8112 *Inorg. Chem.* **2010**, *49*, 8112–8116
DOI: 10.1021/ic1011742

Inorganic Chemistry
Article

Syntheses of Selenolato-Bridged Dinuclear Hydridoplatinum Complexes $[Pt_2H_2(\mu\text{-Se}^t\text{Bu})_2(PPh_3)_2]$ and $[Pt_2H(\text{Se}^t\text{Bu})(\mu\text{-Se}^t\text{Bu})_2(PPh_3)_2]$: Unusual Thermal Reaction of Hydrido(1,1-Dimethylethaneselenolato) Platinum Complex *cis*-$[PtH(\text{Se}^t\text{Bu})(PPh_3)_2]$

Norio Nakata, Takashige Ikeda, and Akihiko Ishii*

Department of Chemistry, Graduate School of Science and Engineering, Saitama University, Shimo-okubo, Sakura-ku, Saitama, 338-8570, Japan

Received June 11, 2010

Novel selenolato-bridged dinuclear hydridoplatinum complexes, *cis*-$[Pt_2H_2(\mu\text{-Se}^t\text{Bu})_2(PPh_3)_2]$ (**2**) and *cis*-$[Pt_2H(\text{Se}^t\text{Bu})(\mu\text{-Se}^t\text{Bu})_2(PPh_3)_2]$ (**3**) were synthesized in 30% and 57% yields, respectively, by the thermolysis of hydrido(1,1-dimethylethaneselenolato) Pt(II) complex *cis*-$[PtH(\text{Se}^t\text{Bu})(PPh_3)_2]$ (**1**) in toluene at 80 °C for 3 h. The structures of dinuclear complexes **2** and **3** were fully characterized on the basis of their NMR and IR spectroscopic data and X-ray crystallography. The two distorted square planar Pt atoms in **2** and **3** are held together by two bridged selenolato ligands, ^{t}Bu groups of which adopt a trans configuration with respect to the four-membered Pt_2Se_2 ring. Each central Pt_2Se_2 ring in **2** and **3** has a hinged arrangement due to the steric repulsion among the two PPh_3 ligands and the ^{t}Bu group lying between them.

Introduction

Oxidative addition of organochalcogen compounds, such as chalcogenols (REH, E = S, Se, and Te) and dichalcogenides (REER) to low-valent transition-metal complexes is considered as an important step in homogeneous catalysis.[1] In the case of the Pt(0)-catalyzed hydroselenation of alkynes, hydrido(selenolato) Pt(II) complex $[PtH(SeR)L_2]$ was proposed as the key intermediate,[2] however, its spectroscopic analysis and structural characterization have not been performed until recently because of the thermal instability of the reactive Pt−H bond. Recently, we succeeded in the first isolation of a stable hydrido(selenolato) Pt(II) complex, $[PtH(SeTrip)(PPh_3)_2]$ (Trip = 9-triptycyl), with cis configuration by the reaction of kinetically stabilized 9-triptyceneselenol (TripSeH) with $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$.[3,4] We also reported a unique thermal reaction of $[PtH(SeTrip)(PPh_3)_2]$ to give a five-membered selenaplatinacycle $[Pt(\eta^2\text{-}C,Se\text{-Trip})(PPh_3)_2]$ by the intramolecular activation of a C−H bond on a benzene group of the triptycyl substituent leading to the cyclometalation.[3] Furthermore, we showed the stoichiometric reaction of $[PtH(SeTrip)(PPh_3)_2]$ with electron-deficient alkynes to proceed in the manner of syn addition.[5]

While a number of dinuclear M_2Se_2 complexes (M = Pd, Pt) containing two bridged selenolato ligands are known, neutral d^8 complexes with the general formula $[Pt_2X_2(\mu\text{-SeR})_2(PR'_3)_2]$ have been attracting widespread interest with respect to their structural properties.[6] Jain and co-workers have reported the preparations of a series of dinuclear Pt_2Se_2 complexes with terminal chloro ligands, *cis*- and *trans*-$[Pt_2Cl_2(\mu\text{-SeR})_2(PR'_3)_2]$.[7]

---

*Corresponding author. E-mail: ishiiaki@chem.saitama-u.ac.jp.

(1) For several recent reviews, see: (a) Kuniyasu, H. In *Catalytic Heterofunctionalization*; Togni, A., Grützmacher, H., Eds.; Wiley-VCH: Weinheim, Germany, 2001; pp 217−251. (b) Beletskaya, I. P.; Moberg, C. *Chem. Rev.* **1999**, *99*, 3435–3461. (c) Kondo, T.; Mitsudo, T. *Chem. Rev.* **2000**, *100*, 3205–3220. (d) Ogawa, A. *J. Organomet. Chem.* **2000**, *611*, 463–474. (e) Kuniyasu, H.; Kambe, N. *Chem. Lett.* **2006**, *35*, 1320–1325. (f) Beletskaya, I. P.; Ananikov, V. P. *Eur. J. Org. Chem.* **2007**, 3431–3444.

(2) Ananikov, V. P.; Malyshev, D. A.; Beletskaya, I. P.; Aleksandrov, G. G.; Eremenko, I. L. *J. Organomet. Chem.* **2003**, *679*, 162–172.

(3) (a) Ishii, A.; Nakata, N.; Uchiumi, R.; Murakami, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 2661–2664. (b) Nakata, N.; Yoshino, T.; Ishii, A. *Phosphorus, Sulfur Silicon Relat. Elem.* **2010**, *185*, 992–999.

