Selective $E$ to $Z$ isomerization of 1,3-Dienes Enabled by A Dinuclear Mechanism

Eiji Kudo$^1$, Kota Sasaki$^1$, Shiori Kawamata$^2$, Koji Yamamoto$^1$ & Tetsuro Murahashi$^1$

The $E/Z$ stereocontrol in a $C\equiv C$ bond is a fundamental issue in olefin synthesis. Although the thermodynamically more stable $E$ geometry is readily addressable by thermal $Z$ to $E$ geometric isomerization through equilibrium, it has remained difficult to undergo thermal geometric isomerization to the reverse $E$ to $Z$ direction in a selective manner, because it requires kinetic trapping of $Z$-isomer with injection of chemical energy. Here we report that a dinuclear Pd$^{1}$–Pd$^{1}$ complex mediates selective isomerization of $E$-1,3-diene to its $Z$-isomer without photoirradiation, where kinetic trapping is achieved through rational sequences of dinuclear elementary steps. The chemical energy required for the $E$ to $Z$ isomerization can be injected from an organic conjugate reaction through sharing of common Pd species.
The E/Z stereocontrol of a C=C moiety has been a central issue in olefin chemistry. Significant efforts have been made to obtain the thermodynamically less stable Z-alkenes as a kinetically preferred product, because Z-alkenes are contained in many natural products, biologically active molecules, and synthons for organic synthesis. Several bond-construction methods have been developed to obtain Z-alkene selectively, such as syn 1,2-addition to alkynes, stereoretentive cross-coupling using Z-vinyl reagents, Z-selective olefin metathesis, modified Wittig reactions, and Z-selective double bond migration. In view of the fact that an E/Z mixture of alkynes in which a thermodynamically more stable E-alkene is the major isomer can be readily obtained by a common alkene construction method such as the Wittig reaction, the E to Z geometric isomerization may also become a powerful method to address to Z-alkenes. Despite its potential usefulness, however, the E to Z geometric isomerization of alkenes is not straightforward. Although photoradiation of several alkenes leads to the E to Z isomerization, Z-stereoselection under photoradiation is sometimes incomplete, mainly because a photophysical E/Z ratio depends on a photodynamic state derived from an excited state structure. Moreover, it has been difficult to undergo E to Z geometric isomerization without photoradiation, because an equilibrium of a reversible E/Z isomerization lies largely to the side of E-alkenes (Fig. 1a). The claim that thermal E to Z isomerization of 1,3-dienes proceeds in the presence of a cobalt catalyst have proven erroneous recently. There has been no rational mechanism that allows kinetic trapping of Z-alkenes through a thermal E/Z isomerization. For example, E/Z geometric isomerization of alkynes is efficiently mediated or catalyzed by a transition metal hydride ([M][H]) or its intermediate, that then gives an equilibrium mixture of an excited state structure, which shows high reactivity with unsaturated hydrocarbons. We chose 1,3-dienes as the alkene substrate, not only because 1,3-dienes become useful starting substrates for many synthetic applications, but also because 1,3-dienes are smoothly introduced to the bridging coordination site of a dinuclear Pd–Pd complex (Fig. 1d). We found that the reaction of 1 with either methyl E-5-methylhexa-2,4-dienoate (E-2) or its Z-isomer (Z-2) immediately gave an equilibrium mixture of transoid-antifacial and cisoid-antifacial isomers of the dinuclear adducts [Pd₂(μ-η⁵-η³-mmd)(CH₃CN)₅][BF₄]₂ (3, mmd = methyl 5-methylhexa-2,4-dienoate) in a 92:8 molar ratio at 25 °C. The molar ratio of 3-transoid-antifacial:3-cisoid-antifacial reached 95:5 at −25 °C (Fig. 2a). The structures of these isomers were assigned by ¹H-NMR and ¹³C-NMR analyses, where the vicinal coupling constant J₁₁₃₋₁₁₄ of the transoid-antifacial isomer (J₁₁₃₋₁₁₄ = 10.4 Hz) is larger than that of cisoid-antifacial one (J₁₁₃₋₁₁₄ = 6.8 Hz), and the η¹-bound ¹³C atom, which is located at the α-position with respect to the COOMe group, appeared at the high-field region (δ = 31 ppm for 3-transoid-antifacial). The molecular structure of the major isomer 3-transoid-antifacial was confirmed by X-ray structure analysis (Fig. 2b). The η¹-bound Pd1 atom and the η¹-bound Pd2 atom are antiplanar with each other, and the conformation around the C3–C4 bond is transoid. The C3–C4 bond length (1.446(12) Å) is longer than those of C1–C2 (1.413(11) Å) and C2–C3 (1.385 (11) Å) due to its single bond character. The minor production of 3-cisoid-antifacial after the dinuclear addition to E-2 indicated that the stereoconversion of the dinuclear adduct 3 proceeded rapidly. That is, the syn dinuclear addition of 1 with E-2 initially gives 3-cisoid-antifacial, and subsequent stereoreversion occurs through the π-σ-π interconversion of the π-¹-allyl Pd moiety, giving the thermodynamically more stable 3-transoid-antifacial in rapid equilibrium (Fig. 2c). As mentioned below, it was confirmed that the dinuclear addition of 1,3-diene to the Pd–Pd moiety proceeds in a stereoretentive (syn) manner when employing a 1,4-disubstituted 1,3-diene as the reactant. The theoretical calculations supported the relative stability of the dinuclear addition products; i.e., 3-transoid-antifacial is more stable by ΔG = 6.9 kJ/mol than 3-cisoid-antifacial, cf. Z-2 is in higher energy by ΔG = 8.3 kJ/mol compared to E-2.

