ORGANOMETALLICS
Article
pubs.acs.org/Organometallics

Carbon(0)-Bridged Pt/Ag Dinuclear and Tetranuclear Complexes Based on a Cyclometalated Pincer Carbodiphosphorane Platform

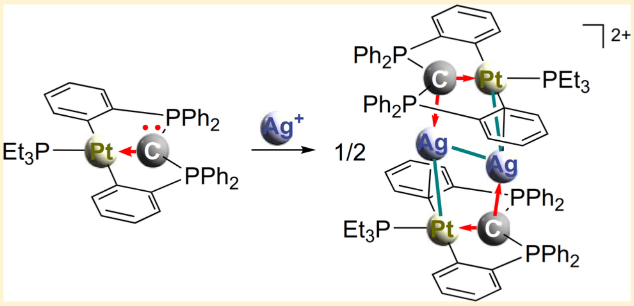
Kazuyuki Kubo,*[†] Hiroyuki Okitsu,[†] Hiroto Miwa,[†] Shoko Kume,[†] Ronald G. Cavell,[‡] and Tsutomu Mizuta*[†]

[†]Department of Chemistry, Graduate School of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8526, Japan

[‡]Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Supporting Information

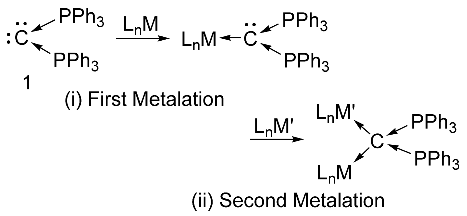
ABSTRACT: A carbon(0)-bridged Pt_2Ag_2 cluster was synthesized from the reaction of a cyclometalated pincer carbodiphosphorane platinum complex with AgOTf, by forming Pt(II)←C(0)→Ag(I) dative bonds along with Pt(II)−Ag(I) and Ag(I)−Ag(I) metal−metal interactions. X-ray diffraction analysis reveals that the cluster adopts an antiparallel sandwich structure with a ladder-shaped PtC/AgAg/CPt core. The coordination plane of the platinum unit is highly distorted due to the in-plane steric repulsion between the PEt_3 ligand on the platinum and the nearest proton on each of the two cyclometalated phenyl rings in the pincer carbodiphosphorane framework. The cluster is very labile and displays different reactivity patterns toward trivalent phosphorus ligands. In the reaction with bulky PPh_3, a dinuclear complex was formed because of coordination of PPh_3 to the silver atom upon cleavage of the tetranuclear core. In contrast, replacement of the PEt_3 on the platinum center by $P(OPh)_3$, which is sterically less demanding, led to a dinuclear complex where the eliminated PEt_3 ligand recoordinated to the silver atom.



INTRODUCTION

Recently, the investigation of carbodiphosphorane (CDP) chemistry has seen a resurgence as the concept of "coordination compounds of carbon(0)" has become widely accepted.[1] Although the first synthesis of CDP, specifically hexaphenylcarbodiphosphorane (**1**; Scheme 1), dates back to 1961[2] and its distinctly bent structure was established by X-ray diffraction analyses some years later,[3] until recently, the general formula L→C(0)←L, where L is a two-electron donor, has infrequently been used to represent the bonding situation in these molecules. Current experimental and theoretical studies have substantiated the donor−acceptor character of the P−C bond and have shown that the central carbon atom preserves its valence electrons as two carbon-centered lone pairs, thereby acting as an excellent donor toward a variety of Lewis acids.[1] Recently, there has been growing interest in extending the utility of this unusual entry of carbon compounds with respect to developing novel catalysts[4−6] and small-molecule transformations.[7,8]

Scheme 1. Metalation of Hexaphenylcarbodiphosphorane



Typically, CDPs coordinate to transition metals as terminal ligands[5,9−33] to afford mononuclear complexes (Scheme 1i); however, the availability of the second lone pair allows them to serve as bridging ligands to form a variety of geminal dinuclear complexes (Scheme 1ii).[10,21,24,34−39] This binucleate property of the CDPs constitutes a noticeable difference from carbenes, in which the central carbon(II) atom possesses only one lone pair. Even so, CDPs are strongly reminiscent of bis(iminophosphorano)methandiide and related dianionic carbon ligands, which produce a number of terminal and bridging alkylidene complexes of various metals.[40] The second metalation of the carbon(0) atom modifies the steric and electronic properties of the ligand framework and may result in enhanced reactivity of the first metal center. Recently, Meek and coworkers have reported the hydroarylation of dienes using a rhodium catalyst containing a carbodicarbene ligand: i.e., a biscarbene complex of carbon(0).[41] The catalytic activity was significantly enhanced by Lewis acidic additives such as CuCl, AgCl, AuCl, and lithium salts. This performance enhancement was rationalized regarding the reversible coordination of the Lewis acid to the second lone pair on the carbon(0) atom so

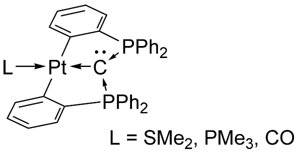
Received: September 3, 2016

DOI: 10.1021/acs.organomet.6b00700

that the electron density on the rhodium center is modulated, enabling facile molecular transformations. Furthermore, multinuclear systems can potentially exhibit fascinating physical and chemical properties or reactivities fundamentally different from those of the corresponding mononuclear units. To explain this distinctive multinuclear behavior, direct interaction between the metals in proximity is often the key.[42] To date, only a limited number of well-defined CDP dinuclear complexes that involve apparent direct metal−metal interactions have been reported, where examples include triangular Au(I)−C(0)−Cu(I),[10] Au(I)−C(0)−Au(I),[10,21] Pd(II)−C(0)−Au(I),[35] and Pd(II)−C(0)−Pd(II)[34] cores.[43]

As illustrated in Chart 1, we[16,19,40h] (L = SMe_2, PMe_3) and others[13] (L = CO) have reported the syntheses and characterization of platinum(II) complexes bearing a dianionic CCC pincer CDP ligand in which one of three phenyl groups attached to each of the two CDP phosphorus atoms is cyclometalated. Given the broad practical and fundamental interest in this molecular architecture, we envisioned that the cyclometalated pincer CDP-platinum platforms might be efficient precursors for promising carbon(0)-containing cluster systems. To date, cyclometalated platinum complexes have received widespread attention because they exhibit remarkable photophysical, photochemical, and biological properties, which may have applications in light-emitting materials,[44] photocatalysts,[45] bioimaging probes,[46] and anticancer drugs.[45,47] In particular, the pincer scaffold is now well recognized as an extremely versatile ligand motif for developing catalysts and materials.[48−51] Furthermore, electron-rich cyclometalated platinum(II) units are frequently employed as valuable building blocks for multinuclear complexes. The d^8 metals in a square-planar geometry can be regarded as pseudo-closed-shell systems, and weak *metallophilic interactions*[52] have been invoked in many multinuclear complexes containing various d^8, d^{10}, or $d^{10}s^2$ (pseudo-) closed-shell systems.[53,54] In addition, the platinum complexes can behave as donors toward a second metal center, forming a Pt→M dative bond[55−57] through the occupied d_{z^2} orbital on the platinum atom.[58,59] The electron-donating ability of the platinum increases with increasing ligand field strength afforded by the ancillary ligands around the platinum center due to the enhancement of antibonding character of the d_{z^2} orbital. Consequently, the cyclometalated system, which contains a strong M−C covalent bond, has proved to be one of the most effective ligand motifs to encourage the formation of Pt→M dative bonds.[56]

Chart 1. CCC Pincer CDP-Platinum Complexes

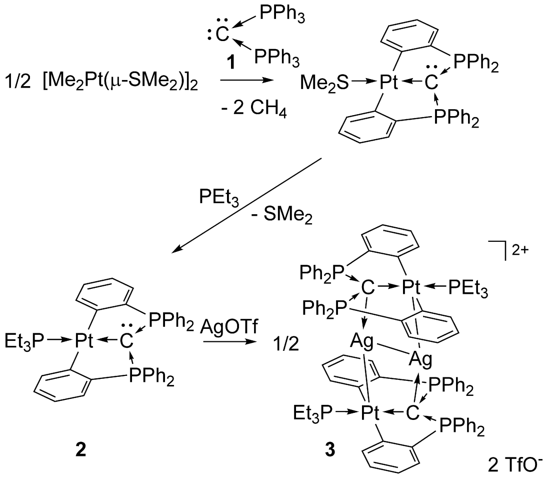


Here we report the synthesis and characterization of a novel heterotetranuclear cluster complex having a sandwich structure based on the pincer CDP−platinum platform. The resulting $Pt^{II}_2Ag^{I}_2$ tetranuclear core is highly labile and is readily converted to two dinuclear components bearing a Pt(II)−C(0)−Ag(I) triangular core after reaction with phosphines. The present work provides further indications of the structural diversity underlying the complexation behavior of the pincer CDP complex with Lewis acids, serving as a foundation for future development of new multinuclear compounds that might exhibit interesting physical properties and catalytic and stoichiometric reactivities.

