Received: 28 September 2018 | Revised: 14 November 2018 | Accepted: 15 November 2018

DOI: 10.1002/hc.21463

SPECIAL ISSUE ARTICLE

WILEY Heteroatom Chemistry

Regio- and stereoselective addition of *trans*-Pt(TeAr)($SiMe_3$)(PEt_3)$_2$ to terminal alkynes leading to *cis*-[(*Z*)-*β*-trimethylsilylalkenyl]platinum(II) complexes

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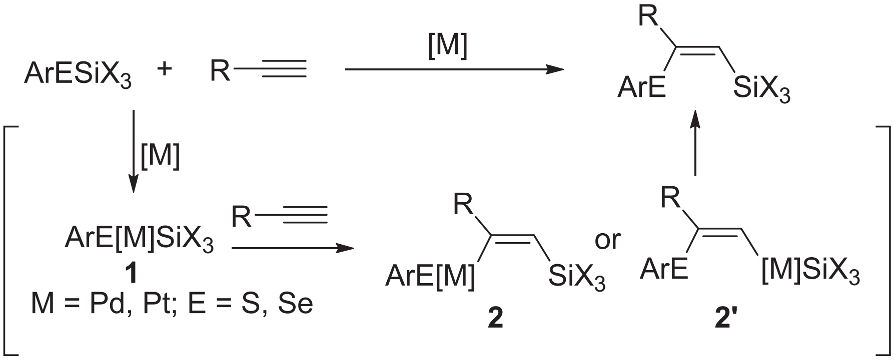
Abstract

Selective insertion of terminal alkynes RC≡CH into the Si—Pt bond of *trans*-Pt(TeAr)($SiMe_3$)(PEt_3)$_2$ took place readily to produce the corresponding novel alkenyl complexes *cis*-Pt(TeAr)[(*Z*)-CR=CH$SiMe_3$](PEt_3)$_2$. The structure of the complex was characterized by an X-ray analysis.

1 | INTRODUCTION

Metal-catalyzed addition of heteroatom compounds to unsaturated carbon—carbon bonds is one of the most straightforward way for the synthesis of new heteroatom chemicals.[1] These reactions are generally envisaged to occur via a catalytic cycle consisting of three elemental steps which are of equal importance: (a) oxidative addition of a heteroatom-containing bond to the metal, (b) insertion of a carbon—carbon unsaturated bond to the metal—heteroatom bond and (c) reductive elimination forming the adduct.[1] The first step of the catalytic cycle has been relatively well studied especially when the adduct generated from the oxidative addition step is isolable. On the other hand, studies dealing with step (ii) or (iii) of the catalytic process are often more complicated and elaborate. Silyl chalcogenides ArESiX_3 (E = S, Se) were able to add to acetylenes in the presence of platinum or palladium catalysts to give the *cis* adducts with the ArE moiety bound to the internal carbons of the acetylenes.[2] These reactions also appear to proceed via similar mechanistic sequences (Scheme 1), since the generation of R_3Si[M]EAr (**1**) by the oxidative addition of the Si—chalcogen bond to the metal has been well established.[3] However, limited information is available about the events that follow the oxidative addition. Intermediate **1** can add to an alkyne either at the Si—Pt bond forming **2** or at the E—Pt bond forming **2′**, both will give the same final product eventually. An attempted detection of these alkenylplatinum species in order to distinguish the two possibilities had not succeeded.



SCHEME 1 Metal-mediated selective addition of ArESiX_3 to alkynes

Herein, we report that *trans*-Pt(TeAr)($SiMe_3$)(PEt_3)$_2$ (**3**) reacts with a terminal alkyne at the Si—Pt bond to afford an alkenylplatinum complex **4**.[4] One of such a complex **4b** was full characterized by X-ray analysis (Chart 1).

