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Properties and Reactivities of Zwitterionic Platinum(II)-ate Complexes Generated by Transforming Coordination of an Alkyne– Bisphosphine Ligand

Kazuhiro Okamoto,* Kohei Sasakura, Satoshi Funasaka, Hiiro Watanabe, Masahiro Suezaki, and Kouichi Ohe*



ABSTRACT: Coordination of an alkyne-bisphosphine ligand with platinum(II) precursors produced a structural reorganization in the ligand backbone to form stable zwitterionic platinum(II) complexes bearing an anionic platinum center. The structural properties and reactivities of these complexes were investigated using X-ray crystallographic analyses, computational studies, and stoichiometric reactions involving oxidative addition and reductive elimination. These studies have shown that the enhanced nucleophilicity of the platinum center to alkyl halides promotes smooth oxidative addition and that the charge rebalance accelerates the dissociation of the halide anion from the platinum(IV) intermediate, which is essential in the carbon-carbon bond-forming step.

INTRODUCTION

Platinum complexes exemplified by Zeise's salt, the firstdiscovered organometallic compound, have been widely studied to gain mechanistic insights into organometallic catalysis because of the higher stability of carbon–platinum bonds against moisture and air in comparison with the case of other transition metals such as palladium.^{1,2} Although various platinum-catalyzed organic reactions such as silylation,³ borylation,⁴ amination,⁵ and carbene-transfer reactions⁶ are well-known these days, there have only been a few reports on the use of platinum complexes as a catalyst for carbon–carbon bond-forming cross-coupling reactions.^{7,8} Recently, key platinum catalysts in these reactions have been considered to be platinum(IV) intermediates (Figure 1), which are rather rare and exhibit unique reactivities in comparison with the



Figure 1. $\ensuremath{\mathsf{Platinum}}(\ensuremath{\mathsf{IV}})$ complexes proposed as catalytic intermediates.

conventional Pt^0/Pt^{II} or Pd^0/Pd^{II} cycles.⁹ Therefore, investigations of the highly efficient platinum(II/IV)-based system involving carbon–carbon bond-forming reactions is of great importance for the fundamental development of organometallic chemistry.

During our studies on the coordination behaviors of alkyne– bisphosphine ligand 1 with various transition metals, cyclobutadiene–dirhodium complex 2 and 1,3-butadiene-1,4-diyl iridium(II) dimer 3 were obtained via the structural change of ligand 1 triggered by π -coordination of alkynes (Scheme 1).^{10,11} Although a variety of bidentate phosphine ligands coordinate to the single metal center while their ligand backbone remains unchanged, ligand 1 undergoes carbon– carbon bond-forming dimerization to afford unique types of dinuclear complexes. Here, we describe how the alkyne moiety reacts with a platinum(II) precursor differently to afford the

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Scheme 1. Alkyne-Containing Bisphosphine Ligand 1 as a Template for Diversity in Complexation



zwitterionic platinum(II) complexes **5**, which undergo oxidative addition with alkyl halides followed by reductive elimination to give the corresponding coupling products. We envisioned that the use of the present zwitterionic complexes having a carbon atom and an anionic charge on the platinum atom would enhance both the nucleophilicity of the platinum center and the carbanion character of the organic ligand bound to the metal center, and thereby the carbon–carbon bond-forming activity would also be enhanced (Scheme 2).¹²

Scheme 2. Reactivity of Zwitterionic Platinum Complexes with an Anionic Metal Center



Moreover, we expect a synergetic effect for zwitterionic platinum complexes bearing both an anionic platinum center and a cationic ligand linkage,^{13,14} which may provide a unique character of the catalytic intermediate because of the rebalancing of charges.

RESULTS AND DISCUSSION

Complexation of Alkyne–Bisphosphine Ligand 1 with Platinum(II) Precursors. As an initial attempt, the reaction of diphenylacetylene-based bisphosphine ligand 1 with $PtCl_2(cod)$ in $CDCl_3$ or CD_2Cl_2 was performed at room temperature (Scheme 3). Crystals of bisphosphine complex 4a immediately precipitated from the reaction mixture. Complex 4a was then dissolved in CD_2Cl_2 and the solution left at room temperature for 15 days to form the new unsymmetrical complex 5a as a precipitate. The structures of complexes 4a and 5a were unambiguously determined using X-ray crystallographic analyses (Figure 2). Complex 4a is a *cis*-chelating Scheme 3. Isolation of Zwitterionic Complexes 5