■ RESULTS AND DISCUSSION

Synthesis and Characterization of Tetranuclear Cluster 3. The pincer-CDP framework can be readily constructed from the successive double-cyclometalation reaction of **1** with 0.5 equiv of $[Me_2Pt(\mu\text{-}SMe_2)]_2$ with the concomitant release of 2 equiv of methane (Scheme 2).[19] $Pt\{C[PPh_2(\textit{o}\text{-}C_6H_4)]_2\text{-}\kappa^3\textit{C,C,C}\}(SMe_2)$ was then reacted with PEt_3 to yield **2** almost quantitatively. The $^{13}C\{^1H\}$ NMR spectrum of **2** gives rise to six characteristic resonances for the cyclometalated aromatic carbons over a 50 ppm range of chemical shifts. The $^{31}P\{^1H\}$ NMR spectrum shows a triplet at 14.6 ppm and a doublet at 28.5 ppm, assignable to mutually coupled PEt_3 and CDP phosphorus, respectively. The signal for PEt_3 is flanked by a large $^{195}Pt{-}^{31}P$ coupling satellite with J_{PtP} = 3174 Hz, confirming the formation of a direct Pt−P bond, whereas that for CDP displays a much smaller ^{195}Pt satellite with J_{PtP} = 147 Hz. The ^1H NMR spectrum is also consistent with the structure for **2**, which we confirmed by X-ray crystallography (vide infra).

Scheme 2. Synthesis of Tetranuclear Cluster 3



The reaction of **2** with an equimolar amount of AgOTf in CH_2Cl_2 at ambient temperature resulted in a rapid color change from yellow to red. After recrystallization, product **3** was isolated as a yellow powder in high yield. In solution, **3** decomposed slowly in the light, forming a black precipitate, suggesting that **3** is light sensitive. The NMR spectra of **3** show somewhat broadened peaks, probably due to the instability of the compound and/or dynamic processes that occur on the NMR time scale; this broadening precluded the satisfactory characterization of the product in solution. VT NMR experiments of **3** in CD_2Cl_2 over the temperature range −70 to +30 °C did not show any remarkable change in the shape of the broad signals, and we could not obtain any meaningful information on the dynamic behavior of **3**. The $^{31}P\{^1H\}$ NMR resonance due to the CDP ligand shifted downfield ($\Delta\delta$ = 4.9 ppm), whereas that assignable to PEt_3 slightly shifted upfield ($\Delta\delta$ = 1.3 ppm), in comparison to the corresponding signals of **2**. Each signal is flanked by a ^{195}Pt satellite with J_{PtP} = 71 Hz for CDP and 3027 Hz for PEt_3, which are both smaller than those observed for **2**. More importantly, the $^{13}C\{^1H\}$ NMR spectrum

DOI: 10.1021/acs.organomet.6b00700

contains several aromatic carbon signals, the observed pattern of which is consistent with the presence of two inequivalent phenyl groups on the CDP phosphorus in addition to the cyclometalated phenyl groups. Since the two cyclometalated $P(Ph)_2C_6H_4$ fragments are equivalent, as indicated by the single CDP signal in the $^{31}P\{^1H\}$ NMR spectrum, the observation of two different environments of the phenyl groups strongly suggests that the silver ion interacts with the platinum complex from one side of the coordination plane, making the phenyl groups above and below the plane inequivalent. However, couplings from ^{107}Ag and ^{109}Ag nuclei were not visible in the NMR spectra because of the line broadening.

The structure of the product was confirmed by single-crystal X-ray diffraction. Precursor **2** was also structurally characterized to allow for comparison with **3**. Molecular diagrams of **2** and **3** are shown in Figures 1 and 2, respectively. Selected bond distances and angles are summarized in Table 1, and full details are provided in the Supporting Information.

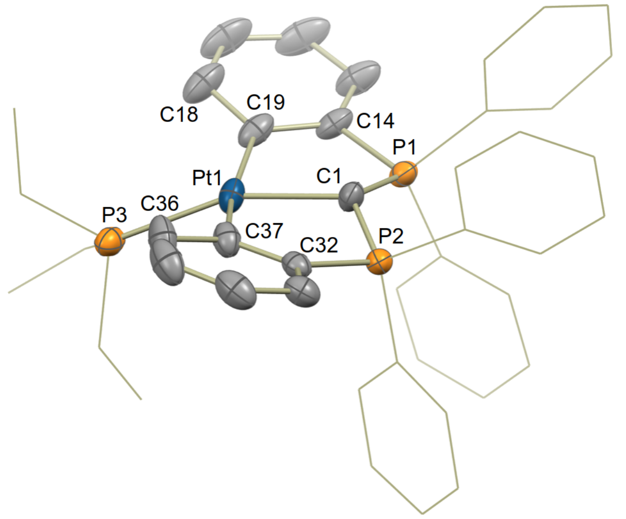


Figure 1. Molecular diagram (50% probability ellipsoids) of **2** showing the crystallographic labeling scheme. All hydrogen atoms and minor disordered components of PEt_3 have been omitted for clarity.

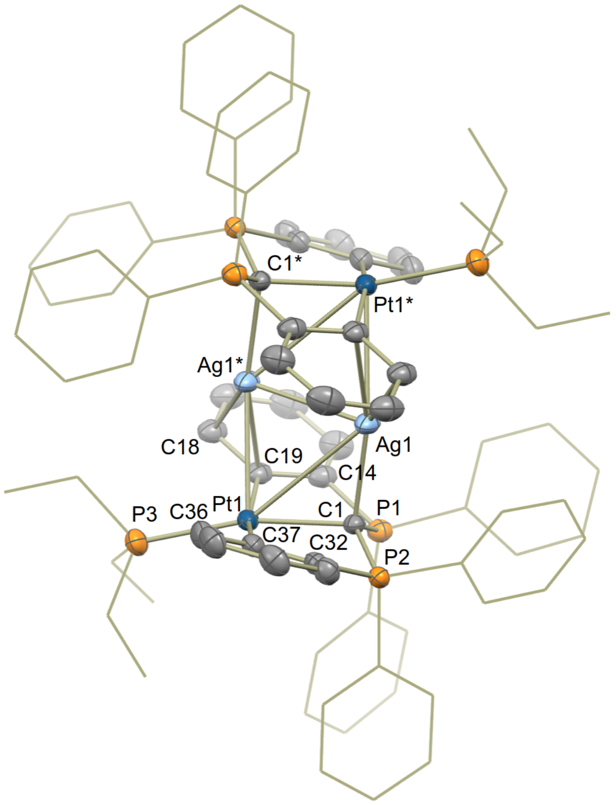


Figure 2. Molecular diagram (50% probability ellipsoids) of **3** showing the crystallographic labeling scheme. Atoms labeled with an asterisk are generated by a crystallographic inversion center. All hydrogen atoms, triflate anions, solvent, and minor disordered components of PEt_3 have been omitted for clarity.

In complex **2**, a highly distorted square planar coordination geometry around the platinum(II) is observed, the doubly cyclometalated CDP ligand adopts a pincer structure, and a PEt_3 ligand is trans to the carbon(0) atom in the CDP. Atom P3 in PEt_3 is located significantly out of the plane defined by the platinum and three carbon atoms of the pincer CDP ligand (C1, C19, and C37), although the location of the PEt_3 ligand is somewhat ambiguous because of disorder associated with the different Et group orientations; the C1−Pt1−P3(P3A) bond is significantly bent with an angle of 159−169°. In addition, the cyclometalated phenyl rings are tilted away from the coordination plane around the metal with torsion angles of 160−162° (C1−Pt1−C37−C36 and C1−Pt1−C19−C18). The pincer framework is significantly warped, with the otherwise planar carbon(0) center being pyramidalized, as demonstrated by the sum of the angles around C1 of 351.16°. Such a distortion cannot be observed for the analogous pincer CDP−platinum complex having CO instead of PEt_3; both the platinum and CDP carbon atoms are almost planar.[13] Preliminary DFT calculations (mPW1PW91, SDD for Pt, 6-31+G(d) for C(0), and 6-31G(d) for all other atoms) on model compounds suggest that this large distortion from square-planar geometry is caused by the strong in-plane steric repulsion between the PEt_3 ligand and the protons on C18 and C36 in the cyclometalated phenyl rings cis to the phosphine (Supporting Information). The optimized geometry of $Pt\{C[PMe_2(o\text{-}C_6H_4)]_2\text{-}\kappa^3C,C,C\}(PEt_3)$ is in good agreement with the observed solid-state structure of **2**, whereas that of $Pt\{C[PMe_2(C_2H_2)]_2\text{-}\kappa^3C,C,C\}(PEt_3)$, having a sterically less demanding pincer framework, is planar at both the platinum and carbon(0) atoms. Since the natural charges on the platinum and carbon(0) atoms are similar in the two models, electronic effects[60] are unlikely to be responsible for the distortion. It is reasonable to assume that the pyramidalization should lead to a partial change in the hybridization of the carbon(0) atom from sp^2 to sp^3, providing the second lone pair of carbon(0) with enhanced donor abilities. The other structural parameters are comparable to those in previously reported analogues.[13,16,19]