We then examined the kinetic trapping of Z-2 from 3-transoid-antifacial through syn elimination (Fig. 2d), although the rapid π-σ-π allyl-Pd interconversion can cause elimination of E-2 via the reverse way of the formation of 3-transoid-antifacial from E-2. Bis(diphenylphosphino)methane (dppm) has been used as a good
Fig. 1 Isomerization of alkenes. a A qualitative energy profile of Z-alkenes and E-alkenes. An M–M complex may promote E to Z geometric isomerization of alkenes through a dinuclear mechanism. The chemical energy required for the E to Z isomerization may come from the reaction energy of a coupled reaction (A + B → C + D), where the common M–M species are shared, making the net reaction exergonic. b A simplified model for the mononuclear metal hydride pathway which is a representative and conventional mechanism for Z to E isomerization. c A dinuclear M–M pathway that enables kinetic trapping of Z-alkene. d The key intermediates for the isomerization of 1,3-diene.
**Fig. 2** The dinuclear addition of a Pd²⁺–Pd⁰ moiety to substituted 1,3-dienes. 

**a** The dinuclear addition to 5-methylhexa-2,4-dienoate (2), and subsequent dinuclear elimination giving Z-diene selectively.  

**b** ORTEP for 3-transoid-antifacial (30% probability ellipsoids; counteranions are omitted for clarity).  

**c** The allyl π-σ-π interconversion for the rapid stereoinversion mechanism.  

**d** The ligand survey for stereoretentive elimination of Z-2. The reactions were carried out in CD₃NO₂ at room temperature. dppm = bis(diphenylphosphino)methane. [a] At −30 °C.  