Figure 2. ORTEP illustration of platinum complexes 4a and 5a-d with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

bisphosphine–platinum(II) dichloride complex with an unconstrained square-planar structure, in which no coordinative interaction of the acetylenic moiety is observed (the C1– C2 bond length is 1.20 Å; the mean of the C3–C1–C2 and C1–C2–C4 angles is 175°). Complex **5a** was found to be a zwitterionic complex with an anionic platinum center and a cationic phosphoindolium moiety. The ligand changes from a κ^2 -P,P- to a κ^2 -C,P-chelating mode by the conversion from complex **4a** to **5a**.¹⁵

NMR studies using $PtMe_2(cod)$ instead of $PtCl_2(cod)$ showed that dimethylplatinum complex **5b** was formed much more quickly (within 120 min) than complex **5a** (Table S1 and Figures S2 and S3 in the Supporting Information). Other platinum precursors such as $PtPh_2(cod)$ and $Pt(C \equiv C'Bu)_2(cod)$ also underwent a similar intramolecular cyclization to form zwitterionic complexes **5c,d** (Scheme 4). Complexes **5b-d** were successfully isolated in good yields (62–82%) by recrystallization from a benzene or toluene pubs.acs.org/Organometallics

Scheme 4. Complexation of Alkyne–Bisphosphine Ligand 1 with $PtR_2(cod)$



solution. Dichloroplatinum complex 5a was alternatively prepared by the treatment of dimethyl complex 5b with hydrochloric acid. The structures of complexes 5b-d were also determined using X-ray crystallographic analyses (Figure 2).

Structural Properties of Zwitterionic Platinum(II) Complexes 5. The characteristic structural parameters of zwitterionic complexes 5 in the X-ray crystal structures are summarized in Table 1. The supporting ligand derived from





alkyne-bisphosphine 1 is composed of two coordination units: phosphoindolium (shown in green) and triarylphosphine (shown in magenta). All zwitterionic complexes have a square-planar structure around the platinum center. The C3-C4 bond lengths in the phosphoindolium ring exhibit a double-bond character, which indicates that the negative charge at the platinum atom and the positive charge at the phosphorus atom are separated.¹⁶ The bond lengths between platinum and the supporting ligands (Pt-C3 and Pt-P1) are considered as indicators of the magnitude of the trans influence, whose strength is in the order Ph > Me \approx ^tBuC \equiv C > Cl. The dihedral angles of the two units in the supporting ligand (C3-C4-C5-C6) are approximately 31° $(X \neq Cl)$ and 23.2° (X = Cl). The phosphoindolium ring unit is also distorted toward the coordination square plane by 42-45°. The distorted coordination structure is important for stabilizing the six-membered platinacycle (Pt-C3-C4-C5-C6-P1).

Oxidative Addition of Alkyl Halides to Zwitterionic Platinum(II) Complexes. As an initial study of the reactivity

of zwitterionic platinum complexes **5**, the oxidative addition reactions of methyl iodide to complexes **5** were performed. At first, the reaction of the dimethylplatinum(II) complex **5b** with 1.1 equiv of MeI was monitored with ¹H and ³¹P NMR analyses at room temperature (Scheme 5 and Figure 3a). After

Scheme 5. Oxidative Addition and Reductive Elimination



Figure 3. Time-dependent percentage amounts of the reaction of zwitterionic platinum complexes (a, 5b; b, 5c; c, 5d) with MeI.

5 min, the two methyl peaks for complex 5b disappeared, whereas three peaks of methyl protons bearing a ${}^{2}J({}^{1}H-{}^{195}Pt)$ satellite coupling corresponding to platinum(IV) species appeared in the ¹H NMR spectrum (Figure S5). As signals of platinum(IV) intermediates gradually decreased over the 2.5 h monitoring period, one new signal for the methyl proton increased, which corresponds to the methyliodo complex 8b formed by reductive elimination, affording ethane. This result clearly indicates the involvement of a fast oxidative addition and a rate-determining reductive elimination via the formation of platinum(IV) intermediates. When the same reaction using deuterated methyl iodide (CD₂I) was performed, three peaks of methyl protons of platinum(IV) species were also observed in the ¹H NMR spectrum, in which the peak intensities were lower than those when CH₃I was used (Table S3 and Figure S6). This result suggests the equilibrium between the hexacoordinate complex 6b and the pentacoordinate complex 7b·X, which caused a rapid exchange of three methyl groups via pseudorotation in 7b·X.

