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Unique stepwise substitution reaction of a mono-(guanidinate)tetraplatinum complex with amidines, giving mono(amidinate)tetraplatinum complexes through mixed-ligand intermediate complexes†

Shinji Tanaka and Kazushi Mashima*

A mono(guanidinate)tetraplatinum complex $[Pt_4(\mu\text{-}OCOCH_3)_7(\mu\text{-}(TolN)_2CN^iPr_2)]$ (**5**: Tol = C_6H_4Me-4) was prepared by treating $[Pt_4(\mu\text{-}OCOCH_3)_8]$ (**1**) with excess amounts of *N,N′*-bis(*p*-tolyl)-*N″*-diisopropylguanidine (**4a**). A substitution reaction of the guanidinate moiety of **5** with *N,N′*-bis(aryl)formamidine (**10**: aryl = C_6H_4Me-4, C_6H_4COMe-4, and C_6H_4OMe-4) *via* mixed-ligand intermediates, *trans*-$[Pt_4(\mu\text{-}OCOCH_3)_6(\mu\text{-}(TolN)_2CN^iPr_2)(\mu\text{-}ArNCHNAr)]$ (**11**: Tol = C_6H_4Me-4; Ar = C_6H_4Me-4, C_6H_4COMe-4, and C_6H_4OMe-4), as a stepwise substitution mechanism, afforded the corresponding mono(amidinate)tetraplatinum complexes $[Pt_4(\mu\text{-}OCOCH_3)_7(\mu\text{-}ArNCHNAr)]$ (**2a**: Ar = C_6H_4Me-4; **2b**: Ar = C_6H_4COMe-4; **2c**: Ar = C_6H_4OMe-4) along with *trans*-bis(amidinate)tetraplatinum complexes *trans*-$[Pt_4(\mu\text{-}OCOCH_3)_6(\mu\text{-}ArNCHNAr)_2]$ (**3a**: Ar = C_6H_4Me-4; **3b**: Ar = C_6H_4COMe-4; **3c**: Ar = C_6H_4OMe-4) as minor products. A Pt_4 dimer complex $[Pt_4(\mu\text{-}OCOCH_3)_7]_2\text{-}\{\mu\text{-}(ArN)_2C(C_6H_4)_2C(NAr)_2\}$ (**13**: Ar = $C_6H_4{}^tBu$-4) was selectively obtained upon treatment of **5** with a bis(amidine) linker ligand, $N^4,N^4,N^{4\prime},N^{4\prime}$-tetrakis(*p*-(*tert*-butyl)phenyl)-[1,1′-biphenyl]-4,4′-dicarboxamidine (**12**). All in-plane acetates of the two Pt_4 cores in **13** were fully substituted by 2,6-dimethylbenzoic acid, 2,4,6-triisopropylbenzoic acid, and ferrocenecarboxylic acid while maintaining its dimer structure to give the corresponding derivatives $[Pt_4(\mu\text{-}OCOCH_3)_4(\mu\text{-}OCOC_6H_3Me_2\text{-}2,6)_3]_2\text{-}\{\mu\text{-}(ArN)_2C(C_6H_4)_2C(NAr)_2\}$ (**14**: Ar = $C_6H_4{}^tBu$-4), $[Pt_4(\mu\text{-}OCOCH_3)_4(\mu\text{-}OCOC_6H_2{}^iPr_3\text{-}2,4,6)_3]_2\text{-}\{\mu\text{-}(ArN)_2C(C_6H_4)_2C(NAr)_2\}$ (**15**: Ar = $C_6H_4{}^tBu$-4), and $[Pt_4(\mu\text{-}OCOCH_3)_4(\mu\text{-}OCOC_5H_4FeCp)_3]_2\text{-}\{\mu\text{-}(ArN)_2C(C_6H_4)_2C(NAr)_2\}$ (**16**: Ar = $C_6H_4{}^tBu$-4). The electrochemistry of the four Pt_4 dimer complexes **13–16** displayed a one-electron process attributed to $Pt_4{}^{9+}/Pt_4{}^{8+}$, and another one-electron process due to Fe^{3+}/Fe^{2+} was observed for the hexaferrocenyl derivative **16**.