**e** Yields of Z-1,3-dienes after isolation. Typically, the diene was added to a CH₃NO₂ solution of 1, and stirred for 30 min. The reaction mixture was cooled to −30 °C, and then COT was added and the mixture was stirred for 15 min. [b] PPh₄I was used instead of COT.
A sequence of syn dinuclear addition and anti-dinuclear elimination. According to the mechanism shown in Fig. 2a, the E to Z isomerization of 1,4-disubstituted 1,3-diienes is not straightforward, because the corresponding dinuclear addition intermediate unlikely undergoes stereoinversion through π-σ-π allyl interconversion that accompanies the exchange of the syn/anti-substituents at the terminal η3-allyl moieties. In fact, it was confirmed that addition of 1 to the (2E,4E)- or the (2Z,4Z)-isomer of methyl 5-phenylpenta-2,4-dienoate (11) in a CD3NO2/CD3CN solution (νν/ν = 9/1) proceeded in a highly stereospecific (syn) manner, yielding the transient-antifacial or cisoid-antifacial dinuclear adduct [Pd2(μ-η3-η1-mpd)L3][BF4] (12-cisoid-antifacial or 12-transoid-antifacial, mpd = methyl 5-phenylpenta-2,4-dienoate) (Fig. 3a). The structure of each isomer of 12 was identified by the 1H NMR analysis, where the vicinal H3-H4 coupling constant of the transoid isomer (J1,3-H4 = 10.4 Hz) is larger than that of the cisoid isomer (J1,3-H4 = 6.0 Hz). We then examined the direct anti elimination from the E-equivalent intermediate 12-cisoid-antifacial that may give (2Z,4E)-11. For the anti elimination, we focused on the free-radical-induced metal elimination, since it is known that a metal–carbon bond undergoes homolysis by addition of radical species. The double homolysis of the C–Pd bonds proceeded by addition of 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) (2 equiv) to 12-cisoid-antifacial in CD3NO2/CD3CN (νν/ν = 9/1) at −30 °C, giving (2Z,4E)-11 (76% yield, (2E,4E)-11: (2Z,4E)-11 = 24:76), where the mononuclear TEMPO-adduct [Pd(η2-TEMPO)(CH3CN)2][BF4] (13) was concomitantly formed (Fig. 3a). The TEMPO adduct 13 was isolated upon treatment of 1 with TEMPO in 91% yield, and its structure was determined by X-ray structure analysis (Fig. 3b). The observed Z-selectivity indicated that association of TEMPO to each PdII center in 12-cisoid-antifacial and subsequent Pd–C bond cleavage occurs with conservation of the cisoid geometry. The partial loss of the stereochemistry may be caused by the TEMPO-induced elimination mechanism, where a palladium moiety could eliminate in a stepwise manner. We confirmed that the treatment of 12-transoid-antifacial with TEMPO gave (2E,4E)-11 selectively (Fig. 3a). It is noted that treatment of 12-transoid-antifacial with COT resulted in the quantitative recovery of (2Z,4E)-11. For the preparative scale, in-situ-generated 12-cisoid-antifacial in CH3NO2/CH3CN (νν/ν = 95/5) from pure (2E,4E)-11 was treated with TEMPO (4 equiv) at −20 °C to give (2Z,4E)-11 in 56% yield (Fig. 3c). Other 1,4-disubstituted (2E,4E)-dienes such as 14, 15, and 16 were also isomerized to the corresponding (2Z,4E)-isomers in 27–64% yields (Fig. 3c). It was reported that UV-irradiation of (2E,4E)-11 at 313 nm gives a mixture of possible four isomers (2Z,4E), (2E,4Z), (2E,4Z), and (2Z,4Z)-11 with low selectivity (18:16:34:32)49.

Injection of chemical energy through conjugate reactions. Finally, we demonstrated that the concept of conjugate reactions is applicable to the present E to Z isomerization of 1,3-diene, where the required chemical energy is injected from a coupled reaction by sharing of a common metal species (Fig. 1a). In biological systems, many endergonic chemical reactions are operated by energetic coupling with an exergonic reaction such as ATP-hydrolysis, that makes the net reaction system exergonic. However, it is rare that the concept of the conjugate reaction system is applied to the reaction-design of artificial metal mediated-hill or catalyzed up-hill organic transformations. Although the above mentioned E to Z isomerization of 2 is driven thermodynamically by the organo-metallic complexation reaction of 1 with COT to yield the complex 4, a conjugate reaction system in which the E to Z isomerization is energetically coupled with a downhill reaction (A + B → C + D in Fig. 1a) could give a net exergonic system. Furthermore, regeneration of 1 after the coupled down-hill reaction is highly desirable. We developed the oxidative double amination of COT by using 1 for the organic coupled reaction. The reaction of 4 with a secondary amine such as pyrrolidine (2 equiv) at 0 °C in the presence of dibenzylideneacetone (dba) (5 equiv) gave a disubstituted 9-aza-barbaralane (17) (58% yield) and Pd2(dbaz) (18) (71% yield) (Fig. 4a). The molecular structure of the fluxional molecule 17 was confirmed by X-ray structure analysis (Fig. 4b). The formation of 17 might involve the nucleophilic amine-attack at one of the η3-allyl moieties in 4, subsequent deprotonation, intramolecular nucleophilic attack at the central carbon of the remaining η3-allyl moiety, and reductive elimination. The resultant Pd0 complex 18 can be converted to the Pd2–Pd4 complex 1 in 90% yield by treatment with [Cp2Fe][BF4] in CH3CN–CH2Cl2 at room temperature (Fig. 4a), although the selective synthesis of a Pd3 complex by one-electron oxidation of Pd0 or one-electron reduction of Pd4 has been rarely reported. Thus, merging the up-hill E to Z isomerization of 1,3-diene and the downhill oxidative double amination of COT gave a net exergonic conjugate reaction system, where delivery of the Pd2–Pd4 species or its equivalent from one reaction to another gives a closed cycle (Fig. 4a).