On the other hand, the reactivity of diphenyl and dialkynyl complexes **5c**,**d** differed from that of dimethyl complex **5b** (Figure 3b,c). The reactions of **5c**,**d** clearly showed first-order kinetics for the conversion of the starting complexes and did not afford observable amounts of platinum(IV) intermediates,¹⁷ which indicates that the rate-determining step is shifted to oxidative addition. The overall reaction rates depend on the R¹ group on the platinum center, which decreases in the order Ph > Me > alkynyl groups. The slowest reaction of **5d** was not completed after 12 h.¹⁸ The resulting platinum(II) complex was successfully analyzed with X-ray crystallography in the case of phenyliodoplatinum(II) complex **8c** (Figure 4). In a



Figure 4. ORTEP illustration of zwitterionic platinum complex **8c** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and solvent atoms are omitted for clarity.

reflection of the difference in *trans* influences discussed above, the phenyl group is located at the position *trans* to the phosphine moiety, which is also supported by the formation of only the isomer observed in NMR analyses. The fact that all of the reactions with MeI proceeded at room temperature is in sharp contrast to the behavior of commercially available platinum complexes such as PtMe₂(dppe) and PtMe₂(cod), which did not afford the coupling product at all even at room temperature (Table S5). Although PtMe₂(dppe) is known to undergo the oxidative addition of MeI to give PtMe₃I(dppe), it is rather stable at room temperature and requires a higher temperature and the use of a polar solvent to cause both C–C formation and C–I reductive elimination.^{19,20} It should be noted that the present zwitterionic complexes undergo a rapid oxidative addition followed by reductive elimination to give ethane in a nonpolar solvent at room temperature with high efficiency.

Diphenyl complex 5c also reacted with allyl halides at ambient temperatures to afford allylbenzene as a major coupling product together with biphenyl as a minor product (Scheme 6a). Iodooctane was less reactive with 5c at room





temperature and underwent a coupling reaction with diphenyl complex **5c** in *o*-dichlorobenzene at 80 $^{\circ}$ C to yield 41% of *n*-octylbenzene and 21% of biphenyl as coupling products (Scheme 6b).

Effect of External Halide Anions on the Reaction Rate. To investigate the influence of the halide anions on the reaction rate, we next carried out the reaction of complex 5b and MeI with the addition of tetrabutylammonium halides as external halide sources (Scheme 7). In comparison with the reaction without additive (condition A), the consumption rate of the intermediates was apparently decreased by the addition of 5.0 equiv of Bu_4NI (condition B). The addition of Bu_4NBr (condition C) and Bu_4NCl (condition D) suppressed the reductive elimination step more significantly in comparison to





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condition B (Figure 5a). The first-order reaction rates estimated from the slopes of linear lines in the logarithmic



Figure 5. Time-dependent percentage amounts of the platinum(IV) intermediate in the presence of Bu_4NX : (a) normal plot; (b) natural logarithm plot and linear approximation. Additive condition: (A) without additive; (B) with Bu_4NI ; (C) with Bu_4NBr ; (D) with Bu_4NCl .

plot are in the order A > B > C > D (Figure 5b), which means that a higher concentration of iodide in the reaction media decreases the reaction rate slightly and that a harder halide anion decreases the rate more significantly than a softer halide. These results suggest that pentacoordinate complex 7•X is the key intermediate leading to complex 8 via reductive elimination (*vide infra*).

Computational Studies of Zwitterionic Platinum Complexes. Density functional theory (DFT) calculations support the charge-separated structure of these complexes visualized with the electrostatic potential diagram and frontier orbitals (Figure 6; see the Supporting Information for details). Zwitterionic complex **Sb** has a charge-separated structure in which the negative charge is localized on the platinum atom and the positive charge is delocalized on the phosphoindolium moiety. Moreover, the highest occupied molecular orbital (HOMO) is mainly composed of the Sd_z^2 orbital of the platinum atom, while the lowest unoccupied molecular orbital (LUMO) is delocalized on the phosphoindolium moiety.



Figure 6. Electrostatic potential and molecular orbitals of zwitterionic platinum complex **5b**: (a) electrostatic potential; (b) HOMO; (c) LUMO. Isovalue for MO: 0.030.

Therefore, it is suggested that the highly nucleophilic nature of the dialkylplatinum(II) center promotes the rapid oxidative addition of electrophiles.