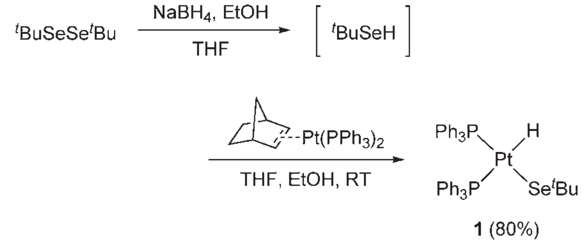
(4) For our applications of Trip group, see:(a) Ishii, A.; Matsubayashi, S.; Takahashi, T.; Nakayama, J. *J. Org. Chem.* **1999**, *64*, 1084–1084. (b) Ishii, A.; Takahashi, T.; Nakayama, J. *Heteroat. Chem.* **2001**, *12*, 198–203. (c) Ishii, A.; Takahashi, T.; Tawata, A.; Furukawa, A.; Oshida, H.; Nakayama, J. *Chem. Commun.* **2002**, 2810–2811. (d) Ishii, A.; Mori, Y.; Uchiumi, R. *Heteroat. Chem.* **2005**, *16*, 525–528. (e) Nakata, N.; Fukazawa, S.; Ishii, A. *Organometallics* **2009**, *28*, 534–538. (f) Nakata, N.; Uchiumi, R.; Yoshino, T.; Ikeda, T.; Kamon, H.; Ishii, A. *Organometallics* **2009**, *28*, 1981–1984. (g) Nakata, N.; Yamamoto, S.; Hashima, W.; Ishii, A. *Chem. Lett.* **2009**, *38*, 400–401.

(5) Ishii, A.; Kamon, H.; Murakami, K.; Nakata, N. *Eur. J. Org. Chem.* **2010**, 1653–1659.

(6) For reviews on dinuclear M_2Se_2 complexes (M = Pd, Pt), see: (a) Aullón, G.; Ujaque, G.; Lledós, A.; Alvarez, S. *Chem.—Eur. J.* **1999**, *5*, 1391–1410. (b) Jain, V. K.; Jain, L. *Coord. Chem. Rev.* **2005**, *249*, 3075–3197.

(7) (a) Jain, V. K.; Kannan, S.; Butcher, R. J.; Jasinski, J. P. *Polyhedron* **1995**, *14*, 3641–3647. (b) Dey, S.; Jain, V. K.; Varghese, B. *J. Organomet. Chem.* **2001**, *623*, 48–55. (c) Dey, S.; Jain, V. K.; Knoedler, A.; Kaim, W. *Inorg. Chim. Acta* **2003**, *349*, 104–110. (d) Kumbhare, L. B.; Jain, V. K.; Phadnis, P. P.; Nethaji, M. *J. Organomet. Chem.* **2007**, *692*, 1546–1556.

Scheme 1



Laitinen,[8] Corrigan,[9] and Woollins[10] also have independently described the syntheses and structural analyses of dinuclear Pt_2Se_2 complexes having terminal selenolato ligands $[Pt_2(SeR)_2(\mu\text{-}SeR)_2(PR'_3)_2]$ of the trans form. However, there is no example of the dinuclear Pt_2Se_2 complex with terminal hydrido ligands, probably due to lack of suitable synthetic methods. In this paper, we present the preparation of new selenolato-bridged dinuclear Pt(II) complexes bearing hydrido ligands by the thermal reaction of hydrido(selenolato) Pt(II) complex *cis*-$[PtH(Se^tBu)(PPh_3)_2]$ (**1**).

Results and Discussion

Hydrido(1,1-dimethylethaneselenolato) Pt(II) complex *cis*-$[PtH(Se^tBu)(PPh_3)_2]$ **1** was prepared as pale-yellow crystals in 80% yield by the reaction of $[Pt(\eta^2\text{-nb})(PPh_3)_2]$ (nb = norbornene)[11] with ^{t}BuSeH, which was generated in situ by the reduction of ^{t}BuSeSe^{t}Bu with an excess amount of $NaBH_4$ in THF followed by quenching with EtOH (Scheme 1). In the ^{1}H NMR spectrum of **1**, the characteristic signals due to the platinum hydride were observed centering at δ −5.94 with splitting by $^{31}P{-}^1H$ ($^2J_{P(cis)-H}$ = 17, $^2J_{P(trans)-H}$ = 179 Hz) and $^{195}Pt{-}^1H$ ($^1J_{Pt-H}$ = 867 Hz) couplings. The $^{31}P\{^1H\}$ NMR spectrum of **1** showed two doublet signals with ^{195}Pt satellites at δ 17.7 ($^2J_{P-P}$ = 14, $^1J_{Pt-P}$ = 3135 Hz) and 29.4 ($^2J_{P-P}$ = 14, $^1J_{Pt-P}$ = 2138 Hz), which were assigned to the phosphorus atoms lying trans to the selenolato ligand and the hydride, respectively. The molecular structure of **1** was confirmed unambiguously by X-ray analysis, as depicted in Figure 1. The X-ray crystallographic analysis of **1** revealed that the platinum center exhibited a square planar environment with distortion of angles due to the steric requirement of the cis-coordinated PPh_3 ligands and the ^{t}Bu group on the selenium atom. The Pt1−Se1 bond length was 2.4157(7) Å, which is slightly shorter than those of stable hydrido(9-triptyceneselenolato) Pt(II) complexes, *cis*-$[PtH(SeTrip)(PPh_3)_2]$ [2.4272(5) Å][3a] and [PtH(SeTrip)(dppe)] [2.4376(8) Å].[3b]

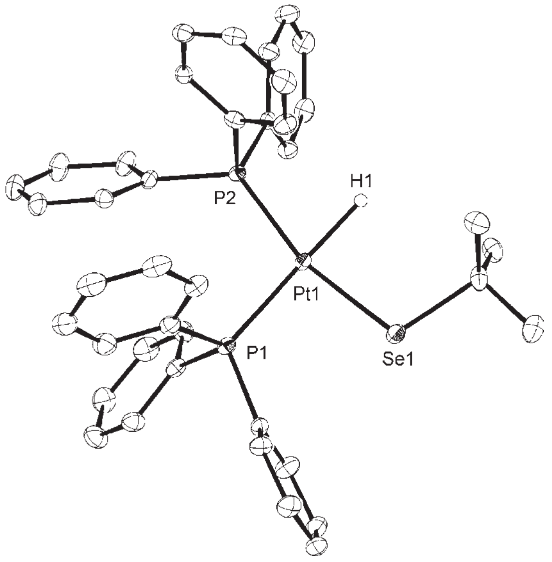


Figure 1. ORTEP drawing of *cis*-$[PtH(Se^tBu)(PPh_3)_2]$ **1** (30% thermal ellipsoids, hydrogen atoms except H1 were omitted for clarity). Selected bond lengths (Å): Pt1−Se1 = 2.4157(7), Pt1−P1 = 2.3239(18), Pt1−P2 = 2.2512(16), Pt1−H1 = 1.732(10), Se1−C1 = 2.017(7). Selected bond angles (°): Se1−Pt1−P1 = 92.69(4), P1−Pt1−P2 = 102.33(6), P2−Pt1−H1 = 78.5(5), Se1−Pt1−H1 = 86.7(5), Se1−Pt1−P2 = 164.32(5), H1−Pt1−P1 = 178(2).