For the anti elimination mechanism, the downhill oxidative protonation reaction of TEMPO becomes the coupled reaction for the up-hill E to Z alkene isomerization of 11. That is, protonation of the TEMPO-adduct 13 with HBF4·Et2O in CH3CN afforded [Pd(CH3CN)2][BF4] (19) in 80% yield with the elimination of [TEMPOH2][BF4] (20). The Pd4 complex 19 was then reduced with Cp2Fe in CH3CN to give 1 in 97% yield.
In summary, we have described $E$ to $Z$ isomerization of 1,3-dienes mediated by the dinuclear $M$–$M$ bonded species. The $E\rightarrow Z$ stereocontrol can be achieved by a rational dinuclear mechanism that allows kinetic trapping of $Z$-1,3-diene. Furthermore, the concept of the conjugate reaction system demonstrated in this work may provide a basis to promote the metal-mediated up-hill organic transformation through energetic coupling with an exergonic reaction.

**Methods**

**General procedure.** All manipulations were conducted under a nitrogen atmosphere using standard Schlenk or drybox techniques. Unless specified, all reagents were purchased from commercial suppliers and used without purification. Solvents were purified according to the standard procedures. For experimental details, spectroscopic characterization data, X-ray crystallographic data, and details of quantum calculations, see the Supplementary Information.

**Isomerization of methyl $E$-2 to $Z$-2.** To a solution of $[Pd_2(CH_3CN)_6][BF_4]_2$ (1, 126.5 mg, 2.66 × 10$^{-3}$ mmol) in CH$_3$NO$_2$, was added methyl (E)-5-methylhexa-2,4-dienoate ($E$-2, 28.0 mg, 2.00 × 10$^{-3}$ mmol) and stirred at room temperature for 30 min. The reaction mixture was cooled to −30 °C and COT (41.7 mg, 4.00 × 10$^{-3}$ mmol, 2 equiv.) was added. After stirring 15 min, the mixture was diluted with diethyl ether, and filtered through a silica gel pad. The solvent was removed in vacuo and the residue was purified by a silica gel column chromatography to give methyl 5-phenylpenta-2,4-dienoate (22/E) as colorless oil (22.4 mg, 1.60 × 10$^{-3}$ mmol, 80% yield, $EZ = <1:99$).

**Isomerization of (2E,4E)-11 to (2Z,4E)-11.** To a solution of $[Pd_2(CH_3CN)_6][BF_4]_2$ (1, 168.1 mg, 2.66 × 10$^{-3}$ mmol) in CH$_3$NO$_2$/CH$_3$CN ($v/v = 95:5$) in CH$_3$NO$_2$/CH$_3$CN ($v/v = 95:5$) was added methyl (2E,4E)-5-phenylpenta-2,4-dienoate (22/E) (50.0 mg, 2.66 × 10$^{-3}$ mmol) and stirred at room temperature for 15 min. The reaction mixture was cooled to −20 °C and a solution of TEMPO (2 equiv) was added and stirred for 5 min.