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Introduction

Supramolecular chemistry continues to attract high interest in the field of inorganic chemistry.[1,2] Well-controlled ligand substitution reactions of metal complexes play a major role in the rational construction of supramolecular complexes *via* a self-assembly process of metal units with the appropriate linker ligands.[2–8] Since Fujita *et al.*[3] and Stang *et al.*[4] independently developed the syntheses of supramolecular assemblies by substitution reactions of a mononuclear Pd(II) complex bearing chelate diamine ligands and a mononuclear Pt(II) complex bearing chelate diphosphine ligands with the appropriate multidentate linker ligands, mainly mononuclear metal entities have been used. On the other hand, to construct supramolecules, metal cluster units are rarely applied except for some dinuclear paddle-wheel complexes,[9–13] trinuclear complexes,[14] and octahedral hexanuclear complexes,[15,16] because of their complicated substitution reactions on a multinuclear core, despite being highly attractive entities due to their redox and magnetic properties.[17–22]

A square planar tetrametal entity, $[Pt_4(\mu\text{-}OCOCH_3)_8]$ (**1**), has four acetate ligands coordinated in-plane of the square Pt_4 core and four other acetate ligands coordinated out-of-plane,[23,24] and the in-plane acetate ligands were selectively replaced by some bridging or chelating ligands due to the *trans*-effect of the platinum ion.[25] We previously reported the unique substitution reaction of **1** with amidines to give mono-(amidinate)tetraplatinum complexes **2** and *trans*-bis(amidinate)tetraplatinum complex **3** (Chart 1), whose electrochemical

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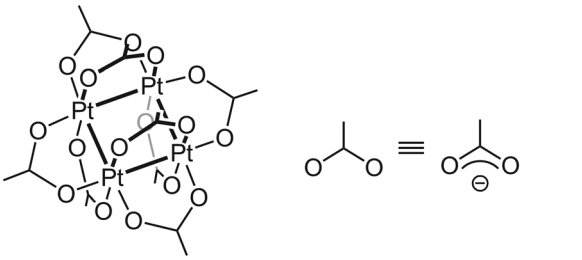
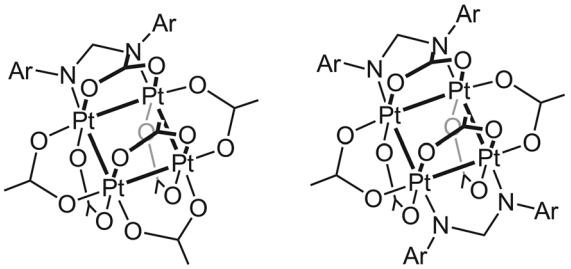
†Electronic supplementary information (ESI) available: X-ray crystallographic data in CIF format, VT-NMR and simulated spectra of complex **5**, tables of crystal data and refinement parameters for **5** and **13**, and ^1H NMR spectra of complexes **5**, **13**, **14**, **15**, and **16**. CCDC 901346, 910750. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt32136j



$[Pt_4(\mu\text{-}OCOCH_3)_8]$(**1**)