Although complex **1** is stable at ambient temperature in the absence of air and moisture, **1** decomposed gradually on heating. Thus, heating of a benzene solution of **1** at 50 °C for 3 h led to the formation of selenolato-bridged dihydrido- and hydrido(selenolato) dinuclear Pt(II) complexes, *cis*-$[Pt_2H_2(\mu\text{-}Se^tBu)_2(PPh_3)_2]$ (**2**) and *cis*-$[Pt_2H(Se^tBu)(\mu\text{-}Se^tBu)_2(PPh_3)_2]$ (**3**) as pale-yellow and orange crystals in 26% and 5% yields, respectively, with recovery of the starting complex **1** (52%). The thermal reaction of **1** in toluene at 80 °C for 3 h proceeded efficiently to give **2** and **3** in 30% and 57% yields, respectively (Scheme 2).[12] In the ^{1}H NMR spectra of **2** and **3**, characteristic hydride signals were observed at δ −12.07 ($^2J_{P-H}$ = 13, $^4J_{P-H}$ = 4 Hz) and −11.54 ($^2J_{P-H}$ = 17, $^4J_{P-H}$ = 5 Hz), respectively, with ^{195}Pt satellites (**2**: $^1J_{Pt-H}$ = 1172 Hz, **3**: $^1J_{Pt-H}$ = 1177 Hz). These $^{195}Pt{-}^1H$ coupling constants are much larger than that of the starting hydrido complex **1** (867 Hz) and within a range of those of the reported terminal hydrido ligand of dinuclear Pt complexes (800−1400 Hz).[13] The $^{31}P\{^1H\}$ NMR spectrum of **2** displayed a singlet signal with ^{195}Pt and ^{77}Se satellites at δ 22.5 ($^1J_{Pt-P}$ = 3819, $^2J_{Se(cis)-P}$ = 36, $^2J_{Se(trans)-P}$ = 125 Hz). In sharp contrast, $^{31}P\{^1H\}$ NMR spectrum of **3** exhibited two nonequivalent doublet signals at δ 9.7 and 21.9 ($^4J_{P-P}$ = 8 Hz) with the $^{195}Pt{-}^{31}P$ coupling constants of 3613 and 3576 Hz and the $^{77}Se{-}^{31}P$ coupling constants of 165 and 124 Hz, respectively. The $^{77}Se\{^1H\}$ NMR spectrum of **2** measured at −20 °C[14] displayed two characteristic signals around δ −82.8 ($^1J_{Se-Pt}$ = 149 Hz) as broad singlet and 229.3 ($^2J_{Se-P}$ = 125 Hz) as broad triplet. The lower field signal (δ 229.3) is assigned to the selenium atom lying trans to the PPh_3 ligand on the basis of agreement with the

---

[8] (a) Oilunkaniemi, R.; Laitinen, R. S.; Ahlgrén, M. *J. Organomet. Chem.* **1999**, *587*, 200–206. (b) Hannu-Kuure, M. S.; Wagner, A.; Bajorek, T.; Oilunkaniemi, R.; Laitinen, R. S.; Ahlgrén, M. *Main Group Chem.* **2005**, *4*, 49–68.

[9] Brown, M. J.; Corrigan, J. F. *J. Organomet. Chem.* **2004**, *689*, 2872–2879.

[10] Aucott, S. M.; Kilian, P.; Robertson, S. D.; Slawin, A. M. Z.; Woollins, J. D. *Chem.—Eur. J.* **2006**, *12*, 895–902.

[11] Petzold, H.; Görls, H.; Weigand, W. *J. Organomet. Chem.* **2007**, *692*, 2736–2742.

[12] The yields of **2** and **3** were evaluated base on the number of selenium atoms.

[13] (a) Brown, M. P.; Puddephatt, R. J.; Rashidi, M.; Seddon, K. R. *J. Chem. Soc., Dalton Trans.* **1978**, 516–522. (b) Bracher, G.; Grove, D. M.; Venanzi, L. M.; Bachechi, F.; Mura, P.; Zambonelli, L. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 778–779. (c) Morris, R. H.; Foley, H. C.; Targos, T. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 7337–7339. (d) Paonessa, R. S.; Trogler, W. C. *J. Am. Chem. Soc.* **1982**, *104*, 3529–3530. (e) Bachechi, F.; Bracher, G.; Grove, D. M.; Kellenberger, B.; Pregosin, P. S.; Venanzi, L. M.; Zambonelli, L. *Inorg. Chem.* **1983**, *22*, 1031–1037. (f) Paonessa, R. S.; Trogler, W. C. *Inorg. Chem.* **1983**, *22*, 1038–1048. (g) McLennan, A. J.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 811–813.

[14] The $^{77}Se\{^1H\}$ NMR of **2** at room temperature showed two broad signals with which we could not confirm ^{195}Pt or ^{31}P satellites, probably due to the fast Pt_2Se_2 ring flipping of **2** in the NMR time scale .