The complex **3** crystallizes as a dicationic Ag_2Pt_2 cluster with $^-$OTf anions and highly disordered ether molecules from the solvent of crystallization. There are no close contacts between the metal centers and the $^-$OTf anions or the solvent molecules. The cluster unit has an antiparallel sandwich structure with a ladder-shaped PtC/AgAg/CPt core, resulting from dimerization of **2** through two silver ions. The two halves of **3** are related by a crystallographic inversion center bisecting the Ag1−Ag1* bond, and the corresponding structural parameters for the dinuclear subunits are thus crystallographically identical. The Pt1−Ag1*−C1* angle of 154.54(8)° deviates substantially from the idealized linear

Table 1. Selected Bond Distances (Å) and Angles (deg) for 2−5[a]

	2	3	4	5a	5b
C1−P1, C1−P2	1.702(2), 1.692(2)	1.745(3), 1.752(3)	1.734(4), 1.739(4)	1.741(4), 1.745(4)	1.746(4), 1.742(4)
av C1−P	1.697	1.749	1.737	1.743	1.744
C1−Pt1	2.067(2)	2.128(3)	2.130(4)	2.105(3)	2.104(4)
C1−Ag1		2.195(3)	2.185(4)	2.224(4)	2.191(4)
Ag1−Pt1		2.7832(4),[b] 3.1946(4)	2.8602(4)	2.8848(4)	2.8829(4)
P1−C1−Pt1	113.88(12)	106.10(15)	111.02(18)	112.14(17)	109.88(18)
P2−C1−P1	124.88(14)	125.29(18)	126.0(2)	122.9(2)	124.9(2)
P2−C1−Pt1	112.40(13)	108.60(15)	106.02(18)	110.73(18)	111.37(18)
sum (around C1)	351.16	339.99	343.0	345.8	346.2
C1−Pt1−P3	159.03(9), 168.87(14)[c]	165.86(8)	167.98(10)	174.19(10)	173.25(11)
Pt1−C1−Ag1		95.27(12)	83.03(13)	83.53(13)	84.30(13)
C1−Pt1−Ag1		92.70(8),[d] 43.17(8)	49.31(10)	49.99(10)	49.13(10)
C1−Ag1−P4			177.02(10)	167.50(10)	172.02(10)

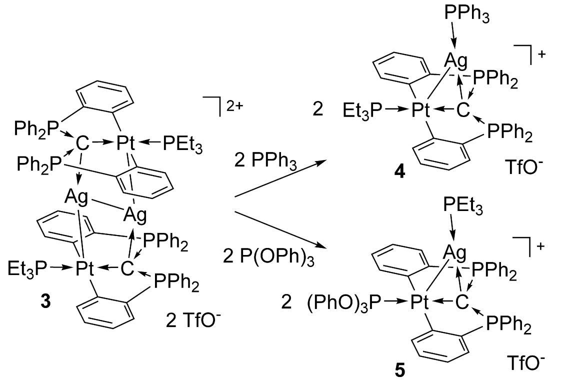
[a] Data for two inequivalent molecules **5a** and **5b**. [b] Ag1*−Pt1. [c] C1−Pt1−P3A for the minor disordered component in **2**. [d] C1−Pt1−Ag1*.

angle expected for two-coordinate Ag(I) complexes, and this bending might result from weak intramolecular interactions between Ag1* and Ag1 (vide infra) and from the coordination of one of the cyclometalated phenyl rings to the silver atom, as indicated by the short C19−Ag1* (2.533(3) Å) and C18−Ag1* (2.675(3) Å) distances, which are significantly less than the sum of the van der Waals radii (3.42 Å).[61] Similar Ag−C(aromatic) contacts have often been observed in related adducts of silver and cyclometalated complexes.[62] The distances for Pt1−Ag1* (2.7832(4) Å) and Pt1−Ag1 (3.1946(4) Å) both fall within the range of Ag−Pt distances found previously for related Ag_2Pt_2 clusters.[63−73] The C1 atom is located 3.582 Å away from Ag1*, and thus, there is no discernible interaction between the two atoms. In contrast, the C1−Ag1 distance of 2.195(3) Å is only slightly longer than those found in $[Ag\{C(PPh_3)_2\}_2]Cl$ (2.115(8) and 2.134(7) Å), where CDPs bind to the silver atom in a terminal mode.[15] The second metalation results in a higher degree of pyramidalization at C1 with the sum of the angles at C1 being 339.99°, associated with slight elongation of the Pt1−C1 (2.128(3) Å), C1−P1 (1.745(3) Å), and C1−P2 (1.752(3) Å) bonds. Frenking et al. have performed detailed theoretical and experimental studies on Lewis acid adducts of CDPs. The P−C bonds are significantly elongated as the number of coordinated Lewis acids A increases (A = halogen cations, H^+, BH_3, CO_2, AuCl; $R_3P{\rightarrow}C{\leftarrow}PR_3 < R_3P{\rightarrow}C(A^1){\leftarrow}PR_3 < R_3P{\rightarrow}C(A^1)(A^2){\leftarrow}PR_3$).[74] This elongation has been rationalized based on a reduced π-back-bonding interaction between the central carbon lone-pair orbitals and the $P{-}C_{phenyl}$ antibonding orbitals, although π-orbital delocalization is intrinsically small in CDPs. These structural changes around the carbon(0) atom are likely to be responsible for the smaller NMR coupling constants of J_{PPt} and J_{PP} in **3** in comparison to those found in **2**. The PEt_3 ligand remains displaced out of the platinum coordination plane (C1−Pt1−P3 = 165.86(8) Å) because of the still severe in-plane steric congestion as in **2**.

It is plausible that the reaction of **2** with AgOTf involves the initial formation of a Pt−Ag dinuclear species that dimerizes to give the tetranuclear cluster **3**. Considering the fact that there is no direct interaction between the cluster unit and ^-OTf in **3**, the formation of **3** can be viewed because of attractive interactions between the two cationic dinuclear units against the charge repulsion. Notably, the Ag1−Ag1* separation of 2.7346(7) Å, which is less than the sum of the van der Waals radii (3.44 Å),[61] is relatively short in comparison to those previously reported for closely related Ag_2Pt_2 clusters,[63−73] suggesting substantial Ag(I)−Ag(I) interactions. This counterintuitive attraction derives partially from *argentophilic interactions*, which often result in the formation of polycationic arrays of silver complexes.[75] The dimerization ultimately resulted in the parallel binding of pincer platinum units to the Ag−Ag component through C(0)−Ag(I) and Pt(II)−Ag(I) bonds, leading to a ladder core. To date, only a few examples of heterodinuclear CDP complexes have been reported[10,35] and, to our knowledge, dimer **3** represents a unique example of a heterotetranuclear cluster supported by bridging CDP ligands.

Reactions of 3 with Trivalent Phosphorus Ligands. From a fundamental view, one of the most salient properties of multinuclear systems that is advantageous for catalysis is the facile generation of coordinatively unsaturated, highly active species, which arise due to the lability of the metal−metal bond. Accordingly, we investigated the reaction of **3** with trivalent phosphorus donors to examine the lability of the tetranuclear core that might lead to incorporation of extraneous substrates (Scheme 3).

Scheme 3. Reactions of 3 with Trivalent Phosphorus Ligands



Complex **3** was treated with 2 equiv of PPh_3 in CH_2Cl_2 at ambient temperature, and the yellow color of the solution immediately became paler. The $^{31}P\{^1H\}$ NMR spectrum of the mixture has two phosphine signals at 12.9 and 17.6 ppm, together with the CDP signal (32.5 ppm), showing characteristic coupling patterns owing to J_{PP}, J_{PPt}, and J_{PAg}. The signals centered at 12.9 ppm appear as two doublets of triplets, one set with J = 510 and 3 Hz and the other with J = 588 and 3 Hz.

The large couplings of 510 and 588 Hz are evidently due to ^{107}Ag and ^{109}Ag nuclei, respectively, indicating the formation of a pair of isotopologues having a direct Ag−P bond. The small 3 Hz coupling is likely due to the to two CDP phosphorus atoms. On the other hand, the signal at 17.6 ppm appears as a triplet of doublets due to two CDP phosphorus atoms (8 Hz) and $^{107/109}$Ag (3 Hz). This signal also exhibits a prominent ^{195}Pt−^{31}P coupling satellite of 3462 Hz, indicative of a Pt−P bond. The same product was obtained on starting from a mixture of complex **2** and Ag(PPh$_3$)OTf, thus allowing confident assignment of the signal at 12.9 ppm for PPh$_3$ attached to Ag and the other at 17.6 ppm for PEt$_3$ attached to Pt. The CDP signal at 32.5 ppm appears as an apparent triplet of doublets arising from couplings to the phosphines and $^{107/109}$Ag. These observations strongly suggest the formation of dinuclear complex **4**, the structure of which was unambiguously determined by X-ray diffraction analysis (vide infra). The ^{1}H and ^{13}C{^{1}H} NMR spectra are also compatible with the formulation of **4**.