**Synthesis of Pd$_4$(dba)$_3$ and 9-aza-barbaralane 17 through double amination of 4.** To a solution of $[Pd_4(CH_3CN)_6][BF_4]_2$ (1, 100.0 mg, 1.60 × 10$^{-3}$ mmol) in CH$_3$CN was added the COT (17.3 mg, 1.70 × 10$^{-3}$ mmol) and stirred at room temperature. After 30 min, dba (185.1 mg, 7.90 × 10$^{-3}$ mmol) was added to the
reaction mixture, and then the reaction mixture was cooled at 0 °C. After addition of pyrrolidine (22.4 mg, 3.20 × 10–3 mmol) at 0 °C, the reaction mixture was stirred at the temperature for 2 h. The violet precipitate in suspension was then separated by decantation, and the supernatant was concentrated in vacuo. The solution was filtered through a silica gel pad. The silica gel pad was washed with CH2Cl2 and diethyl ether and dried in vacuo to yield Pd2(dba)3 (18) in 71% yield (Yield was determined by the free dba/Pd2(dba)3 molar ratio from 1H NMR).

Data availability

The authors declare that the data supporting the findings of this study are available within the paper and its supplementary information files, as well as from the corresponding author upon reasonable request. The X-ray crystallographic coordinates for structures reported in this study (3-transoid-antifacial, 13, and 17) have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers 2003060–2003062. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The experimental data are available in Supplementary Information.

Received: 4 August 2020; Accepted: 2 February 2021; Published online: 05 March 2021

Fig. 4 The conjugate reaction system for the uphill E to Z isomerization. a E to Z isomerization of 1,3-diene is energetically coupled with oxidative double amination of cyclooctatetraene. The reaction conditions: CH3CN, 0 °C, 2 h, for 4 to 18, CH3CN/CH2Cl2, r.t., 1 h for 18 to 1, b ORTEP for 17 (30% probability ellipsoids).