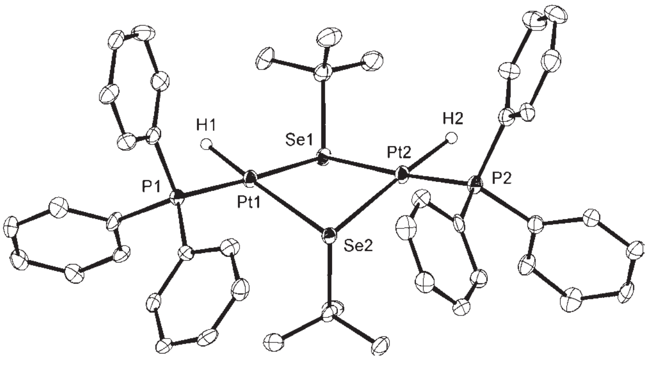


Figure 2. ORTEP drawing of *cis*-[Pt$_2$H$_2$(μ-Se^{t}Bu)$_2$(PPh$_3$)$_2$] **2** (30% thermal ellipsoids, a solvated CH$_2$Cl$_2$ molecule, and hydrogen atoms except H1 and H2 were omitted for clarity). Selected bond lengths (Å): Pt1−Se1 = 2.4494(11), Pt1−Se2 = 2.5109(10), Pt2−Se1 = 2.4469(10), Pt2−Se2 = 2.5088(11), Pt1−P1 = 2.217(3), Pt2−P2 = 2.210(2), Pt1−H1 = 1.56(8), Pt2−H2 = 1.596(10), Se1−C1 = 2.008(10), Se2−C5 = 2.014(9). Selected bond angles (°): Se1−Pt1−Se2 = 83.71(3), Se1−Pt2−Se2 = 83.81(3), Pt1−Se1−Pt2 = 92.74(3), Pt1−Se2−Pt2 = 89.82(3), P1−Pt1−Se2 = 101.59(6), P1−Pt1−H1 = 86(3), Se1−Pt1−H1 = 88(3), P2−Pt2−Se2 = 99.24(7), P2−Pt2−H2 = 78(4), Se1−Pt2−H2 = 99(4), Pt1−Se1−C1 = 110.1(3), Pt2−Se1−C1 = 107.8(3), Pt1−Se2−C5 = 106.8(2), Pt2−Se2−C5 = 107.9(3); Pt$_2$Se$_2$ folding angle (°): 147.5.

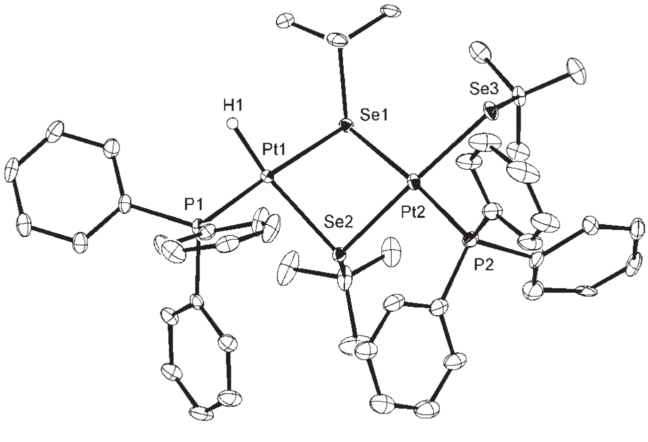
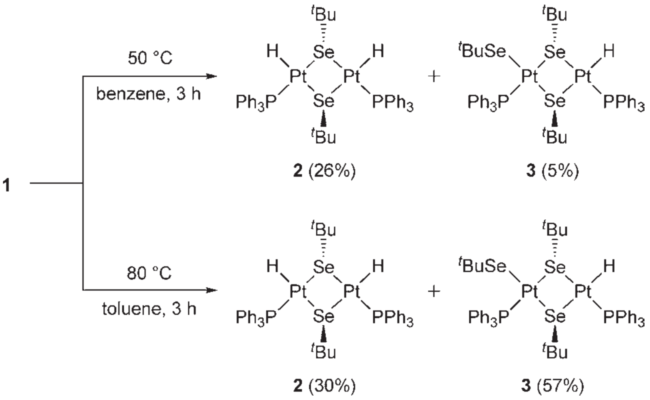


Figure 3. ORTEP drawing of *cis*-[Pt$_2$H(Se^{t}Bu)(μ-Se^{t}Bu)$_2$(PPh$_3$)$_2$] **3** (30% thermal ellipsoids, hydrogen atoms except H1 were omitted for clarity). Selected bond lengths (Å): Pt1−Se1 = 2.481(5), Pt1−Se2 = 2.4974(5), Pt2−Se1 = 2.436(5), Pt2−Se2 = 2.4713(5), Pt2−Se3 = 2.4689(5), Pt1−P1 = 2.2125(13), Pt2−P2 = 2.2358(14), Pt1−H1 = 1.596(10), Se1−C1 = 2.017(14), Se2−C6 = 2.031(5), Se3−C9 = 2.120(16). Selected bond angles (°): Se1−Pt1−Se2 = 78.74(14), Se1−Pt2−Se2 = 80.11(11), Pt1−Se1−Pt2 = 88.90(15), Pt1−Se2−Pt2 = 87.741(16), P1−Pt1−Se2 = 98.40(4), P1−Pt1−H1 = 83(2), Se1−Pt1−H1 = 100(2), P2−Pt2−Se2 = 95.46(4), P2−Pt2−Se3 = 85.20(4), Se1−Pt2−Se3 = 99.28(11), Pt1−Se1−C1 = 105.2(4), Pt2−Se1−C1 = 114.3(5), Pt1−Se2−C6 = 109.61(17), Pt2−Se2−C6 = 107.34(17); Pt$_2$Se$_2$ folding angle (°): 129.7.