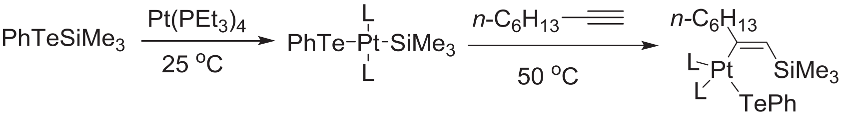
3 (L = PEt_3)
3a: Ar = Ph
3b: Ar = 4-PhC_6H_4

4 (L = PEt_3)
4a: Ar = Ph; R = *n*-C_6H_{13}
4b: Ar = Ph; R = *t*-$BuCH_2$
4c: Ar = 4-PhC_6H_4; R = *n*-C_6H_{13}

CHART 1 Structures of the Pt-complexes

2 | RESULTS AND DISCUSSION

To complex **3a**, quantitatively generated by treating $PhTeSiMe_3$ (0.59 mmol) with Pt(PEt_3)$_4$ (0.16 mmol) at room temperature for 10 minutes in dry degassed benzene-d_6 (0.50 mL),[3] was added 1-octyne (0.40 mmol) and the solution was heated at 50°C for 5 hours. ^1H NMR spectroscopy of the resulted pale yellow solution showed that **3a** was completely consumed to generate a new complex **4a** in 87% yield (Equation 1). Pumping off the starting materials and other volatiles under high vacuum at room temperature left a pale yellow oil. ^{31}P NMR spectroscopy confirmed the *cis* configuration at the platinum center; two phosphorus atoms are observed at δ −5.21 (J_{PP} 16.3, J_{PPt} 3290 Hz) and δ 0.57 (J_{PP} 16.3, J_{PPt} 1627 Hz), both as doublets. The regio- and stereochemistry concerning the carbon—carbon double bond of **4a** was also easily deduced from its ^{13}C and ^1H NMR spectra; first, the olefinic carbon directly bound to platinum (δ 175.1, J_{CP} 9.0 and 97.6 Hz, J_{CPt} 645.6 Hz) is a quaternary carbon, as indicated by a DEPT (θ = 135°) experiment. Secondly, the olefinic proton signal centered at δ 6.59 (J_{HP} 23.6, J_{HPt} 87.2 Hz) is a doublet due to the coupling with phosphorus and displays satellite bands with a large coupling constant with platinum, characteristic of olefinic protons *trans* to platinum.[5] The two allylic protons are not equivalent in ^1H NMR spectroscopy, displaying signals at 2.34 and 2.67 ppm, respectively. An NOE experiment by irradiation at the δ 2.67 signal resulted in a 3.4% enhancement of the olefinic proton signal at δ 6.59, which further substantiates the Z configuration of the double bond being generated through the *cis*-addition of the Pt-Si bond.



(1)

3a (L = PEt_3) **4a** (L = PEt_3)

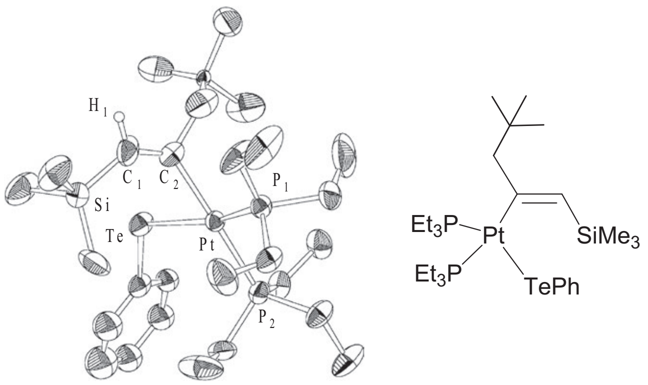


FIGURE 1 Molecular structure of complex **4b**. Selected distances (Å) and angles (°): Pt—Te 2.645(5), Pt—P(1) 2.278(3), Pt—P(2) 2.351(3), Pt—C(2) 2.14(1), Si—Tc 3.75(2); Te—Pt—P(1) 164.4(1), P(2)—Pt—C(2) 172.2(3), Tc—Pt—P(2) 94.3(9), Te—Pt—C(2) 78.5(8), C(2)—Pt—P(1) 87.5(3), P(1)—Pt—P(2) 94.3(9), Te—Pt—C(2) 78.5(8), C(2)—Pt—P(1) 87.5(3), P(1)—Pt—P(2) 99.7(1)

Other terminal alkynes such as phenylacetylene, 3-phenyl-1-propyne reacted similarly with **3** to give the corresponding alkenylplatinum complexes. Disappointingly, however, all of these products were oil. On the other hand, an internal alkyne, diphenylacetylene did not undergo the addition reaction with **3a** at all. *After extensive trials and errors, very fortunately, we finally succeeded in obtaining a crystalline product.* Thus, treating **3a** with 4,4-dimethyl-1-pentyne followed by recrystallization from pentane (0.5 mL), a pale yellow crystal of alkenylplatinum complex **4b** suitable for X-ray analysis was obtained! The X-ray analysis of **4b** unambiguously confirmed its *cis* configuration at platinum and the regio- and stereochemistry at the double bond (Figure 1).[a]