The preference of zwitterionic complexes in the oxidative addition has also been elucidated using DFT calculation studies assessing the $5d_{z^2}$ orbital (Table 2). Molecular orbitals

Table 2. Parameters of Calculated Structures of Complexes Sb-d and $PtMe_2(dppe)$ for an Indication of Nucleophilicity at the Platinum Center

| R | МО | $5d_{z^2}$ | energy (eV) |
|-------|------------------------|----------------------------------------|--------------------------------------------------------|
| Me | номо | 0.597 | -4.64 |
| Ph | HOMO-2 | 0.547 | -4.97 |
| MeC≡C | HOMO-4 | 0.72 | -5.36 |
| | НОМО | 0.183 | -5.28 |
| | HOMO-3 | 0.468 | -6.02 |
| | R Me Ph MeC≡C | RMOMeHOMOPhHOMO-2MeC≡CHOMO-4HOMOHOMO-3 | $\begin{array}{c c c c c c c c c c c c c c c c c c c $ |

of 5c,e and PtMe₂(dppe) are shown for reference (Figure 7). The energy levels of the $5d_{z^2}$ orbital of zwitterionic complexes **5b** (R = Me), **5c** (R = Ph), and **5e** ($R = MeC \equiv C-$) instead of 5d are -4.64, -4.97, and -5.36 eV, respectively, which are higher than that of the typical platinum(II) complex $PtMe_2(dppe)$ (-6.02 eV). These energy levels are closely correlated with the first oxidation potentials measured using cyclic voltammetry (0.47 V for 5b, 0.82 V for 5c, 0.94 V for 5d), which obviously reflects the higher nucleophilicity of zwitterionic complexes 5b-d (Figure S9). The energy levels of the $5d_{z^2}$ orbital are also negatively correlated with the s character of the alkyl, aryl, and alkynyl ligands. The negatively charged platinum center having the κ^2 -C,P-chelating ligand is considered to raise the occupied $5d_{z^2}$ orbital level so that its effective interaction with the LUMO of the alkyl halide C-X σ^* orbital promotes the S_N2-type oxidative addition.

Measurement of UV–Vis Absorption Spectra. An increase in the occupied molecular orbitals involving $5d_{z^2}$ was also observed in the UV–vis spectra of a series of zwitterionic platinum complexes. In all zwitterionic complexes, wide absorption peaks or shoulders were observed in the visible region (380–530 nm) (Figure 8a). TD-DFT calculations for the optimized structure of dimethylplatinum

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Figure 7. Molecular orbitals of a series of platinum complexes: (a) HOMO of $PtMe_2(dppe)$; (b) HOMO-3 of $PtMe_2(dppe)$: (c) HOMO-2 of complex 5c; (d) HOMO-4 of complex 5e. Isovalue for MO: 0.030.

complex **5b** demonstrated two weak sets of oscillator strengths in the visible region, which is in good accordance with the actual absorption spectrum (Figure 8b). Major transitions are attributed to the charge transfer from the platinum-centered occupied orbitals (HOMO to HOMO-2) to the LUMO spreading around the phosphoindolium moiety of the ligand (MLCT), which reflects the upward trend of the occupied orbitals in zwitterionic complexes so that the HOMO–LUMO gap becomes narrow to lower the energy for the MLCT transition.

Mechanistic Considerations. A proposed mechanism for the present oxidative addition and reductive elimination system using zwitterionic platinum complexes on the basis of the experimental and theoretical studies described above is summarized in Scheme 8. First, the reversible oxidative addition of organic halides to dialkylplatinum(II) zwitterionic complex 5 gives the pentacoordinate platinum(IV) species 7·X, which is in fast equilibrium with hexacoordinate platinum(IV) species 6. The pentacoordinate intermediate 7·X is susceptible to reductive elimination to afford the coupling product R^1-R^2 and monoalkyl complex 8.

The present system is typical of sequential reactions, and its rate laws were derived using suitable approximations depending on the R¹ substituents (eqs 1 and 2; full derivation is given in the Supporting Information). In the case of $R^1 = Me (eq 1)$, the decrease in the platinum(IV) species in an equilibrium between 6 and 7·X ([int] = [6] + [7]) obeys first-order kinetics because the oxidative addition is much faster than reductive elimination. The observed rate constant, k_{obs} , is proportional to the rate constant for reductive elimination (k_3) and is also dependent on both the concentration of halide $[X^-]$ and the association equilibrium constant (K_{eq}) . This equation clearly explains the experimental results concerning the halide source and its concentration as described above (Scheme 7 and Figure 5). On the one hand, a low concentration of halide (decrease in $[X^-]$) and soft halide anions (decrease of K_{eq}) increase the observed rate constant (k_{obs}) , in which the