Scheme 2



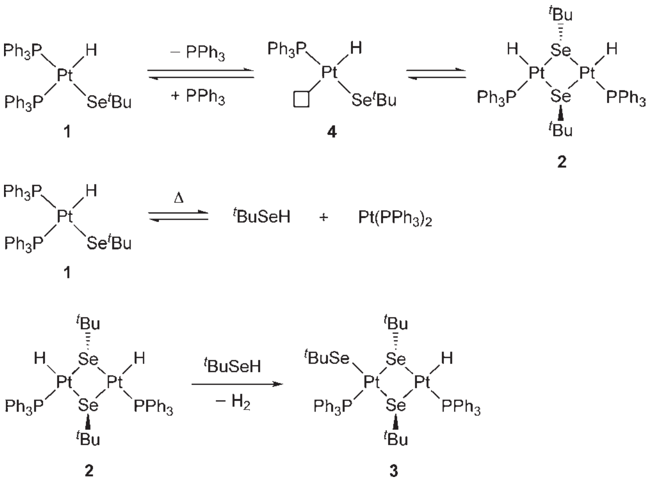
^{77}Se−^{31}P coupling constant value observed in the ^{31}P{^{1}H} NMR spectrum. On the other hand, the ^{77}Se{^{1}H} NMR spectrum of **3** obtained at room temperature showed two doublet signals at δ −4.8 ($^2J_{\text{Se-P}}$ = 7, $^1J_{\text{Se-Pt}}$ = 124, 96 Hz) and 182.1 ($^2J_{\text{Se-P}}$ = 7 Hz) and a doublet of doublets signal at δ 162.4 ($^2J_{\text{Se-P}}$ = 165, 124 Hz). According to the ^{77}Se−^{31}P and ^{77}Se−^{195}Pt coupling constant values, the resonances at δ −4.8 and 162.4 are assignable to the bridged selenolato ligands lying each trans to the hydrido and the PPh$_3$ ligands, respectively, while the remaining lower one (δ 182.1) can be attributed to the terminal selenolato ligand. Furthermore, in the IR spectra, the Pt−H stretching vibration of **2** (2088 cm^{-1}) was observed at a lower wavenumber compared to that of **3** (2120 cm^{-1}). The molecular structures of **2** and **3** were finally determined by X-ray crystallography, as shown in Figures 2 and 3. In **2** and **3**, two distorted square planar Pt atoms are held together by two bridged selenolato ligands, which adopt trans configuration with respect to the four-membered ring. Two PPh$_3$ ligands in **2** and **3** take mutually a cis configuration. The four-membered Pt$_2$Se$_2$ rings of **2** and **3** feature nonplanar geometries with the hinged angles of 147.5° and 129.7°, respectively. The hinged angle of **3** (129.7°) is smaller than those of the related selenolato-bridged dinuclear Pt complexes having a hinged Pt$_2$Se$_2$ ring, *trans*-[Pt$_2$Cl$_2$(μ-SeCH$_2$Ph)$_2$(PPr$_3$)$_2$] (131.1°)[7b] and *trans*-[PtCl(SeCH$_2$CH$_2$CH$_2$NMe$_2$)]$_2$ (159.3°).[15] These hinged arrangements are considered to be caused by the steric repulsion among two PPh$_3$ ligands and the ^{t}Bu group lying between them. In the hinged four-membered Pt$_2$Se$_2$ rings in **2** and **3**, the Se−Pt−Se angles (**2**: Se(1)−Pt(1)−Se(2) = 83.71(3), Se(1)−Pt(2)−Se(2) = 83.81(3)°; **3**: Se(1)−Pt(1)−Se(2) = 78.74(14), Se(1)−Pt(2)−Se(2) = 80.11(11)°) are reduced significantly from the ideal value of 90°, while the Pt−Se−Pt angles (**2**: Pt(1)−Se(1)−Pt(2) = 92.74(3), Pt(1)−Se(2)−Pt(2) = 89.82(3)°; **3**: Pt(1)−Se(1)−Pt(2) = 88.90(15), Pt(1)−Se(2)−Pt(2) = 87.741(16)°) are near 90°. The Pt1···Pt2 distances (**2**: 3.5439(8) Å, **3**: 3.4435(3) Å) are significantly longer than the sum of metallic radii (2.78 Å),[16] indicating no direct Pt−Pt bonding interaction. The Pt−Se bonds trans to the PPh$_3$ ligand in **2** (Pt(1)−Se(1) = 2.4494(11), Pt(2)−Se(1) = 2.4469(10) Å) as well as **3** (Pt(1)−Se(1) = 2.482(5) Å) are shortened compared with the bond trans to the hydrido ligands (**2**: Pt(1)−Se(2) = 2.5109(10), Pt(2)−Se(2) = 2.5088(11) Å; **3**: Pt(1)−Se(2) = 2.4974(5) Å), suggesting that the hydrido ligand has a stronger trans influence than the phosphine ligand. Again, the Pt−Se bond trans to the terminal selenolato ligand in **3** (Pt(2)−Se(2) = 2.4713(5) Å) is longer than the bond trans to the PPh$_3$ ligand due to the stronger trans influence of the selenolato ligand. The terminal Pt(2)−Se(3) bond length of **3** (2.4689(5) Å) is close to those reported for *trans*-[Pt(SeR)(PPh$_3$)(μ-SeR)$_2$Pt(SeR)(PPh$_3$)] (R = Bu: 2.457(1) Å, R = 2-thienyl: 2.4395(13) Å).[8] The Pt−P bonds of **2** (Pt(1)−P(1) = 2.217(3), Pt(2)−P(2) = 2.210(2) Å) and **3** (Pt(1)−P(1) = 2.2125(13), Pt(2)−P(2) = 2.2358(14) Å) are almost equal. While the phosphido-bridged dinuclear platinum complexes with terminal hydrido ligands, *cis*- and *trans*-[Pt$_2$H$_2$(μ-PPh$_2$)$_2$(PEt$_3$)$_2$], *trans*-[Pt$_2$H$_2$(μ-P^{t}Bu$_2$)$_2$(PEt$_3$)$_2$], and *trans*-[Pt$_2$H$_2$(μ-PPh$_2$)$_2$(PCy$_3$)$_2$], were

---

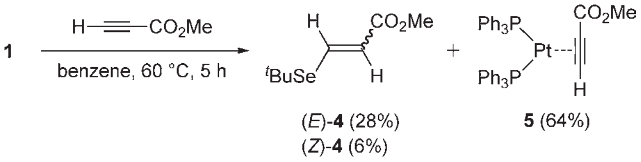
[15] Dey, S.; Jain, V. K.; Butcher, R. J. *Inorg. Chim. Acta* **2007**, *360*, 2653–2660.