Platinum complex **4b** has a distorted square-planar structure with bond angles of Te—Pt—P(1) and P(2)—Pt—C(2)

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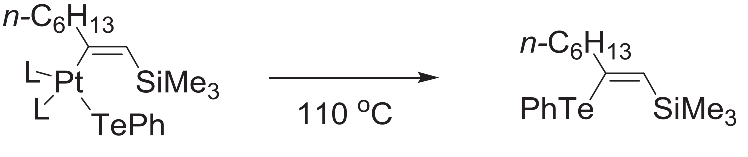
[a] *Crystal data for **4b***: $C_{28}H_{56}P_2PtSiTe$, $M = 805.47$, monoclinic, space group *P*21/n(#14), $a = 10.025(2)$, $b = 20.174(2)$, $c = 17.053(2)$ Å, $\beta = 96.88$ (1)°, $V = 3424.1(8)$ Å^3, $T = -120.0$°C, $Z = 4$, $D_c = 1.562$ g/cm^3, $\mu = 50.59$ cm^{-1}, 6722 reflections measured, 4929 observed [$I > 3\sigma(I)$], 273 parameters. Empirical absorption corrections (ψscan) were applied. Final *R* factor = 0.063, *R*w = 0.103. The PhTe group was disordered into two positions. Average values of distances and angles containing Te were shown in Figure 1. CCDC171714 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

being 164.4(1) and 172.2(3), respectively. The bond distances of Pt—P(1) and Pt—P(2) are 2.278(3) and 2.351(3) Å, respectively, reflecting the stronger *trans* influence of the alkenyl group as compared to TePh.[6]

The stable *cis* geometry of organotelluroplatinum species such as **4** is unusual since all other PtR(TeR')$(PEt_3)_2$-type complexes so far obtained adopt *trans* geometry.[3,6] Although *cis*-PtPh(Te*i*-Pr)$(PEt_3)_2$ could be observed at the beginning of the reaction of *i*-PrTePh with $Pt(PEt_3)$[3,6] this complex was not stable and isomerized quickly to its *trans* isomer even at room temperature. A possible driving force for this remarkable feature of **4** preferring the *cis* geometry may come from an interaction between tellurium and silicon.[7] Indeed, the molecular structure of **4b** has revealed the distance between silicon and tellurium is 3.990(7) Å, which is shorter than the sum of their van der Waals radii 4.16 Å,[8] indicating such an interaction.

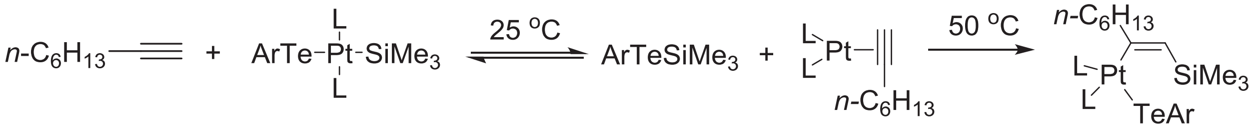
A careful analysis of the reaction between complex **3b**[3] and 1-octyne revealed a more detailed process of the alkyne insertion. Thus, **3b** (40 mg) was allowed to react with 1-octyne (1.5 equiv.) in benzene-d_6, at 25°C for 1 hour. NMR spectroscopy showed no insertion took place at all. However, the formation of $ArTeSiMe_3$ (**3b**/$ArTeSiMe_3$ = 70/30) and an equivalent amount alkyne-platinum complex **5** were observed, indicating an equilibrium as illustrated in Equation 2.[b]



(3)

4a (L = PEt_3)

7



(2)