Complex **3** also rapidly reacted with 2 equiv of P(OPh)$_3$ under conditions similar to those employed for the reaction with PPh$_3$. Interestingly, however, the main product shows the signal for the added P(OPh)$_3$ at 97.8 ppm as a triplet (J_{PP} = 12 Hz) flanked by a large ^{195}Pt−^{31}P coupling satellite with J_{PtP} = 5752 Hz in the ^{31}P{^{1}H} NMR spectrum. This large satellite coupling confirms that the P(OPh)$_3$ is directly bonded to the platinum center. Instead, the signal for PEt$_3$ at 11.1 ppm appears as two doublets with large ^{107}Ag−^{31}P (J_{PAg} = 517 Hz) and ^{109}Ag−^{31}P (J_{PAg} = 597 Hz) couplings, indicating that the PEt$_3$ is attached to the silver center. The observed coupling pattern is consistent with the formulation of **5**, where the PEt$_3$ initially bound to the platinum center is replaced by added P(OPh)$_3$ and then recoordinated to the silver. The reaction mixture contained small amounts of unidentified compounds, but no signal assignable to a byproduct containing a Ag−P(OPh)$_3$ bond was observed.

The structures of **4** and **5** were confirmed by single-crystal X-ray diffraction analyses, and the molecular diagrams are shown in Figures 3 and 4, respectively. In the crystal of **4**, the asymmetric unit contains a cationic dinuclear unit of **4** and $^-$OTf together with a dichloromethane solvent molecule. The dinuclear unit can be viewed as being composed of a half-molecule of the tetranuclear cluster **3** and a PPh$_3$ ligand coordinated to the silver center. The platinum center exhibits a heavily distorted square planar environment, the structural parameters of which are comparable to those of **3**. The C1−Ag1 distance of 2.185(4) Å is also similar to that in **3**, but the geometry around the silver atom is essentially linear, with a C1−Ag1−P4 angle of 177.02(10)°, and it appears that there is no interaction between the silver atom and the cyclometalated phenyl ring such as that as found in **3**. The Pt1−Ag1 distance of 2.8602(4) Å in **4** is within the range of those observed in related PtAg dinuclear complexes,[64,70,72,76−85] suggesting the presence of an intramolecular metal−metal interaction. Correspondingly, the linear silver moiety is slightly tilted toward the platinum atom, as indicated by the smaller angle of Pt1−C1−Ag1 (83.03(13)°) in comparison to that in **3** (95.27(12)°), and this value is the smallest in the similar M−C(0)−M′ frameworks (86.80(11)−98.44(11)°) reported previously for the related dinuclear CDP complexes.[10,21,34,35]

The crystal of **5** contains two crystallographically independent molecules together with a dichloromethane solvent molecule in the asymmetric unit; one of the cationic dinuclear units is shown in Figure 4. Complex **5** has structural features similar to those seen for **4**, except that the PEt$_3$ ligand, which is initially coordinated to platinum, is located on the silver atom and the added P(OPh)$_3$ ligand is bonded to the platinum atom instead. The C1−Pt1−P3 angle of 173.7° (av) approaches linearity, implying the alleviation of steric crowding around the platinum center. The C1−Ag1−P4 angle of 169.8° (av)

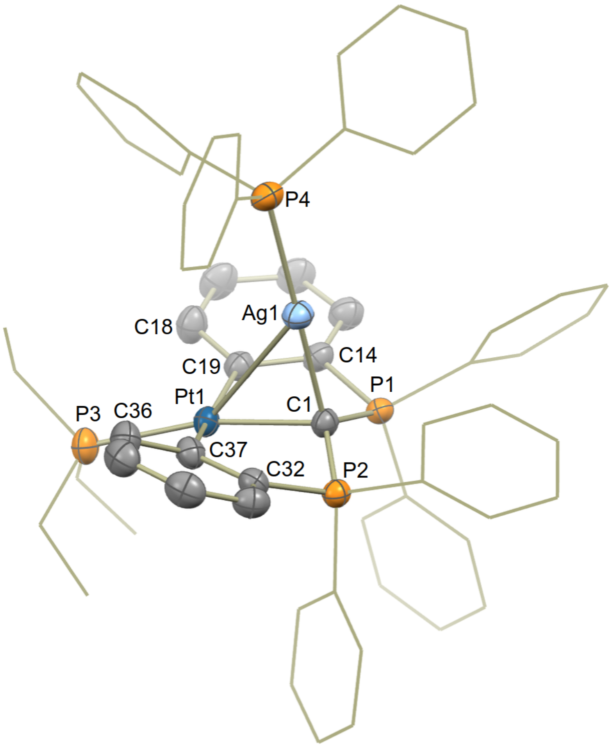


Figure 3. Molecular diagram (50% probability ellipsoids) of **4** showing the crystallographic labeling scheme. All hydrogen atoms, the triflate anion, the solvent molecule, and minor disordered components of PEt$_3$ have been omitted for clarity.

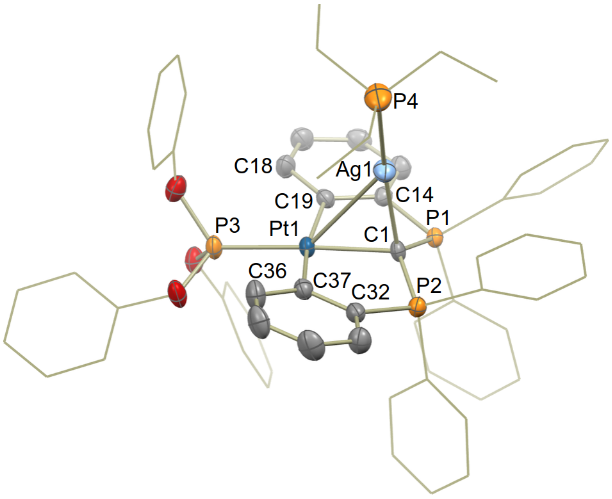
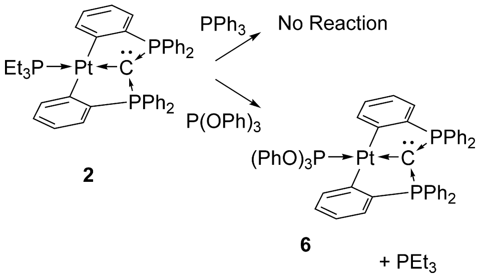


Figure 4. Molecular diagram (50% probability ellipsoids) of **5** showing the crystallographic labeling scheme. One of the two crystallographically independent molecules in the asymmetric unit is shown. All hydrogen atoms, the triflate anions, solvent molecules, and minor disordered components of PEt$_3$ have been omitted for clarity.

indicates that the PEt_3 ligand is bent away from the $P(OPh)_3$ ligand, probably because of steric repulsion between them.

Since the identity of **3** in solution is not yet known, a detailed discussion of the mechanism must await additional investigation. To gain further insight into the origin of the different reactivities of **3** against PPh_3 and $P(OPh)_3$, we investigated the reactions of **2** with the phosphorus ligands (Scheme 4). The $^{31}P\{^1H\}$ NMR studies revealed that complex **2** failed to react with PPh_3 but rapidly reacted with $P(OPh)_3$, eliminating PEt_3 from platinum to produce **6**.[86] This result strongly suggests that the difference in reactivity of **3** with each phosphorus ligand reflects the inherent reactivity of the pincer CDP−platinum subunit. Generally, the electron-donating ability of trivalent phosphorus ligands increases in the order $P(OPh)_3 < PPh_3 < PEt_3$, whereas the ligand size increases in the order $P(OPh)_3 < PEt_3 < PPh_3$.[87] Therefore, one might reasonably anticipate that the substitution reaction of PEt_3 by less electron donating and more sterically demanding PPh_3 is unlikely to occur, considering the crowded environment around platinum in **3** (vide supra). In contrast, this steric congestion would facilitate PEt_3 substitution by the less bulky phosphite $P(OPh)_3$, despite the weaker electron donating ability of $P(OPh)_3$.

Scheme 4. Reactions of 2 with Trivalent Phosphorus Ligands



■ CONCLUSIONS

In summary, we have demonstrated that the platinum complex **2** bearing a cyclometalated pincer CDP ligand serves as a valuable building block for mixed-metal multinuclear complexes. The platinum coordination plane in **2** is severely distorted from planarity because of the in-plane steric congestion. This distortion eventually leads to appreciable pyramidalization at the carbon(0) atom in the pincer framework and thus may enhance the donor ability of the second lone pair on carbon. The reaction of **2** with AgOTf affords the Pt_2Ag_2 tetranuclear cluster **3**. The cluster exhibits an antiparallel sandwich structure with two planar platinum units connected by two silver ions, where the core array contains Pt(II)←C(0)→Ag(I) dative bonds and Pt(II)−Ag(I) and Ag(I)−Ag(I) metal−metal interactions, thereby forming a three-rung ladder core.

Cluster **3** proved to be highly reactive with donor ligands. The reactions of **3** with PPh_3 and with $P(OPh)_3$ provide dinuclear complexes **4** and **5**, respectively, which have different coordination patterns. The sterically demanding and less electron donating PPh_3 coordinates to the silver atom upon the cleavage of the tetranuclear core, whereas the sterically less demanding $P(OPh)_3$ displaces the PEt_3 ligand from the platinum coordination plane to alleviate the steric congestion around platinum.