References

1. Molloy, J. J., Morack, T. & Gilmour, R. Positional and geometrical isomerisation of alkenes: the pinnacle of atom economy. Angew. Chem. Int. Ed. 58, 13654–13664 (2019).
2. Siau, W.-Y., Zhang, Y. & Zhao, Y. Stereoselective synthesis of Z-alkenes. Top. Curr. Chem. 327, 33–58 (2012).
3. Negeishi, E. et al. Recent advances in efficient and selective synthesis of di-, tri-, and tetra-substituted alkenes via Pd-catalyzed alkynylation-carbonylation formylation synergy. Acc. Chem. Res. 41, 1474–1485 (2008).
4. Negishi, E. et al. Recent advances in efficient and selective synthesis of di-, tri-, and tetra-substituted alkenes via Pd-catalyzed allynylation-carbonylation formylation synergy. Acc. Chem. Res. 41, 1474–1485 (2008).
5. Negishi, E. et al. Recent advances in efficient and selective synthesis of di-, tri-, and tetra-substituted alkenes via Pd-catalyzed formylation synergy. Acc. Chem. Res. 41, 1474–1485 (2008).
6. Negishi, E. et al. Recent advances in efficient and selective synthesis of di-, tri-, and tetra-substituted alkenes via Pd-catalyzed formylation synergy. Acc. Chem. Res. 41, 1474–1485 (2008).
7. Negishi, E. et al. Recent advances in efficient and selective synthesis of di-, tri-, and tetra-substituted alkenes via Pd-catalyzed formylation synergy. Acc. Chem. Res. 41, 1474–1485 (2008).
8. Negishi, E. et al. Recent advances in efficient and selective synthesis of di-, tri-, and tetra-substituted alkenes via Pd-catalyzed formylation synergy. Acc. Chem. Res. 41, 1474–1485 (2008).
9. Negishi, E. et al. Recent advances in efficient and selective synthesis of di-, tri-, and tetra-substituted alkenes via Pd-catalyzed formylation synergy. Acc. Chem. Res. 41, 1474–1485 (2008).
10. Negishi, E. et al. Recent advances in efficient and selective synthesis of di-, tri-, and tetra-substituted alkenes via Pd-catalyzed formylation synergy. Acc. Chem. Res. 41, 1474–1485 (2008).
11. Negishi, E. et al. Recent advances in efficient and selective synthesis of di-, tri-, and tetra-substituted alkenes via Pd-catalyzed formylation synergy. Acc. Chem. Res. 41, 1474–1485 (2008).
12. Negishi, E. et al. Recent advances in efficient and selective synthesis of di-, tri-, and tetra-substituted alkenes via Pd-catalyzed formylation synergy. Acc. Chem. Res. 41, 1474–1485 (2008).
13. Negishi, E. et al. Recent advances in efficient and selective synthesis of di-, tri-, and tetra-substituted alkenes via Pd-catalyzed formylation synergy. Acc. Chem. Res. 41, 1474–1485 (2008).
14. Negishi, E. et al. Recent advances in efficient and selective synthesis of di-, tri-, and tetra-substituted alkenes via Pd-catalyzed formylation synergy. Acc. Chem. Res. 41, 1474–1485 (2008).
15. Negishi, E. et al. Recent advances in efficient and selective synthesis of di-, tri-, and tetra-substituted alkenes via Pd-catalyzed formylation synergy. Acc. Chem. Res. 41, 1474–1485 (2008).
16. Negishi, E. et al. Recent advances in efficient and selective synthesis of di-, tri-, and tetra-substituted alkenes via Pd-catalyzed formylation synergy. Acc. Chem. Res. 41, 1474–1485 (2008).
17. Negishi, E. et al. Recent advances in efficient and selective synthesis of di-, tri-, and tetra-substituted alkenes via Pd-catalyzed formylation synergy. Acc. Chem. Res. 41, 1474–1485 (2008).
18. Negishi, E. et al. Recent advances in efficient and selective synthesis of di-, tri-, and tetra-substituted alkenes via Pd-catalyzed formylation synergy. Acc. Chem. Res. 41, 1474–1485 (2008).
10. Holland, P. L. Distinctive reaction pathways at base metals in high-spin organometallic catalysts. Acc. Chem. Res. 48, 1696–1702 (2015).
11. Singh, K., Staig, S. I., & Weaver, J. D. Facile synthesis of Z-Alkenes via uphill catalysis. J. Am. Chem. Soc. 136, 5275–5278 (2014).
12. Metternich, J. B. & Gilmour, R. A bio-inspired, catalytic E → Z isomerization of activated olefins. J. Am. Chem. Soc. 137, 11254–11257 (2015).
13. Molloy, J. J. et al. Boron-enamed geometric isomerization of alkenes via selective energy-transfer catalysis. Science 369, 302–306 (2020).
14. Meier, H. The photochemistry of stilbeneoid compounds and their role in materials technology. Angew. Chem. Int. Ed. 31, 1399–1420 (1992).
15. Arai, T. & Tocumaru, K. Photochemical one-way adiabatic isomerization of aromatic olefins. Chem. Rev. 93, 23–39 (1993).
16. Pünner, F., Schmidt, A. & Hilt, G. Corrigendum: Up the Hill: selective double bond isomerization of terminal 1,3-dienes towards Z,1,3-dienes as Z,2,4-dienes. Angew. Chem. Int. Ed. 58, 17103–17104 (2019).
17. Larionov, E., Li, H. & Mazet, C. Well-defined transition metal hydrides in catalytic isomerizations. Chem. Commun. 50, 9816–9826 (2014).
18. Cramer, R. & Lindsey, R. V. The mechanism of isomerization of olefins with transition metal catalysts. J. Am. Chem. Soc. 88, 3534–3544 (1966).
19. Kapar, A., Spregler, T., Guven, S. & Schoenebeck, F. E-olefins through intramolecular radical relocation. Science 363, 391–396 (2019).
20. Tan, E. H. P., Lloyd-Jones, G. C., Harvey, J. N., Lennox, A. J. J. & Mills, B. M. [(RCN)PdCl2] catalyzed E/Z isomerization of alkenes: a non-hydride binuclear addition-elimination pathway. Angew. Chem. Int. Ed 50, 9602–9606 (2011).
21. Sen, A. & Lai, T. C. Isomerization of alkynes by palladium(II) compounds. An alternative mechanistic view. Inorg. Chem. 20, 4036–4038 (1981).
22. Vedejs, E. & Fuchs, P. L. Inversion of acyclic olefins by the phosphorus betaine method: scope and limitations. J. Am. Chem. Soc. 95, 822–825 (1973).
23. Lamb, J. R., Hubbell, A. K., MacMillan, S. N. & Coates, G. W. Carboxylative catalytic deoxygenation of 2,3-disubstituted epoxides with inversion of stereochemistry: an alternative alkene isomerization method. J. Am. Chem. Soc. 142, 8029–8035 (2020).
24. Maeda, K., Shinoziku, H. & Oshima, K. Olefin inversion: stereoorganic olefin synthesis from vicinal alkoxylidioales with butyllithium by an E2 syn mechanism. J. Org. Chem. 61, 6770–6771 (1996).
25. Murahashi, T. et al. Stereoretentive elimination and trans-olefination of the dicaticonic palladium moiety [Pd2L4]2+ bound on 1,3,5-trienes. J. Am. Chem. Soc. 128, 4377–4388 (2006).
26. Kreiter, C. G. & Lips, W. Cleavage of a metal-metal bond by 1,3-butadiene under photochemical conditions. Angew. Chem. Int. Ed. 20, 201–202 (1981).
27. Murahashi, T., Nagai, T., Nakashima, H., Tomiyasu, S. & Kurosawa, H. Dinuclear addition of the Pd–Pd moieties to 1,3-dienes. Chem. Lett. 35, 754–755 (2006).
28. Murahashi, T., Nagai, T., Okuno, T., Matsutani, T. & Kurosawa, H. Synthesis and ligand substitution reaction of homoleptic acetonitrile dipalladium(I) complex. Chem. Commun. 1698–1699 (2000).
29. Leoni, P. et al. Reaction of phosphide-bridged palladium(I) dimers containing secondary phosphines with ethylene and isoprene: coordination vs. insertion. Organometallics 12, 4503–4508 (1993).
30. Murahashi, T., Kannehisa, N., Kai, Y., Otani, T. & Kurosawa, H. Rational synthesis of anionic, neutral, and cationic palladium(I) dinuclear complexes containing bridging conjugated dienes. Chem. Commun. 825–826 (1996).
31. Murahashi, T., Otani, T., Mochizuki, E., Kai, Y. & Kurosawa, H. Remarkably wide range of bond distance adjustment of Pd–Pd-Pd interactions to change stereochemistry: an alternative alkene isomerization method. J. Am. Chem. Soc. 139, 5194–5200 (2017).
32. Schramm, R. F. & Wayland, B. B. Oxidation of metallic palladium by nitrosyl tetrafluoroborate. Chem. Commun. 898–899 (1968).