Figure 8. (a) UV–vis spectra of complexes 5, dissolved in MeCN (5.0 \times 10⁻⁴ M). (b) Comparison of the observed absorption spectrum and the calculated values of oscillator length in complex 5b. Oscillator lengths for the excitation of complex 5b are estimated with TD-DFT calculations by using the optimized structure of complex 5b.





equilibrium is forced to favor pentacoordinate complex 7b·X, which readily undergoes reductive elimination. On the other hand, the steady-state approximation can be applied to the case of \mathbb{R}^1 = Ph, alkynyl (eq 2), in which the observed rate constant (k_{obs}) is correlated to the rate constants of oxidative addition

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 (k_1) , inverse oxidative addition (k_{-1}) , and reductive elimination (k_3) .

$$R^{1} = Me: \frac{d[\mathbf{8}]}{dt} = -\frac{d[int]}{dt} = k_{obs}[int]$$
$$k_{obs} = \frac{k_{3}}{1 + K_{eq}[X^{-}]}$$
(1)

$$R^{l} = Ph, alkynyl: \frac{d[8]}{dt} = -\frac{d[5]}{dt} = k_{obs}[5][R^{2}-X]$$

$$k_{obs} = \frac{k_{1}k_{3}}{k_{-1} + k_{3}}$$
(2)

As mentioned above, the sequential reaction of zwitterionic complex 5b with methyl iodide is remarkably faster than those of other dimethylplatinum(II) complexes such as PtMe2(dppe).¹⁸ On the basis of previous studies on the reactivity of PtMe₂(dppe), the hexacoordinate platinum(IV) complex PtMe₃I(dppe) is far less reactive toward reductive elimination due to the fast association rate of halide anion (k_2) $\gg k_{-2}$) in comparison with zwitterionic platinum(IV) intermediates 6 and 7.X. Therefore, it forms a mixture of both ethane and MeI because of the competitive reverse oxidative addition with reductive elimination $(k_{-1} \approx k_3)$.¹⁸ In the present zwitterionic system, the negative charge on the platinum center would enhance the nucleophilicity of the platinum center to alkyl halides and accelerate the dissociation of iodide anion by charge rebalancing to produce the coupling product R¹-R².

CONCLUSION

In conclusion, we have found the formation of zwitterionic platinum complexes from an alkyne-containing bisphosphine ligand and demonstrated the stoichiometric reactivities in fundamental organometallic reactions. On the basis of kinetic studies, X-ray crystallographic analyses, and DFT calculation studies, the advantages of the zwitterionic platinum complexes are ascribed to the acceleration of oxidative addition by the higher level of the Pt $5d_{z^2}$ orbital and the highly dissociative lability of the halide anion in the platinum(IV) intermediate, leading to the selective C–C bond-forming reductive elimination. Further studies aiming at more general and novel catalytic reactions of the present and modified zwitterionic platinum complexes are ongoing.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00759.

Details on experimental procedures for the catalytic reactions, spectroscopic data for the products, and crystallographic data (PDF)

Cartesian coordinates from DFT calculation results (XYZ)

Accession Codes

CCDC 2047309–2047314 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

- Kazuhiro Okamoto Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan; orcid.org/ 0000-0001-8562-3167; Email: kokamoto@scl.kyotou.ac.jp
- Kouichi Ohe Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan; orcid.org/0000-0001-8893-8893; Email: ohe@scl.kyoto-u.ac.jp

Authors

- Kohei Sasakura Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan
- Satoshi Funasaka Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan
- Hiiro Watanabe Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan
- Masahiro Suezaki Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.organomet.0c00759

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) For reviews on platinum-catalyzed organometallic reactions, see: (a) Zhang, L.; Sun, J.; Kozmin, S. A. Gold and Platinum Catalysis of Enyne Cycloisomerization. *Adv. Synth. Catal.* **2006**, 348, 2271. (b) Fürstner, A.; Davies, P. A. Catalytic Carbophilic Activation: Catalysis by Platinum and Gold π Acids. *Angew. Chem., Int. Ed.* **2007**, 46, 3410.

(2) For relativistic effects of platinum, see: Bond, G. C. Relativistic Phenomena in the Chemistry of the Platinum Group Metals. *Platinum Metals Rev.* **2000**, *44*, 146.

