged.

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