Acknowledgements
H. Nakashima is acknowledged for his initial contribution to the 1,4-disubstituted 1,3-diene system. This work was supported by the grants-in-aid for scientific research from JSPS (15H02465, 17H04805, 19H01073, 19H04565), and by JST-CREST (JP17C00286).

Author contributions
Chemical reaction experiments were performed by E.K., K.S., S.K., and K.Y. Theoretical characterization of Pd2(dba)-2 complexes. J. Am. Chem. Soc. 135, 8388–8393 (2013).
Johansson seechurn, C. C. C., Spregler, T., Scrase, T. G., Schoenebeck, F. & Colcokt, J. Understanding the unusual reduction mechanism of Pd(II) to Pd(I): uncovering hidden species and implications in catalytic cross-coupling reactions. J. Am. Chem. Soc. 139, 5194–5200 (2017).
Kapadi, A. R. & et al. The elusive structure of Pd2(dba)2. Examination by isotopic labeling, NMR spectroscopy, and X-ray diffraction analysis: synthesis and characterization of Pd2(dba-2)2 complexes. J. Am. Chem. Soc. 135, 5194–5200 (2017).

Schramm, R. F. & Wayland, B. B. Oxidation of metallic palladium by nitrosyl tetrafluoroborate. Chem. Commun. 898–899 (1968).

Competing interests
The authors declare no competing interests.

Additional information
Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41467-021-21720-4.
Correspondence and requests for materials should be addressed to T.M.

Peer review information Nature Communications thanks the anonymous reviewer(s) for their contribution to the peer review of this work.

Reprints and permission information is available at http://www.nature.com/reprints

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.