The intriguing molecular architecture of the present double-cyclometalated CDP−platinum system might offer great potential applications in metal cluster chemistry. Future studies will focus on exploring catalytic applications as well as examining photophysical characteristics of mixed-metal complexes based on the cyclometalated pincer CDP platform.

■ EXPERIMENTAL SECTION

General Considerations. All manipulations were conducted under an N_2 atmosphere using standard Schlenk techniques. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Tetrahydrofuran, diethyl ether, hexane, and toluene were distilled under an N_2 atmosphere from sodium or sodium benzophenone ketyl. Dichloromethane was dried over P_2O_5 and distilled under N_2. $Pt\{C[PPh_2(o\text{-}C_6H_4)]_2\text{-}\kappa^3C,C,C\}(SMe_2)$ was synthesized as previously reported.[19] NMR spectra were recorded on a JEOL Lambda 300 spectrometer, and chemical shifts are reported in ppm. ^1H and $^{13}C\{^1H\}$ NMR chemical shifts were referenced to tetramethylsilane using residual ^1H and ^{13}C signals of the deuterated solvents as internal standards. $^{31}P\{^1H\}$ NMR chemical shifts were referenced to an external 85% H_3PO_4 standard sample. Elemental analyses were performed on a PerkinElmer 2400 Series II CHNS/O Elemental Analyzer.

X-ray Crystal Structure Determinations. Single crystals of **2** were grown by slow evaporation from tetrahydrofuran, while those of **3**−**5** were obtained by slow diffusion of ether into dichloromethane solutions. For X-ray measurement, each crystal was coated with an inert oil, mounted on a MiTeGen polyimide MicroMount, and transferred to a low-temperature nitrogen stream. Intensity data were collected on a Bruker APEX-II Ultra CCD diffractometer using the Apex2 software.[88] The structures were solved using direct methods and refined against F^2 by full-matrix least-squares techniques using the SHELX[89] and Olex2[90] program packages. Non-hydrogen atoms other than those in heavily disordered components were refined anisotropically. The disordered atoms were restrained and refined isotropically with a set of restraints. Hydrogen atoms were placed in ideal positions and refined isotropically as riding atoms. Molecular diagrams were generated with the Mercury CSD 3.8 program.[91,92] Further details of the crystallographic works are available in the Supporting Information.

Synthesis of 2. To a toluene solution (40 mL) of $Pt\{C[PPh_2(o\text{-}C_6H_4)]_2\text{-}\kappa^3C,C,C\}(SMe_2)$ (3.52 g, 4.44 mmol) was added PEt_3 (0.65 mL, 4.84 mmol) at ambient temperature, and the resulting mixture was stirred for 1 h. The volatile compounds were then removed under vacuum. The residue was washed twice with hexane (20 mL × 2) and dried under vacuum to give **2** as a yellow powder. Yield: 3.72 g (99%). ^1H NMR (δ, in C_6D_6): 0.98 (dt, J_{HP} = 15.2 Hz, J_{HH} = 7.6 Hz, 9H, PCH_2CH_3), 1.90 (quint, $J_{HH} = J_{HP}$ = 7.8 Hz, 6H, PCH_2CH_3), 6.82−8.35 (m, 28H, PC_6H_5 and PC_6H_4). $^{13}C\{^1H\}$ NMR (δ, in C_6D_6): 9.4 (s, J_{CPt} = 29 Hz, PCH_2CH_3), 18.7 (d, J_{CP} = 29 Hz, J_{CPt} = 29 Hz, PCH_2CH_3), 121.4 (t, J_{CP} = 7 Hz, PC_6H_4), 127.9 (d, J_{CP} = 6 Hz, PC_6H_5), 129.4 (s, PC_6H_4), 129.5 (t, J_{CP} = 11 Hz, PC_6H_4), 130.1 (s, PC_6H_5), 132.9 (t, J_{CP} = 5 Hz, PC_6H_5), 135.4 (m, PC_6H_5), 142.4 (m, PC_6H_4), 155.8 (m, PC_6H_4), 172.6 (m, PC_6H_4). $^{31}P\{^1H\}$ NMR (δ, in C_6D_6): 14.6 (t, J_{PP} = 8 Hz, J_{PPt} = 3174 Hz, PEt_3), 28.5 (d, J_{PP} = 7 Hz, J_{PPt} = 147 Hz, PCP). Anal. Calcd for $C_{43}H_{43}P_3Pt$: C, 60.92; H, 5.11. Found: C, 60.97; H, 5.20.

Synthesis of 3. A solution of **2** (155 mg, 0.18 mmol) in dichloromethane (7 mL) was added by cannula to a stirred solution of AgOTf (48 mg, 0.19 mmol) in dichloromethane (3 mL) at ambient temperature. The solution immediately changed from yellow to red. After it was stirred for 1 h, the resulting mixture was filtered to remove a black powder that had formed; then, all volatiles were removed under vacuum. The remaining solid was recrystallized twice using dichloromethane (2 mL) and diethyl ether (15 mL) and dried under vacuum to give **3** as a yellow powder. Yield: 181 mg (90%). ^1H NMR (δ, in CD_2Cl_2): 0.64 (dt, J_{HH} = 7.7 Hz, J_{HP} = 16.0 Hz, 18H, PCH_2CH_3), 1.67 (br, 12H, PCH_2CH_3), 6.91−7.84 (m, 56H, PC_6H_5 and PC_6H_4). $^{13}C\{^1H\}$ NMR (δ, in CD_2Cl_2): 9.2 (d, J_{CP} = 3 Hz, J_{CPt} = 19 Hz, PCH_2CH_3), 19.3 (d, J_{CP} = 32 Hz, J_{CPt} = 30 Hz, PCH_2CH_3), 121.3 (q, J_{CF} = 322 Hz, CF_3), 125.4 (br, PC_6H_5), 126.4 (br, PC_6H_4), 127.8 (br, PC_6H_5), 128.7 (br, PC_6H_5), 130.0 (br, PC_6H_5), 132.2 (br, PC_6H_5), 132.8 (br, PC_6H_5), 133.9 (br, PC_6H_5), 140.8 (br, PC_6H_4), 153.0 (br, PC_6H_4), 156.2 (br, J_{CPt} = 604 Hz, PC_6H_4). $^{31}P\{^1H\}$ NMR (δ, in CD_2Cl_2): 13.3 (br, J_{PPt} = 3027 Hz, PEt_3), 33.4 (br, J_{PPt} = 71 Hz, PCP). Anal. Calcd for $C_{88}H_{86}Ag_2F_6O_6P_6Pt_2S_2$: C, 47.84; H, 3.92. Found: C, 47.95; H, 3.93.

Synthesis of 4. To a stirred solution of **3** (131 mg, 0.059 mmol) in dichloromethane (5 mL) was added a solution of PPh_3 (31 mg, 0.12 mmol) in dichloromethane (5 mL) at ambient temperature. The solution immediately faded to pale yellow. After 30 min of stirring, all volatiles were removed under vacuum. The resulting solid was recrystallized twice using dichloromethane (1 mL) and diethyl ether (10 mL) and dried under vacuum to give **4** as a yellow powder. Yield: 115 mg (71%). Compound **4** was also obtained from the reaction of **2** (148 mg, 0.18 mmol) with $Ag(PPh_3)OTf$ (93 mg, 0.18 mmol) in 10 mL of dichloromethane and recrystallization using dichloromethane/diethyl ether. Yield: 220 mg (92%). ^1H NMR (δ, in $CDCl_3$): 1.07 (dt, J_{HP} = 16.3 Hz, J_{HH} = 7.8 Hz, 9H, PCH_2CH_3), 2.13 (quint, $J_{\mathrm{HP}} = J_{\mathrm{HH}}$ = 7.8 Hz, 6H, PCH_2CH_3), 6.95–7.94 (m, 43H, $AgPC_6H_5$, $C^0PC_6H_5$ and PC_6H_4). $^{13}C\{^1H\}$ NMR (δ, in $CDCl_3$): 9.3 (s, J_{CPt} = 27 Hz, PCH_2CH_3), 18.3 (d, J_{CP} = 31 Hz, J_{CPt} = 32 Hz, PCH_2CH_3), 121.1 (q, J_{CF} = 321 Hz, SCF_3), 122.8 (t, J_{CP} = 7 Hz, CPC_6H_4), 126.3 (dd, J = 8 Hz, J = 2 Hz, $C^0PC_6H_5$), 127.3 (dd, J = 8 Hz, J = 2 Hz, $C^0PC_6H_5$), 128.3 (t, J_{CP} = 6 Hz, $C^0PC_6H_5$), 129.1 (t, J_{CP} = 6 Hz, $C^0PC_6H_5$), 129.3 (d, J = 11 Hz, $AgPC_6H_5$), 130.8 (br, PC_6H_4), 131.3 (d, J = 2 Hz, $AgPC_6H_5$), 131.4 (s, $C^0PC_6H_5$), 132.3 (t, J_{CP} = 5 Hz, $C^0PC_6H_5$), 132.5 (t, J_{CP} = 4 Hz, $C^0PC_6H_5$), 132.7 (s, $C^0PC_6H_5$), 133.4 (dd, J = 17 Hz, J = 2 Hz, $AgPC_6H_5$), 141.8 (m, PC_6H_4), 152.1 (m, J_{CPt} = 43 Hz, PC_6H_4), 166.8 (m, J_{CPt} = 648 Hz, PC_6H_4). $^{31}P\{^1H\}$ NMR (δ, in $CDCl_3$): 12.9 (2 × dt, $J_{\mathrm{P}^{109}\mathrm{Ag}}$ = 588 Hz, $J_{\mathrm{P}^{107}\mathrm{Ag}}$ = 510 Hz, J_{PP} = 3 Hz, J_{PPt} = 70 Hz, PPh_3), 17.6 (td, J_{PP} = 8 Hz, J_{PAg} = 3 Hz, J_{PPt} = 3462 Hz, PEt_3), 32.5 (td, $J_{\mathrm{PP}} = J_{\mathrm{PAg}}$ = 8 Hz, J_{PP} = 3 Hz, J_{PPt} = 107 Hz, PCP). Anal. Calcd for $C_{62}H_{58}AgF_3O_3P_4PtS$: C, 54.47; H, 4.28. Found: C, 54.05; H, 4.28.