2a: Ar = C_6H_4Me-4
2b: Ar = C_6H_4COMe-4

3a: Ar = C_6H_4Me-4
3b: Ar = C_6H_4COMe-4

Chart 1

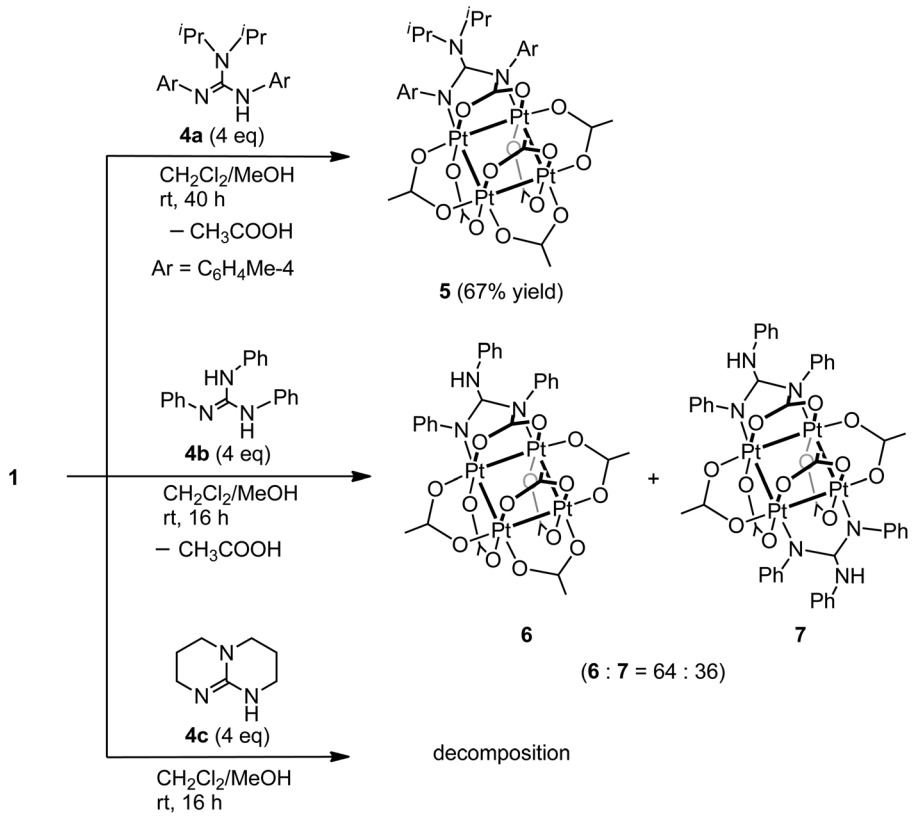
properties were elucidated.[26,27] Herein we report the synthesis and structure of a mono(guanidinate)tetraplatinum complex and its substitution reactions with carboxylic acids and amidines. Based on the substitution pattern of guanidinate bound to the Pt_4 unit with amidines, we synthesized a Pt_4 dimer complex by treatment with a bis(amidine) linker.

Results and discussion

A mono(guanidinate)tetraplatinum complex, $[Pt_4(\mu\text{-}OCOCH_3)_7(\mu\text{-}(TolN)_2CN^iPr_2)]$ (**5**: Tol = C_6H_4Me-4), was prepared in 67% yield by treating $[Pt_4(\mu\text{-}OCOCH_3)_8]$ (**1**) with 4 equiv. of a guanidine, *N*,*N*′-bis(*p*-tolyl)-*N*″-diisopropylguanidine (**4a**), in a mixture of dichloromethane and methanol for 16 h followed by removal of excess amounts of **4a** by washing with Et_2O and then with hexane (Scheme 1). Excess amounts of **4a** were essential for full conversion of **1**; however, to our surprise, further substitution of the monosubstituted product **5** was not detected even when 10 equiv. of **4a** was added. Complex **5** was characterized by NMR spectroscopy, ESI-MS, and combustion analysis together with its single crystal X-ray analysis. The ^{1}H NMR spectrum of **5** in $CDCl_3$ exhibited five singlets due to magnetically nonequivalent acetate protons at δ 1.67, 1.76, 1.82, 2.38, and 2.40 in a 2 : 1 : 1 : 2 : 1 integral ratio. Proton signals assignable to two ^{i}Pr groups bound to the nitrogen atom of the guanidinate ligand were observed as two doublets at δ 0.74 and 0.77 ($^3J_{HH}$ = 6.8 Hz), indicating that rotation around the $(^iPr)_2N\text{–}C(NAr)_2$ bond was locked in solution at 30 °C. These two doublets gradually coalesced as the temperature was increased, and a doublet at δ 0.80 was observed at 60 °C. The activation energy ($\Delta G^{\ddagger}$ = 16.9 kcal mol^{-1} at 30 °C) of rotation of the $(^iPr)_2N\text{–}C(NAr)_2$ bond was estimated by NMR shape analysis at varying temperatures (Fig. S1†). Hindered rotation of the N–C bond of a guanidinate ligand bridged to a Rh_2 unit was reported by Turro *et al*.[28] Fig. 1 shows the molecular structure of **5**, in which the guanidinate ligand coordinates to the in-plane side of the Pt_4 core. The mean Pt–N distance (2.11 Å) is shorter than that (2.17 Å) of **2a** due to a stronger donative nature of the guanidinate ligand. Notably, the sp^2 nature of the nitrogen atom in the guanidinate ligand is decreased as indicated by smaller values for the sum (ϕ) of the angles around the nitrogen atom in **5** (355.0° and 357.8°) than in **2a** (359.4° and 358.5°),[26b] presumably due to the steric hindrance between tolyl groups and a bulky $N(^iPr)_2$ group attached to the central carbon of the NCN moiety in **5**. This deviation around the nitrogen atoms of the guanidinate ligand leads to the distortion of the planar geometry of the Pt_4 core, resulting in a smaller value of the sum (θ) of the internal angles of the Pt_4 square in **5** (355.8°). The mean Pt–^{eq}O bond distance (2.23 Å) between the oxygen atom of the *trans*-positioned acetate and each platinum atom is longer by 0.06 Å than that (2.17 Å) between the oxygen atom of the *cis*-positioned acetate and each platinum atom, due to a *trans*-influence of the guanidinate ligand through the Pt–Pt bond.[26b]