[16] Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, U.K., 1984.

Scheme 3



Scheme 4



reported by Osakada and co-workers,[17,18] complexes **2** and **3** are the first examples of the selenolato-bridged dinuclear hydridoplatinum complexes having bent Pt_2Se_2 ring structures.

A plausible reaction pathway for the formation of dinuclear complexes **2** and **3** is shown in Scheme 3. In the first step, mononuclear complex **1** undergoes dissociation of a PPh_3 ligand to form an intermediary, coordination-unsaturated Pt complex **4**, where the ligand trans to hydrido would be detached due to the stronger trans influence of the hydrido ligand than that of the selenolato ligand. Then, dimerization of the resulting intermediate **4** readily occurs to give **2**. The equilibrium between the mono- and dinuclear complexes in solution was clearly confirmed by the thermal reaction of **1** in the presence of free PPh_3 ligand (2 equiv) that resulted in the quantitative recovery of **1** without formation of either **2** or **3**. The formation of terminal selenolato dinuclear complex **3** can be explained by the reaction of **2** with ^{t}BuSeH that was produced by the reductive elimination of **1** during the thermolysis (Scheme 3). Consequently, the thermal reaction of **1** at 50 °C was dominated by the dissociation of a PPh_3 ligand to give **2** as the major product. By contrast, the thermal reaction of **1** at 80 °C was promoted by the reductive elimination of ^{t}BuSeH from **1**, and then ^{t}BuSeH readily reacted with **2** to give **3** as the major product. In a control experiment, the reaction of **2** with 2 equiv of ^{t}BuSeH in a mixed solvent of toluene and hexane at 80 °C afforded complex **3** in 40% yield. Evolution of H_2 occurs at this stage.

Since mono- and dinuclear hydridoplatinum complexes **1**−**3** are considered as key intermediates in the Pt(0)-catalyzed hydroselenation, we examined the stoichiometric reactions of **1**−**3** with electron-deficient alkyne, such as methyl propiolate (MP). The reaction of **1** with MP in benzene at 60 °C for 5 h gave an (*E*)/(*Z*) mixture of vinyl selenide **4** in low yield (28% and 6% NMR yields, respectively), together with $[Pt(mp)(PPh_3)_2]$ **5** in 64% NMR yield (Scheme 4).[19] The formation of (*Z*)-**4** result can be explained partly by the thermal reaction between MP and ^{t}BuSeH that was generated by the reductive elimination of **1**. In fact, the thermal reaction of ^{t}BuSeH with MP at 60 °C for 5 h produced a mixture of (*E*)- and (*Z*)-**4** in a ratio of 1: 2. On the other hand, the reactions of **2** or **3** with MP under the above conditions afforded a complicated mixture, and no hydroselenated products were detected.

In conclusion, we have demonstrated that the thermal reaction of hydrido(1,1-dimethylethaneselenolato) Pt(II) complex **1** in toluene at 80 °C for 3 h resulted in the formations of selenolato-bridged dinuclear hydridoplatinum complexes, *cis*-$[Pt_2H_2(\mu\text{-}Se^tBu)_2(PPh_3)_2]$ **2** and *cis*-$[Pt_2H(Se^tBu)(\mu\text{-}Se^tBu)_2(PPh_3)_2]$ **3** with novel structures. X-ray analyses of **2** and **3** revealed that each central Pt_2Se_2 ring has a hinged arrangement due to the steric repulsion between the ^{t}Bu group in the bridged selenolato ligands and the neighboring PPh_3 ligands. The sterically bulky ^{t}Bu group on the Se atom retarded isomerization **1**, **2**, or **3** and their further reactions with ^{t}BuSeH to give mononuclear diselenolato complexes $[Pt(Se^tBu)_2(PPh_3)_2]$, trans isomer *trans*-$[Pt_2H_2(\mu\text{-}Se^tBu)_2(PPh_3)_2]$, or a dinuclear diselenolato complex $[Pt_2(Se^tBu)_2(\mu\text{-}Se^tBu)_2(PPh_3)_2]$. Further investigations on the reactivity of **2** and **3** are currently in progress.

Experimental Section

General Procedure. All experiments were performed under an argon atmosphere unless otherwise noted. Solvents were dried by standard methods and freshly distilled prior to use. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker DPX-400 or DRX-400 (400.1, 100.6, and 162.1 MHz, respectively) spectrometers using $CDCl_3$ as the solvent at room temperature. $^{77}Se\{^1H\}$ NMR spectra were recorded on Bruker AVANCE 500 or DRX-400 (95.4 or 76.3 MHz) spectrometers using $CDCl_3$ as the solvent at −20 °C or room temperature, and the chemical shifts (ppm) are referenced to Me_2Se. IR spectra were obtained on a Perkin-Elmer System 2000 FT-IR spectrometer. Elemental analyses were carried out at the Molecular Analysis and Life Science Center of Saitama University. All melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. $[Pt(\eta^2\text{-nb})(PPh_3)_2]$ was prepared according to the reported procedure.[11]

***cis*-$[PtH(Se^tBu)(PPh_3)_2]$ (1).** 1,1-Dimethylethaneselenol (^{t}BuSeH) was prepared in situ by the reduction of ^{t}BuSeSe^{t}Bu with an excess amount of $NaBH_4$. Thus, a solution of ^{t}BuSeSe^{t}Bu (109.0 mg, 0.41 mmol) in THF (2 mL) was added slowly to a suspension of $NaBH_4$ (61.0 mg, 1.60 mmol) in THF (1 mL) at 0 °C, and the mixture was stirred for 1 h at room temperature and then quenched with ethanol (1 mL). The resulting solution of ^{t}BuSeH (0.81 mmol) was added to a solution of $[Pt(\eta^2\text{-nb})(PPh_3)_2]$ (663 mg, 0.82 mmol) in THF (7 mL), and the mixture was stirred for 3 h at room temperature to form a pale-yellow solution. After removal of the solvent under reduced pressure, the residue was dissolved in benzene (ca. 3 mL), which was filtered through a pad of Celite and rinsed with benzene (ca. 3 mL). After removal of the solvent of the filtrate under reduced pressure, the residual pale-yellow solid was washed three times with ether (ca. 3 mL) to give analytically pure *cis*-$[PtH(Se^tBu)(PPh_3)_2]$ **1** (558 mg, 80%) as pale-yellow crystals. **1**: Mp 102−104 °C (dec.). ^1H NMR (400.1 Hz, $CDCl_3$): δ −5.94 (dd, $^2J_{P-H}$ = 179, 17, $^1J_{Pt-H}$ = 867 Hz, 1H), 1.59 (s, 9H), 7.08−7.17 (m, 12H),

---

[17] Itazaki, M.; Nishihara, Y.; Osakada, K. *Organometallics* **2004**, *23*, 1610–1621.