(3) Silylation: (a) Berthon-Gelloz, G.; Schumers, J.-M.; De Bo, G.; Marko, I. E. Highly β -(*E*)-Selective Hydrosilylation of Terminal and Internal Alkynes Catalyzed by a (IPr)Pt(diene) Complex. *J. Org. Chem.* **2008**, 73, 4190. (b) Tsukada, N.; Hartwig, J. F. Intermolecular and Intramolecular, Platinum-Catalyzed, Acceptorless Dehydrogenative Coupling of Hydrosilanes with Aryl and Aliphatic Methyl C-H Bonds. *J. Am. Chem. Soc.* **2005**, 127, 5022. (c) Parker, S. E.; Borgel, J.; Ritter, T. 1,2-Selective Hydrosilylation of Conjugated Dienes. *J. Am. Chem. Soc.* **2014**, 136, 4857. (4) Borylation: (a) Ishiyama, T.; Matsuda, N.; Miyaura, N.; Suzuki, A. Platinum(0)-catalyzed diboration of alkynes. J. Am. Chem. Soc. **1993**, 115, 11018. (b) Yamamoto, Y.; Fujikawa, R.; Yamada, A.; Miyaura, N. A Regio- and Stereoselective Platinum(0)-Catalyzed Hydroboration of Allenes Controlled by Phosphine Ligands. Chem. Lett. **1999**, 28, 1069. (c) Furukawa, T.; Tobisu, M.; Chatani, N. C–H Functionalization at Sterically Congested Positions by the Platinum-Catalyzed Borylation of Arenes. J. Am. Chem. Soc. **2015**, 137, 12211.

(5) (a) Bender, C. F.; Widenhoefer, R. A. Platinum-Catalyzed Intramolecular Hydroamination of Unactivated Olefins with Secondary Alkylamines. J. Am. Chem. Soc. 2005, 127, 1070. (b) Karshtedt, D.; Bell, A. T.; Tilley, T. D. Platinum-Based Catalysts for the Hydroamination of Olefins with Sulfonamides and Weakly Basic Anilines. J. Am. Chem. Soc. 2005, 127, 12640. (c) McBee, J. L.; Bell, A. T.; Tilley, T. D. Mechanistic Studies of the Hydroamination of Norbornene with Electrophilic Platinum Complexes: The Role of Proton Transfer. J. Am. Chem. Soc. 2008, 130, 16562.

(6) π -Acidic platinum catalysis: (a) Nakanishi, Y.; Miki, K.; Ohe, K. Transition metal-catalyzed pentannulation of propargyl acetates via styrylcarbene intermediates. *Tetrahedron* **2007**, *63*, 12138. (b) Saito, K.; Sogou, H.; Suga, T.; Kusama, H.; Iwasawa, N. Platinum(II)-Catalyzed Generation and [3 + 2] Cycloaddition Reaction of α,β -Unsaturated Carbene Complex Intermediates for the Preparation of Polycyclic Compounds. *J. Am. Chem. Soc.* **2011**, *133*, 689.

(7) Crespo, M.; Martinez, M.; Sales, J. Effect of fluorine substituents in intramolecular activation of carbon-fluorine and carbon-hydrogen bonds by platinum(II). *Organometallics* **1993**, *12*, 4297.

(8) (a) Bedford, R. B.; Hazelwood, S. L.; et al. Platinum Catalysts for Suzuki Biaryl Coupling Reactions. Organometallics 2002, 21, 2599. (b) Oh, C. H.; Lim, Y. M.; You, C. H. Platinum-catalyzed crosscouplings of organoboronic acids with aryl iodides. Tetrahedron Lett. 2002, 43, 4645. (c) Lillo, V.; Mata, J. A.; Segarra, A. M.; Peris, E.; Fernandez, E. The active role of NHC ligands in platinum-mediated tandem hydroboration-cross coupling reactions. Chem. Commun. 2007, 2184. (d) Wang, T.; Love, J. A. Insight into the Mechanism of Platinum-Catalyzed Cross-Coupling of Polyfluoroaryl Imines. Organometallics 2008, 27, 3290. (e) Wang, T.; Keyes, L.; Patrick, B. O.; Love, I. A. Exploration of the Mechanism of Platinum(II)-Catalyzed C-F Activation: Characterization and Reactivity of Platinum(IV) Fluoroaryl Complexes Relevant to Catalysis. Organometallics 2012, 31, 1397. (f) Wagner, A. M.; Hickman, A. J.; Sanford, M. S. Platinum-Catalyzed C-H Arylation of Simple Arenes. J. Am. Chem. Soc. 2013, 135, 15710.

(9) Johansson Seechurn, C. C. C.; Kitching, M. O.; Colacot, T. J.; Snieckus, V. Palladium-Catalyzed Cross-Coupling: A Historical Contextual Perspective to the 2010 Nobel Prize. *Angew. Chem., Int. Ed.* **2012**, *51*, 5062.