Synthesis of 5·CH_2Cl_2. To a stirred solution of **3** (128 mg, 0.058 mmol) in dichloromethane (5 mL) was added a solution of $P(OPh)_3$ (0.045 mL, 0.17 mmol) in dichloromethane (5 mL) at ambient temperature. The solution immediately faded to pale yellow. After 1 h of stirring, all volatiles were removed under vacuum. The resulting solid was recrystallized three times using dichloromethane (1 mL) and diethyl ether (2 mL) and dried under vacuum to give **5** as a yellow powder. Yield: 89 mg (51%). ^1H NMR (δ, in $CDCl_3$): 0.68 (dt, J_{HP} = 19.3 Hz, J_{HH} = 7.7 Hz, 9H, PCH_2CH_3), 1.38 (quintd, $J_{\mathrm{HP}} = J_{\mathrm{HH}}$ = 7.9 Hz, J_{HAg} = 4.8 Hz, 6H, PCH_2CH_3), 6.99–8.48 (m, 43H, POC_6H_5, PC_6H_5 and PC_6H_4). $^{13}C\{^1H\}$ NMR (δ, in $CDCl_3$): 9.1 (dd, J = 4 Hz, J = 2 Hz, PCH_2CH_3), 16.5 (dd, J_{CP} = 22 Hz, J_{CAg} = 5 Hz, PCH_2CH_3), 120.6 (d, J_{CP} = 6 Hz, POC_6H_5), 121.0 (q, J_{CF} = 321 Hz, SCF_3), 123.6 (t, J_{CP} = 7 Hz, PC_6H_4), 124.6 (s, POC_6H_5), 126.1 (d, J = 4 Hz, PC_6H_5), 127.1 (d, J = 4 Hz, PC_6H_5), 128.4 (t, J_{CP} = 6 Hz, PC_6H_5), 129.2 (t, J_{CP} = 6 Hz, PC_6H_5), 129.5 (s, POC_6H_5), 131.2 (s, PC_6H_4), 131.4 (s, PC_6H_5), 132.1 (t, J_{CP} = 5 Hz, PC_6H_5), 132.5 (t, J_{CP} = 4 Hz, PC_6H_5), 133.0 (s, PC_6H_5), 143.1 (m, PC_6H_4), 150.1 (m, J_{CPt} = 50 Hz, PC_6H_4), 151.1 (d, J_{CP} = 7 Hz POC_6H_5), 163.9 (m, J_{CPt} = 629 Hz, PC_6H_4). $^{31}P\{^1H\}$ NMR (δ, in $CDCl_3$): 11.1 (2 × d, $J_{\mathrm{P}^{109}\mathrm{Ag}}$ = 597 Hz, $J_{\mathrm{P}^{107}\mathrm{Ag}}$ = 517 Hz, J_{PPt} = 60 Hz, PEt_3), 36.0 (t, $J_{\mathrm{PP}} = J_{\mathrm{PAg}}$ = 9 Hz, J_{PPt} = 118 Hz, PCP), 97.8 (t, J_{PP} = 12 Hz, J_{PPt} = 5752 Hz, $P(OPh)_3$). Anal. Calcd for $C_{62}H_{58}AgF_3O_6P_4PtS{\bullet}CH_2Cl_2$: C, 50.44; H, 4.03. Found: C, 50.65; H, 3.62.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00700.

Summary of X-ray crystallographic data, NMR spectra for **2**–**5**, and computational data (PDF)

Crystallographic data for **2**–**5** (CIF)

Cartesian coordinates for calculated structures (XYZ)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail for K.K.: kkubo@sci.hiroshima-u.ac.jp.

*E-mail for T.M.: mizuta@sci.hiroshima-u.ac.jp.

ORCID

Kazuyuki Kubo: 0000-0002-3889-5802

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by JSPS KAKENHI Grant Number 23550079. Elemental analyses were performed on a PerkinElmer 2400 Series II CHNS/O analyzer at the Natural Science Center for Basic Research and Development (N-BARD), Hiroshima University.

■ REFERENCES

(1) For recent overviews on carbodiphosphoranes and related carbon(0) chemistry, see: (a) Frenking, G.; Hermann, M.; Andrada, D. M.; Holzmann, N. *Chem. Soc. Rev.* **2016**, *45*, 1129–1144. (b) Petz, W. *Coord. Chem. Rev.* **2015**, *291*, 1–27. (c) Fliedel, C.; Schnee, G.; Avilés, T.; Dagorne, S. *Coord. Chem. Rev.* **2014**, *275*, 63–86. (d) Frenking, G.; Tonner, R.; Klein, S.; Takagi, N.; Shimizu, T.; Krapp, A.; Pandey, K. K.; Parameswaran, P. *Chem. Soc. Rev.* **2014**, *43*, 5106–5139. (e) Schmidbaur, H.; Schier, A. *Angew. Chem., Int. Ed.* **2013**, *52*, 176–186. (f) Alcarazo, M. *Dalton Trans.* **2011**, *40*, 1839–1845. (g) Melaimi, M.; Soleilhavoup, M.; Bertrand, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 8810–8849. (h) Patel, D. S.; Bharatam, P. V. *Curr. Sci.* **2010**, 425–426. (i) Petz, W.; Frenking, G. Carbodiphosphoranes and Related Ligands. In *Transition Metal Complexes of Neutral η^1-Carbon Ligands*; Chauvin, R., Canac, Y., Eds.; Springer: Berlin, Germany, 2010; Vol. *30*, pp 49–92. (j) Dyker, C. A.; Bertrand, G. *Nat. Chem.* **2009**, *1*, 265–266. (k) Kaufhold, O.; Hahn, F. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 4057–4061.

(2) Ramirez, F.; Desai, N. B.; Hansen, B.; McKelvie, N. *J. Am. Chem. Soc.* **1961**, *83*, 3539–3540.

(3) (a) Vincent, A. T.; Wheatley, P. J. *J. Chem. Soc., Dalton Trans.* **1972**, 617–622. (b) Vincent, A. T.; Wheatley, P. J. *J. Chem. Soc. D* **1971**, 582a–582a.

(4) El-Hellani, A.; Bour, C.; Gandon, V. *Adv. Synth. Catal.* **2011**, *353*, 1865–1870.

(5) Corberán, R.; Marrot, S.; Dellus, N.; Merceron-Saffon, N.; Kato, T.; Peris, E.; Baceiredo, A. *Organometallics* **2009**, *28*, 326–330.

(6) Tonner, R.; Frenking, G. *Chem. Commun.* **2008**, 1584–1586.

(7) Dobrovetsky, R.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2013**, *52*, 2516–2519.

(8) Alcarazo, M.; Gomez, C.; Holle, S.; Goddard, R. *Angew. Chem., Int. Ed.* **2010**, *49*, 5788–5791.

(9) Pranckevicius, C.; Iovan, D. A.; Stephan, D. W. *Dalton Trans.* **2016**, *45*, 16820–16825.

(10) Alcarazo, M.; Radkowski, K.; Mehler, G.; Goddard, R.; Fürstner, A. *Chem. Commun.* **2013**, *49*, 3140–3142.

(11) Reitsamer, C.; Stallinger, S.; Schuh, W.; Kopacka, H.; Wurst, K.; Obendorf, D.; Peringer, P. *Dalton Trans.* **2012**, *41*, 3503–3514.

(12) Petz, W.; Neumüller, B.; Klein, S.; Frenking, G. *Organometallics* **2011**, *30*, 3330–3339.

(13) Petz, W.; Neumüller, B. *Polyhedron* **2011**, *30*, 1779–1784.

(14) Petz, W.; Neumüller, B. *Eur. J. Inorg. Chem.* **2011**, *2011*, 4889–4895.

(15) Petz, W.; Öxler, F.; Neumüller, B. *J. Organomet. Chem.* **2009**, *694*, 4094–4099.