3b, Ar = 4-PhC_6H_4; L = PEt_3

5

4c

Subsequent heating of the solution at 50°C for 2.5 hours resulted in a complete consumption of **3b**, affording the Si-Pt addition product **4c** in 87% NMR yield. This insertion was retarded, though not completely, by the addition of free PEt_3. Thus, when the reaction was run in the presence of an additional PEt_3 (1.5 equiv relative to **3b**) under otherwise identical conditions, ca. 20% of **3b** remained unreacted and **4c** was formed in only 58% NMR yield. This result resembles the behavior of bissilylplatinum complexes[4] and may suggest that the alkyne insertion to the Si—Pt bond of **3** proceeds via a three-coordinate platinum species generated by the dissociation of a PEt_3 ligand. In agreement with this assumption, $Pt(TePh)(SiMe_3)(dmpe)$ [**6**, dmpe = 1,2-bis(dimethylphosphino)ethane] bearing a tightly chelating phosphine ligand did not undergo such an insertion reaction with 1-octyne at 50°C.[b]

Finally, it is noted that when the reaction shown in Equation 1 was further continued at an elevated temperature (110°C, 6 hours), **4a** completely disappeared to reductively eliminate vinyl telluride **7**[b] in 67% yield based on **3a** used. This result together with the others herein described intimates the possibility of a catalytic addition of silyl tellurides to alkynes, which has never been realized so far. Studies along this line are in progress.[c]

3 | CONCLUSION

A Pt(0) complex easily oxiditively inserts to the Te-Si bond of $ArTeSiMe_3$ compound to generate a complex bearing a backbone of Si-Pt-Te bond. This Si-Pt-Te complex adds to a terminal alkyne by the selective *cis*-addition of the Si-Pt bond (not the Te-Pt bond) to the triple bond to give a new complex with the Si moiety bonding to the terminal carbon and the Pt moiety bonding to the internal carbon. Upon heating the new complex at an elevated temperature, the corresponding *cis*-alkenylteruride is obtained.

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[b] Selected NMR data for **5, 6** and **7**. **5**: ^{31}P NMR (C_6D_6) δ 16.5 (J_{PP} = 39.2, J_{PPt} = 3459 Hz), 13.1 (J_{PP} 39.2, J_{PPt} 3243 Hz). **6** ($CDCl_3$): ^{1}H NMR δ 7.89–7.91 (m, 2 H), 7.12–7.14 (m, 1 H), 6.98–7.00 (m, 2 H), 1.68 (d, 6 H, J_{HP} 9.7, J_{HPt} 38.2 Hz), 1.59–1.65 (m, 2 H), 1.40–1.45 (m, 2 H), 0.99 (d, 6 H, J_{HP} 8.2, J_{HPt} 15.3 Hz), 0.33 (s, 9 H, J_{HPt} 17.7 Hz); ^{31}P NMR δ 34.6 (d, J_{PP} 6.2 Hz, J_{PPt} 1313.5 Hz), 24.7 (d, J_{PP} 6.2 Hz, J_{PPt} 2963.7 Hz). **7** ($CDCl_3$): ^{1}H NMR δ 7.74–7.76 (m, 2 H), 7.20–7.31 (m, 3 H), 6.55 (s, 1 H, J_{HTe} 72.8 Hz), 2.29 (t, 2 H, *J* 7.7 Hz), 1.17–1.48 (m, 8 H), 0.86 (t, 3 H, *J* 7.4 Hz), 0.22 (s, 9 H); ^{13}C NMR δ 141.0, 140.9, 138.8, 129.2, 127.7, 114.0, 46.7, 31.7, 29.6, 28.3, 22.6, 14.1, −0.10; ^{29}Si NMR δ −8.14; ^{125}Te NMR δ −370.4.

[c] Partial of this work was first disclosed in the XIXth Internatinal Conferenve on Organometallic Chemistry, Shanghai, July, 2000. A catalytic addition of PhTeTMS to acetylenes has not been achieved yet, partly due to the decomposition of the current Te-Pt complexes that leads to the deactivation of the catalyst (ref 3). The reason for the regioselectivity of complex **3** with a terminal alkyne generating complex **4** was not clear, though a steric repulsion of the bulky TMS group may play a crucial role.

ACKNOWLEDGEMENT

We thank Professor Masato Tanaka for useful discussions.

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How to cite this article: Han L-B, Mirzaei F, Shimada S. Regio- and stereoselective addition of *trans*-Pt(TeAr)($SiMe_3$)(PEt_3)$_2$ to terminal alkynes leading to *cis*-[(*Z*)-*β*-trimethylsilylalkenyl]platinum(II) complexes. *Heteroatom Chem*. 2018;e21463. https://doi.org/10.1002/hc.21463