(10) (a) Okamoto, K.; Omoto, Y.; Sano, H.; Ohe, K. Alkynecoordinating tridentate ligands: structural properties and reactivity of their rhodium complexes. Dalton Trans. 2012, 41, 10926. (b) Sasakura, K.; Okamoto, K.; Ohe, K. Incorporation of Monatomic Cations onto an Ir-Ir Bond in a Dimeric Iridium(II) Complex Having a 1,3-Diene-1,4-diyl Backbone. Organometallics 2018, 37, 2319-2324. (c) Sasakura, K.; Okamoto, K.; Sakaki, S.; Ohe, K. The Reaction Pathway Leading to Dinuclear Rhodium and Iridium Complexes from Alkyne-Containing Bisphosphine Ligands. Bull. Chem. Soc. Jpn. 2020, 93, 794-798. (d) Sasakura, K.; Okamoto, K.; Ohe, K. Bimetallic Reactivities of Dinuclear Iridium and Rhodium Complexes Generated from Two Types of Alkyne-Containing Bisphosphine Ligands. Eur. J. Inorg. Chem. 2020, 2020, 1894-1901. (e) Federmann, P.; Richter, T.; Waderpohl, H.; Ballmann, J. Synthesis and Reactivity of [PCCP]-Coordinated Group 5 Alkyl and Alkylidene Complexes Featuring a Metallacyclopropene Backbone. Organometallics 2019, 38, 4307-4318.

(11) For reviews on η^2 -alkyne complexes, see: (a) Belluco, U.; Bertani, R.; Michelin, R. A.; Mozzon, M. Platinum—alkynyl and alkyne complexes: old systems with new chemical and physical perspectives. J. Organomet. Chem. **2000**, 600, 37. (b) Organometallic Chemistry of the Transition Metals; Crabtree, R. H., Ed.; WileyInterscience: Hoboken, NJ, 2005; pp 183–198. (c) Organometallics; Eisenbroich, C., Ed.; Wiley-VCH: Weinheim, Germany, 2006; pp 425–435. (d) Organotransition Metal Chemistry: From Bonding to Catalysis; Hartwig, J. F., Ed.; University Science Books: 2010; pp 47–57. (e) Verhoeven, D. G. A.; Moret, M.-E. Metal–ligand cooperation at tethered π -ligands. Dalton Trans. 2016, 45, 15762.

(12) For selected examples for nucleophilic transformation of alkenes or dienes using ate-type transition-metal complexes as catalysts, see: (a) Terao, J.; Watanabe, H.; Ikumi, A.; Kuniyasu, H.; Kambe, N. Nickel-Catalyzed Cross-Coupling Reaction of Grignard Reagents with Alkyl Halides and Tosylates: Remarkable Effect of 1,3-Butadienes. J. Am. Chem. Soc. 2002, 124, 4222. (b) Iwasaki, T.; Takagawa, H.; Singh, S. P.; Kuniyasu, H.; Kambe, N. Co-Catalyzed Cross-Coupling of Alkyl Halides with Tertiary Alkyl Grignard Reagents Using a 1,3-Butadiene Additive. J. Am. Chem. Soc. 2013, 135, 9604. (c) Iwasaki, T.; Miyata, Y.; Akimoto, R.; Fujii, Y.; Kuniyasu, H.; Kambe, N. Diarylrhodates as Promising Active Catalysts for the Arylation of Vinyl Ethers with Grignard Reagents. J. Am. Chem. Soc. 2014, 136, 9260.

(13) Many zwitterionic complexes bearing an anionic metal center based on ylide ligands have been reported. See: (a) Schmidbauer, H. Phosphorus Ylides in the Coordination Sphere of Transition Metals: An Inventory. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 907. (b) Chauvin, R. Zwitterionic Organometallates. *Eur. J. Inorg. Chem.* **2000**, *2000*, 577. However, the catalytic behavior of zwitterionic complexes bearing a negative charge on the metal center has hardly been studied to date.

(14) The catalytic behavior of zwitterionic complexes bearing a positive charge on the metal center has been studied. See: (a) Thomas, C. J.; Peters, J. C. Benzene C-H Activation at a Charge Neutral Zwitterionic Platinum(II) Complex. J. Am. Chem. Soc. 2001, 123, 5100. (b) Stradiotto, M.; Hesp, K. H.; Lundgren, R. J. Zwitterionic Relatives of Cationic Platinum Group Metal Complexes: Applications in Stoichiometric and Catalytic σ -Bond Activation. Angew. Chem., Int. Ed. 2010, 49, 494.