[18] Tanabe, M.; Itazaki, M.; Kitami, O.; Nishihara, Y.; Osakada, K. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 1288–1290.

[19] Mochida, K.; Karube, H.; Nanjo, M.; Nakadaira, Y. *Organometallics* **2005**, *24*, 4734–4741.

7.18−7.28 (m, 6H), 7.33−7.47 (m, 12H). $^{13}C\{^1H\}$ NMR (100.6 Hz, $CDCl_3$): δ 34.3 (dd, $^3J_{P-C}$ = 10, 2 Hz), 37.0 (d, $^4J_{P-C}$ = 2, $^3J_{Pt-C}$ = 33 Hz), 127.5 (d, $^2J_{P-C}$ = 20 Hz), 127.6 (d, $^2J_{P-C}$ = 21 Hz), 129.5, 129.6, 132.0 (dd, $^1J_{P-C}$ = 44, $^3J_{P-C}$ = 1, $^2J_{Pt-C}$ = 19 Hz), 134.2 (d, $^3J_{P-C}$ = 11 Hz), 134.3 (d, $^2J_{P-C}$ = 11 Hz), 135.1 (dd, $^3J_{P-C}$ = 3, $^1J_{P-C}$ = 52, $^2J_{Pt-C}$ = 35 Hz). $^{31}P\{^1H\}$ NMR (162.1 Hz, $CDCl_3$): δ 17.7 (d, $^2J_{P-P}$ = 14, $^1J_{Pt-P}$ = 3135 Hz), 29.4 (d, $^2J_{P-P}$ = 14, $^1J_{Pt-P}$ = 2138 Hz). IR (KBr) ν 2088 cm^{-1} (Pt−H). Anal. calcd for $C_{40}H_{40}P_2PtSe$: C, 56.08; H, 4.71. Found: C, 55.67; H, 4.56.

Thermal Reaction of Hydrido Complex 1. A solution of complex **1** (31.4 mg, 0.036 mmol) in toluene (2 mL) was heated at 80 °C for 3 h, and the solvent was removed under reduced pressure. The residue was subjected to silica-gel column chromatography (hexane/CH_2Cl_2 = 1:1) to give analytically pure *cis*-$[Pt_2H_2(\mu\text{-}Se^tBu)_2(PPh_3)_2]$ **2** (6.5 mg, 0.0055 mmol, 30%, R_f = 0.65) as pale-yellow crystals and *cis*-$[Pt_2H(Se^tBu)(\mu\text{-}Se^tBu)_2(PPh_3)_2]$ **3** (9.1 mg, 0.0069 mmol, 57%, R_f = 0.50) as orange crystals. **2**: Mp 140−142 °C (dec.). ^1H NMR (400.1 MHz, $CDCl_3$): δ −12.07 (dd, $^2J_{P-H}$ = 13, $^4J_{P-H}$ = 4, $^1J_{Pt-H}$ = 1172 Hz, 2H), 0.89 (s, 9H), 1.74 (s, 9H), 7.23−7.27 (m, 12H), 7.30−7.34 (m, 6H), 7.57−7.62 (m, 12H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 33.0 ($^3J_{Pt-C}$ = 25 Hz), 37.7, 41.0, 41.2, 127.7 (d, $^2J_{P-C}$ = 11 Hz), 129.8, 134.0 (d, $^1J_{P-C}$ = 55 Hz), 134.4 (d, $^3J_{P-C}$ = 12 Hz). $^{31}P\{^1H\}$ NMR (162.1 MHz, $CDCl_3$): δ 22.5 (s, $^2J_{Se(cis)-P}$ = 36, $^2J_{Se(trans)-P}$ = 125, $^1J_{Pt-P}$ = 3819 Hz). $^{77}Se\{^1H\}$ NMR (95.4 MHz, $CDCl_3$, −20 °C): δ −84.5 (br s, $^1J_{Se-Pt}$ = 149 Hz), 215.6 (t, $^2J_{Se-P}$ = 125 Hz). IR (KBr) ν 2088 cm^{-1} (Pt−H). Anal. calcd for $C_{44}H_{50}P_2Pt_2Se_2$: C, 44.45; H, 4.24. Found: C, 44.51; H, 4.20. **3**: Mp 132−134 °C (dec.). ^1H NMR (400.1 MHz, $CDCl_3$): δ −11.54 (dd, $^2J_{P-H}$ = 17, $^4J_{P-H}$ = 5, $^1J_{Pt-H}$ = 1177 Hz, 1H), 0.92 (s, 9H), 1.20 (s, 9H), 1.97 (s, 9H), 7.12−7.19 (m, 6H), 7.24−7.38 (m, 12H), 7.54−7.67 (m, 12H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 35.6, 36.8, 36.9, 38.3, 44.3, 47.6, 127.5 (d, $^2J_{C-P}$ = 10 Hz), 127.8 (d, $^2J_{C-P}$ = 10 Hz), 129.3 (d, $^4J_{C-P}$ = 2 Hz), 130.0 (d, $^4J_{C-P}$ = 2 Hz), 132.4 (d, $^1J_{C-P}$ = 56 Hz), 133.7 (d, $^1J_{C-P}$ = 55 Hz), 134.4 (d, $^3J_{C-P}$ = 7 Hz), 134.5 (d, $^3J_{C-P}$ = 6 Hz). $^{31}P\{^1H\}$ NMR (162.1 MHz, $CDCl_3$): δ 9.7 (d, $^4J_{P-P}$ = 8, $^2J_{Se-P}$ = 165, $^1J_{Pt-P}$ = 3576 Hz), 21.9 (d, $^4J_{P-P}$ = 8, $^2J_{Se-P}$ = 124, $^1J_{Pt-P}$ = 3613 Hz). $^{77}Se\{^1H\}$ NMR (76.3 MHz, $CDCl_3$): δ −4.8 (br d, $^2J_{Se-P}$ = 7, $^1J_{Se-Pt}$ = 124, 96 Hz), 162.4 (dd, $^2J_{Se-P}$ = 165, 124 Hz), 182.1 (d, $^2J_{Se-P}$ = 7 Hz). IR (KBr) ν 2120 cm^{-1} (Pt−H). Anal. calcd for $C_{48}H_{58}P_2Pt_2Se_3$: C, 43.55; H, 4.42. Found: C, 43.07; H, 4.38.