(16) Cavell, R. G. Pincer and chelate carbodiphosphorane complexes of noble metals. In *The Chemistry of Pincer Compounds*; Morales-

Morales, D., Jensen, C. M., Eds.; Elsevier: Amsterdam, The Netherlands, 2007; Chapter 15, pp 347−355.

(17) Stallinger, S.; Reitsamer, C.; Schuh, W.; Kopacka, H.; Wurst, K.; Peringer, P. *Chem. Commun.* **2007**, 510−512.

(18) Marrot, S.; Kato, T.; Gornitzka, H.; Baceiredo, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 2598−2601.

(19) Kubo, K.; Jones, N. D.; Ferguson, M. J.; McDonald, R.; Cavell, R. G. *J. Am. Chem. Soc.* **2005**, *127*, 5314−5315.

(20) Petz, W.; Kutschera, C.; Neumüller, B. *Organometallics* **2005**, *24*, 5038−5043.

(21) Vicente, J.; Singhal, A. R.; Jones, P. G. *Organometallics* **2002**, *21*, 5887−5900.

(22) Petz, W.; Weller, F.; Uddin, J.; Frenking, G. *Organometallics* **1999**, *18*, 619−626.

(23) Sundermeyer, J.; Weber, K.; Peters, K.; von Schnering, H. G. *Organometallics* **1994**, *13*, 2560−2562.

(24) Schmidbaur, H.; Scherbaum, F.; Huber, B.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 419−421.

(25) Endrich, K.; Alburquerque, P.; Korswagen, R. P.; Ziegler, M. L. *Z. Naturforsch., B: J. Chem. Sci.* **1988**, *43*, 1293−1306.

(26) Bruce, A. E.; Gamble, A. S.; Tonker, T. L.; Templeton, J. L. *Organometallics* **1987**, *6*, 1350−1352.

(27) Zybill, C.; Müller, G. *Organometallics* **1987**, *6*, 2489−2494.

(28) Müller, G.; Krüger, C.; Zybill, C.; Schmidbauer, H. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1986**, *42*, 1141−1144.

(29) Schmidbaur, H.; Zybill, C. E.; Müller, G.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 729−730.

(30) Baldwin, J. C.; Kaska, W. C. *Inorg. Chem.* **1979**, *18*, 686−691.

(31) Kaska, W. C.; Mitchell, D. K.; Reichelderfer, R. F.; Korte, W. D. *J. Am. Chem. Soc.* **1974**, *96*, 2847−2854.

(32) Kaska, W. C.; Reichelderfer, R. F. *J. Organomet. Chem.* **1974**, *78*, C47−C50.

(33) Kaska, W. C.; Mitchell, D. K.; Reichelderfer, R. F. *J. Organomet. Chem.* **1973**, *47*, 391−402.

(34) Reitsamer, C.; Schuh, W.; Kopacka, H.; Wurst, K.; Ellmerer, E. P.; Peringer, P. *Organometallics* **2011**, *30*, 4220−4223.

(35) Reitsamer, C.; Schuh, W.; Kopacka, H.; Wurst, K.; Peringer, P. *Organometallics* **2009**, *28*, 6617−6620.

(36) Kaska, W. C. *Coord. Chem. Rev.* **1983**, *48*, 1−58.

(37) Schmidbaur, H.; Costa, T.; Milewski-Mahrla, B. *Chem. Ber.* **1981**, *114*, 1428−1441.

(38) Schmidbaur, H.; Costa, T. *Chem. Ber.* **1981**, *114*, 3063−3069.

(39) Schmidbaur, H.; Gasser, O. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 502−503.

(40) For selected reviews, see: (a) Gessner, V. H.; Becker, J.; Feichtner, K.-S. *Eur. J. Inorg. Chem.* **2015**, *2015*, 1841−1859. (b) Ephritikhine, M. *C. R. Chim.* **2013**, *16*, 391−405. (c) Liddle, S. T.; Mills, D. P.; Wooles, A. J. *Chem. Soc. Rev.* **2011**, *40*, 2164−2176. (d) Harder, S. *Coord. Chem. Rev.* **2011**, *255*, 1252−1267. (e) Panda, T. K.; Roesky, P. W. *Chem. Soc. Rev.* **2009**, *38*, 2782−2804. (f) Cantat, T.; Mézailles, N.; Auffrant, A.; Le Floch, P. *Dalton Trans.* **2008**, 1957−1972. (g) Cavell, R. G. Pincer, chelate and spirocyclic metal carbene complexes from bis(iminophosphorano)methane ligands. In *The Chemistry of Pincer Compounds*; Morales-Morales, D., Jensen, C. M., Eds.; Elsevier: Amsterdam, The Netherlands, 2007; Chapter 14, pp 311−346. (h) Jones, N. D.; Cavell, R. G. *J. Organomet. Chem.* **2005**, *690*, 5485−5496. (i) Cavell, R. G.; Kamalesh Babu, R. P.; Aparna, K. *J. Organomet. Chem.* **2001**, *617−618*, 158−169. (j) Cavell, R. G. *Curr. Sci.* **2000**, *78*, 440−451.

(41) Roberts, C. C.; Matías, D. M.; Goldfogel, M. J.; Meek, S. J. *J. Am. Chem. Soc.* **2015**, *137*, 6488−6491.

(42) For recent reviews, see: (a) Buchwalter, P.; Rosé, J.; Braunstein, P. *Chem. Rev.* **2015**, *115*, 28−126. (b) Mata, J. A.; Hahn, F. E.; Peris, E. *Chem. Sci.* **2014**, *5*, 1723−1732. (c) Bratko, I.; Gómez, M. *Dalton Trans.* **2013**, *42*, 10664−10681. (d) Park, J.; Hong, S. *Chem. Soc. Rev.* **2012**, *41*, 6931−6943. (e) Cooper, B. G.; Napoline, J. W.; Thomas, C. M. *Catal. Rev.: Sci. Eng.* **2012**, *54*, 1−40. (f) Thomas, C. M. *Comments Inorg. Chem.* **2011**, *32*, 14−38. (g) Ritleng, V.; Chetcuti, M. J. *Chem. Rev.* **2007**, *107*, 797−858.

(43) For some related examples, see: (a) Morosaki, T.; Suzuki, T.; Fujii, T. *Organometallics* **2016**, *35*, 2715−2721. (b) Morosaki, T.; Fujii, T. *Phosphorus, Sulfur Silicon Relat. Elem.* **2016**, *191*, 159−162. (c) Morosaki, T.; Wang, W.-W.; Nagase, S.; Fujii, T. *Chem. - Eur. J.* **2015**, *21*, 15405−15411. (d) Alcarazo, M.; Lehmann, C. W.; Anoop, A.; Thiel, W.; Fürstner, A. *Nat. Chem.* **2009**, *1*, 295−301.

(44) For recent reviews, see: (a) Yam, V. W.-W.; Au, V. K.-M.; Leung, S. Y.-L. *Chem. Rev.* **2015**, *115*, 7589−7728. (b) Huo, S.; Carroll, J.; Vezzu, D. A. K. *Asian J. Org. Chem.* **2015**, *4*, 1210−1245. (c) Yang, X.; Yao, C.; Zhou, G. *Platinum Met. Rev.* **2013**, *57*, 2−16. (d) Kalinowski, J.; Fattori, V.; Cocchi, M.; Williams, J. A. G. *Coord. Chem. Rev.* **2011**, *255*, 2401−2425. (e) Díez, l.; Lalinde, E.; Moreno, M. T. *Coord. Chem. Rev.* **2011**, *255*, 2426−2447. (f) Chi, Y.; Chou, P.-T. *Chem. Soc. Rev.* **2010**, *39*, 638−655.

(45) To, W.-P.; Zou, T.; Sun, R. W.-Y.; Che, C.-M. *Philos. Trans. R. Soc., A* **2013**, *371*, 20120126.

(46) For recent reviews, see: (a) Mauro, M.; Aliprandi, A.; Septiadi, D.; Kehr, N. S.; Cola, L. D. *Chem. Soc. Rev.* **2014**, *43*, 4144−4166. (b) Baggaley, E.; Weinstein, J. A.; Williams, J. A. G. *Coord. Chem. Rev.* **2012**, *256*, 1762−1785. (c) Lo, K. K.-W.; Choi, A. W.-T.; Law, W. H.-T. *Dalton Trans.* **2012**, *41*, 6021−6047. (d) Thorp-Greenwood, F. L. *Organometallics* **2012**, *31*, 5686−5692. (e) Zhao, Q.; Huang, C.; Li, F. *Chem. Soc. Rev.* **2011**, *40*, 2508−2524.

(47) For recent reviews, see: (a) Omae, I. *Coord. Chem. Rev.* **2014**, *280*, 84−95. (b) Cutillas, N.; Yellol, G. S.; de Haro, C.; Vicente, C.; Rodríguez, V.; Ruiz, J. *Coord. Chem. Rev.* **2013**, *257*, 2784−2797.

(48) *The Privileged Pincer-Metal Platform: Coordination Chemistry & Applications*; van Koten, G., Gossage, R. A., Eds.; Springer: Cham, Switzerland, 2016; Vol. *54*.