(15) Complexes 5 may be formed through the following pathways: (1) dissociation of the one phosphine moiety forming a phosphinealkyne bidentate complex and (2) nucleophilic attack of the liberated phosphine moiety to the acetylenic carbon activated by a π -acidic platinum center. Similar cyclization reactions affording phosphoindoliums or their derivatives have been reported. See: Fukazawa, A.; Yamada, H.; Yamaguchi, S. Phosphonium- and Borate-Bridged Zwitterionic Ladder Stilbene and Its Extended Analogues. Angew. Chem., Int. Ed. 2008, 47, 5582-5585. (b) Fukazawa, A.; Yamaguchi, E.; Ito, E.; Yamada, H.; Wang, J.; Irle, S.; Yamaguchi, S. Zwitterionic Ladder Stilbenes with Phosphonium and Borate Bridges: Intramolecular Cascade Cyclization and Structure-Photophysical Properties Relationship. Organometallics 2011, 30, 3870-3879. (c) Ge, Q.; Zong, J.; Li, B.; Wang, B. Copper-Mediated Annulation of Phosphorus-Containing Arenes with Alkynes: An Approach to Phosphindolium Salts. Org. Lett. 2017, 19, 6670-6673. (d) Arndt, S.; Hansmann, M. M.; Motloch, P.; Rudolph, M.; Rominger, F.; Hashmi, A. S. K. Intramolecular anti-Phosphinoauration of Alkynes:An FLP-Motivated Approach to Stable Aurated PhosphindoliumComplexes. Chem. - Eur. J. 2017, 23, 2542. (e) Arndt, S.; Hansmann, M. M.; Rominger, F.; Rudolph, M.; Hashmi, A. S. K. Direct Access to p-Extended Phosphindolium Salts by Simple Proton-Induced Cyclization of (o-Alkynylphenyl)phosphanes. Chem. - Eur. J. 2017, 23, 5429-5433. (f) Wang, Q.; Tinnermann, H.; Tan, S.; Young, R. D. Late-Stage Generation of Bidentate .³ Benzophosphorine-Phosphino Ligands from a Rhodium PC_{carbene}P Pincer Complex and Their Use in the Catalytic Hydrosilylation of Alkynes. Organometallics 2019, 38, 3512-3520.



(16) Due to the C3–C4 double-bond character of the indicated structure of complex 5, its resonance form (charge-neutralized biscarbene complex) contributes rather less to the real electronic structure.



(17) At lower temperature (0 °C), intermediates **6c** and **7c** were observed as only very minor species. ¹H NMR (400 MHz, CDCl₃, 0 °C): δ 1.70 ppm (d, $J_{\text{Pt-H}}$ = 66.3 Hz, $J_{\text{P-H}}$ = 7.3 Hz).

(18) The consumption of 5d was completed by heating the reaction mixture at 50 °C for an additional 12 h.

(19) The reductive elimination requires a higher temperature and the use of a polar solvent. Both C-C and C-I bond-forming reductive eliminations occur to give a mixture of ethane and MeI as shown in the scheme below. See: (a) Goldberg, K. I.; Yan, J.; Winter, E. L. J. Competitive Carbon-Carbon Reductive Elimination and Carbon-Iodide Bond Formation from a Pt(IV) Complex. J. Am. Chem. Soc. 1994, 116, 1573. (b) Goldberg, K. I.; Yan, J.; Breitung, E. M. Energetics and Mechanisms of Carbon-Carbon and Carbon-Iodide Reductive Elimination from a Pt(IV) Center. J. Am. Chem. Soc. 1995, 117, 6889. (c) Williams, B. S.; Holland, A. W.; Goldberg, K. I. Direct Observation of C-O Reductive Elimination from Pt(IV). J. Am. Chem. Soc. 1999, 121, 252. (d) Williams, B. S.; Goldberg, K. I. Studies of Reductive Elimination Reactions To Form Carbon-Oxygen Bonds from Pt(IV) Complexes. J. Am. Chem. Soc. 2001, 123, 2576.



(20) (a) Kaphan, D. M.; Levin, M. D.; Bergman, R. G.; Raymond, K. N.; Toste, F. D. A supramolecular microenvironment strategy for transition metal catalysis. *Science* 2015, 350, 1235–1238. (b) Levin, M. D.; Kaphan, D. M.; Hong, C. M.; Bergman, R. G.; Raymond, K. N.; Toste, F. D. Scope and Mechanism of Cooperativity at the Intersection of Organometallic and Supramolecular Catalysis. *J. Am. Chem. Soc.* 2016, 138, 9682–9693.