Reaction of Hydrido Complex 1 with Methyl Propiolate. To a solution of **1** (97.0 mg, 0.11 mol) in benzene (3 mL) was added methyl propiolate (9.5 mg, 10.0 μL, 0.11 mmol) under argon. The mixture was heated at 60 °C for 5 h, and then the solvent was removed in vacuo. The ^1H NMR spectrum of the reaction mixture confirmed the formation of (*E*)- and (*Z*)-**4** together with **5**.[19] The NMR yields of (*E*)- and (*Z*)-**4** and **5** were calculated on the basis of the integral ratio in the ^1H NMR spectrum as 28, 6, and 64%, respectively. Although we tried the purification of (*E*)- and (*Z*)-**4** and **5** by silica-gel column chromatography, the separation of the mixture was unsuccessful due to the instability of (*E*)- and (*Z*)-**4** on silica gel. (*E*)-**4**: ^1H NMR (400.1 MHz, $CDCl_3$): δ 1.55 (s, 9H), 3.72 (s, 3H), 6.20 (d, ^3J = 16 Hz, 1H), 8.23 (d, ^3J = 16 Hz, 1H). (*Z*)-**4**: ^1H NMR (400.1 MHz, $CDCl_3$): δ 1.51 (s, 9H), 3.74 (s, 3H), 6.36 (d, ^3J = 10 Hz, 1H), 7.83 (d, ^3J = 10 Hz, 1H).

X-ray Crystallographic analyses of 1−3. Pale-yellow single crystals of **1** and **2** and orange ones of **3** were grown by slow evaporation of their saturated CH_2Cl_2 and hexane solutions. The intensity data were collected at 103 K for **1**−**3** on a Bruker AXS SMART diffractometer employing graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELX-97).[20] Hydrogen atoms, except for PtH hydrogen of **1**−**3** were located by assuming ideal geometry and were included in the structure calculations without further refinement of the parameters. The structures of **3** involved disorders in a bridged ^{t}BuSe ligand, two ^{t}Bu groups on Se2 and Se3 atoms, and a phenyl group of a PPh_3 ligand. The occupancies of each fragment were refined with constraints where their sum is 1 (0.542(15): 0.458(15) for the bridged ^{t}BuSe ligand, 0.589(15): 0.411(15) for the ^{t}Bu group on Se2 atom, 0.525(9): 0.475(9) for the ^{t}Bu group on Se3 atom, and 0.481(16): 0.519(16) for the phenyl group). Crystal data (see also Supporting Information) for **1** at 103 K: $C_{40}H_{40}P_2PtSe$, MW = 856.71, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 10.4447(6)$, $b = 21.0275(11)$, $c = 16.5542(9)$ Å, $\beta = 105.2180(10)°$, $V = 3508.2(3)$ Å^3, $D_{calcd} = 1.622$ g·cm^{-3}, $\mu = 5.155$ mm^{-1}, $2\theta_{max} = 51.00°$, R_1 ($I > 2\sigma(I)$) = 0.0414, wR_2 (all data) = 0.1082 for 6529 reflections, 404 parameters, and 2 restraints, GOF = 1.037. Crystal data for **2** at 103 K: $C_{44}H_5P_2Pt_2Se_2\cdot CH_2Cl_2$, MW = 1273.81, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 16.169(3)$, $b = 10.802(2)$, $c = 26.764(5)$ Å, $\beta = 105.471(4)°$, $V = 4505.0(15)$ Å^3, $D_{calcd} = 1.878$ g·cm^{-3}, $\mu = 8.040$ mm^{-1}, $2\theta_{max} = 51.00°$, R_1 ($I > 2\sigma(I)$) = 0.0509, wR_2 (all data) = 0.1247 for 8365 reflections, 492 parameters, and 1 restraint, GOF = 1.034. Crystal data for **3** at 103 K: $C_{48}H_{58}P_2Pt_2Se_3$, MW = 1323.94, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 10.5887(4)$, $b = 19.0090(8)$, $c = 23.1157(10)$ Å, $\beta = 90.2250(10)°$, $V = 4652.7(3)$ Å^3, $D_{calcd} = 1.890$ g·cm^{-3}, $\mu = 8.454$ mm^{-1}, $2\theta_{max} = 52.00°$, R_1 ($I > 2\sigma(I)$) = 0.0304, wR_2 (all data) = 0.0690 for 9136 reflections, 648 parameters, and 1 restraint, GOF = 1.004.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research (no. 21550035) and that on Priority Areas (nos. 19027014 and 20036013, Synergy Elements) from the Ministry of Education, Science, Sports, and Culture of Japan.

Supporting Information Available: NMR spectra for **2** and **3** (PDF), and tables of crystallographic data including atomic positional and anisotropic displacement parameters for **1**−**3** as PDF and CIF formats. Crystallographic data for **1**−**3** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

---

[20] Sheldrick, G. M. *SHELXL-97*, Program for Crystal Structure Refinement; University of Göttingen: Göttingen, Germany, 1997.