(49) *Pincer and Pincer-Type Complexes: Applications in Organic Synthesis and Catalysis*; Szabó, K. J., Wendt, O. F., Eds.; Wiley-VCH: Weinheim, Germany, 2014.

(50) *Organometallic pincer chemistry*; van Koten, G., Milstein, D. M., Eds.; Springer: Berlin, Germany, 2013; Vol. *40*.

(51) *The chemistry of pincer compounds*; Morales-Morales, D., Jensen, C. M., Eds.; Elsevier: Amsterdam, The Netherlands, 2007.

(52) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597−636.

(53) Doerrer, L. H. *Dalton Trans.* **2010**, *39*, 3543−3553.

(54) For some theoretical calculations on d^{8}−d^{10} metallophilic interactions see: (a) Pan, Q.-J.; Guo, Y.-R.; Zhang, H.-X. *Organometallics* **2010**, *29*, 3261−3270. (b) Mendizabal, F. *Int. J. Quantum Chem.* **2008**, *108*, 1164−1172. (c) Xia, B.-H.; Zhang, H.-X.; Jiao, Y.-Q.; Pan, Q.-J.; Li, Z.-S.; Sun, C.-C. *J. Chem. Phys.* **2004**, *120*, 11487−11492. (c) Xia, B.-H.; Zhang, H.-X.; Che, C.-M.; Leung, K.-H.; Phillips, D. L.; Zhu, N.; Zhou, Z.-Y. *J. Am. Chem. Soc.* **2003**, *125*, 10362−10374.

(55) Bauer, J.; Braunschweig, H.; Dewhurst, R. D. *Chem. Rev.* **2012**, *112*, 4329−4346.

(56) Moret, M.-E. Organometallic Platinum(II) and Palladium(II) Complexes as Donor Ligands for Lewis-Acidic d^{10} and s^{2} Centers. In *Higher Oxidation State Organopalladium and Platinum Chemistry*; Canty, A. J., Ed.; Springer: Berlin, Germany, 2011; Vol. *35*, pp 157−184.

(57) Usón, R.; Forniés, J. *Inorg. Chim. Acta* **1992**, *198-200*, 165−177.

(58) Aullón, G.; Alvarez, S. *Inorg. Chem.* **1996**, *35*, 3137−3144.

(59) Mealli, C.; Pichierri, F.; Randaccio, L.; Zangrando, E.; Krumm, M.; Holtenrich, D.; Lippert, B. *Inorg. Chem.* **1995**, *34*, 3418−3424.

(60) Some electronic effects were noted on pyramidalization of a methanediide carbon. See: (a) Gessner, V. H.; Meier, F.; Uhrich, D.; Kaupp, M. *Chem. - Eur. J.* **2013**, *19*, 16729−16739. (b) Cantat, T.; Mézailles, N.; Ricard, L.; Jean, Y.; Le Floch, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 6382−6385.

(61) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441−451.

(62) See the examples in ref 64 and references therein.

(63) Moussa, J.; Chamoreau, L. M.; Gullo, M. P.; Esposti, A. D.; Barbieri, A.; Amouri, H. *Dalton Trans.* **2016**, *45*, 2906−2913.

(64) Baya, M.; Belío, r.; Forniés, J.; Martín, A.; Perálvarez, M.; Sicilia, V. *Inorg. Chim. Acta* **2015**, *424*, 136−149.

(65) Forniés, J.; Sicilia, V.; Casas, J. M.; Martín, A.; López, J. A.; Larraz, C.; Borja, P.; Ovejero, C. *Dalton Trans.* **2011**, *40*, 2898−2912.
(66) Jamali, S.; Mazloomi, Z.; Nabavizadeh, S. M.; Dalibor, M.; Kia, R.; Rashidi, M. *Inorg. Chem.* **2010**, *49*, 2721−2726.
(67) Moret, M.-E.; Chen, P. *J. Am. Chem. Soc.* **2009**, *131*, 5675−5690.
(68) Chen, Y.-D.; Zhang, L.-Y.; Shi, L.-X.; Chen, Z.-N. *Inorg. Chem.* **2004**, *43*, 7493−7501.
(69) Vicente, J.; Chicote, M. T.; Huertas, S.; Bautista, D.; Jones, P. G.; Fischer, A. K. *Inorg. Chem.* **2001**, *40*, 2051−2057.
(70) Forniés, J.; Martín, A.; Navarro, R.; Sicilia, V.; Villarroya, P.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1998**, 3721−3726.
(71) Forniés, J.; Martínez, F.; Navarro, R.; Urriolabeitia, E. P. *Organometallics* **1996**, *15*, 1813−1819.
(72) Uson, R.; Fornies, J.; Menjon, B.; Cotton, F. A.; Falvello, L. R.; Tomas, M. *Inorg. Chem.* **1985**, *24*, 4651−4656.
(73) Uson, R.; Fornies, J.; Tomas, M.; Cotton, F. A.; Falvello, L. R. *J. Am. Chem. Soc.* **1984**, *106*, 2482−2483.
(74) Examples include: (a) Petz, W.; Kuzu, I.; Frenking, G.; Andrada, D. M.; Neumüller, B.; Fritz, M.; Münzer, J. E. *Chem. - Eur. J.* **2016**, *22*, 8536−8546. (b) Takagi, N.; Tonner, R.; Frenking, G. *Chem. - Eur. J.* **2012**, *18*, 1772−1780. (c) Esterhuysen, C.; Frenking, G. *Chem. - Eur. J.* **2011**, *17*, 9944−9956. (d) Petz, W.; Öxler, F.; Neumüller, B.; Tonner, R.; Frenking, G. *Eur. J. Inorg. Chem.* **2009**, *2009*, 4507−4517. (e) Frenking, G.; Tonner, R. *Pure Appl. Chem.* **2009**, *81*, 597−614. (f) Tonner, R.; Frenking, G. *Chem. - Eur. J.* **2008**, *14*, 3273−3289. (g) Tonner, R.; Öxler, F.; Neumüller, B.; Petz, W.; Frenking, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 8038−8042.
(75) Schmidbaur, H.; Schier, A. *Angew. Chem., Int. Ed.* **2015**, *54*, 746−784.
(76) Martín, A.; Belío, r.; Fuertes, S.; Sicilia, V. *Eur. J. Inorg. Chem.* **2013**, *2013*, 2231−2247.
(77) Forniés, J.; Ibáñez, S.; Lalinde, E.; Martín, A.; Moreno, M. T.; Tsipis, A. C. *Dalton Trans.* **2012**, *41*, 3439−3451.
(78) Forniés, J.; Ibáñez, S.; Martín, A.; Sanz, M.; Berenguer, J. R.; Lalinde, E.; Torroba, J. *Organometallics* **2006**, *25*, 4331−4340.
(79) Usón, R.; Forniés, J.; Tomás, M.; Ara, I. *Inorg. Chem.* **1994**, *33*, 4023−4028.
(80) Albinati, A.; Chaloupka, S.; Demartin, F.; Koetzle, T. F.; Ruegger, H.; Venanzi, L. M.; Wolfer, M. K. *J. Am. Chem. Soc.* **1993**, *115*, 169−175.
(81) Usón, R.; Forniés, J.; Tomás, M.; Ara, I. *Inorg. Chim. Acta* **1991**, *186*, 67−71.
(82) Usón, R.; Forniés, J.; Tomás, M.; Ara, I.; Casas, J. M.; Martín, A. *J. Chem. Soc., Dalton Trans.* **1991**, 2253−2264.
(83) Usón, R.; Forniés, J.; Tomás, M.; Ara, I.; Casas, J. M. *Inorg. Chem.* **1989**, *28*, 2388−2392.
(84) (a) Cotton, F. A.; Falvello, L. R.; Usón, R.; Forniés, J.; Tomás, M.; Casas, J. M.; Ara, I. *Inorg. Chem.* **1987**, *26*, 1366−1370. (b) Usón, R.; Forniés, J.; Tomás, M.; Casas, J. M.; Cotton, F. A.; Falvello, L. R. *J. Am. Chem. Soc.* **1985**, *107*, 2556−2557.
(85) Usón, R.; Forniés, J.; Tomás, M.; Casas, J. M.; Cotton, F. A.; Falvello, L. R. *Inorg. Chem.* **1986**, *25*, 4519−4525.
(86) $^{31}P\{^1H\}$ NMR spectrum (δ, in CH_2Cl_2) of **6**: 33.8 (d, J_{PP} = 9 Hz, J_{PPt} = 176 Hz, PCP), 107.9 (t, J_{PP} = 9 Hz, J_{PPt} = 5143 Hz, $P(OPh)_3$).
(87) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−348.
(88) *Apex2, Version 2009.9-0*; Bruker AXS Inc., Madison, WI, 2009.
(89) Sheldrick, G. *Acta Crystallogr., Sect. C: Struct. Chem.* **2015**, *C71*, 3−8.
(90) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339−341.
(91) Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A. *J. Appl. Crystallogr.* **2008**, *41*, 466−470.
(92) Macrae, C. F.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Shields, G. P.; Taylor, R.; Towler, M.; van de Streek, J. *J. Appl. Crystallogr.* **2006**, *39*, 453−457.