In contrast to the successful synthesis of **5**, treatment of **1** with 4 equiv. of triphenylguanidine **4b** resulted in a 64 : 36 mixture of monosubstituted complex **6** and *trans*-disubstituted complex **7**, and no product could be separated (Scheme 1). The second substitution of a stronger donative guanidinate ligand to the Pt_4 core did not complete, even in the presence of an excess of **4b**, presumably due to the *trans*-effect of the guanidinate ligand rather than steric effects. In fact, we previously reported that the reaction of **1** with excess amounts of amidines selectively afforded *trans*-disubstituted products **3**.[26b] Furthermore, the reaction of **1** with a cyclic guanidine, 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-α]pyrimidine (**4c**), which is a highly donative ligand used for paddle-wheel type dinuclear complexes,[29] resulted in decomposition.

We conducted substitution reactions of **5** with 2,6-dimethylbenzoic acid and *N*,*N*′-(*p*-aryl)formamidine **10a–c** to competitively replace the guanidinate ligand and in-plane acetate ligands of **5** (Scheme 2). When excess amounts of 2,6-dimethylbenzoic acid were added to **5**, a trisubstituted complex **8** bearing the guanidinate ligand and a tetrasubstituted complex **9**, in which four 2,6-dimethylbenzoic acids were located in-plane of the square Pt_4 core and there was no guanidinate ligand, were obtained in an 87 : 13 ratio. Its ^{1}H NMR spectrum displayed a new set of signals centered at δ 1.68, 1.76, and 1.80 due to ^{ax}OAc with a 2 : 1 : 1 integral ratio, assignable to complex **8**, and a singlet at δ 2.06 due to ^{ax}OAc of **9** together with signals due to the dissociated guanidine **4a**. Because the major product was **8**, the guanidinate ligand of **5** was too inert for a substitution reaction with 2,6-dimethylbenzoic acid compared with in-plane acetates. When 1 equiv. of amidine *N*,*N*′-(*p*-tolyl)formamidine (**10a**) was added to **5**, the guanidinate ligand **4a** was gradually dissociated to give an 83 : 17 mixture of mono(amidinate) complex **2a** and *trans*-bis(amidinate) complex **3a**. Similarly, the reaction of **5** with



Scheme 1 Reactions of **1** with some guanidines.

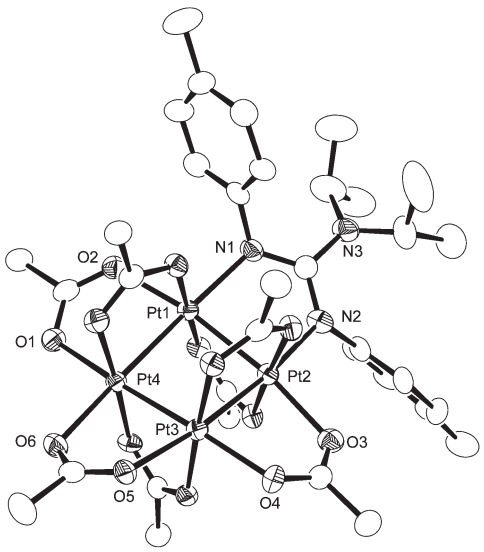
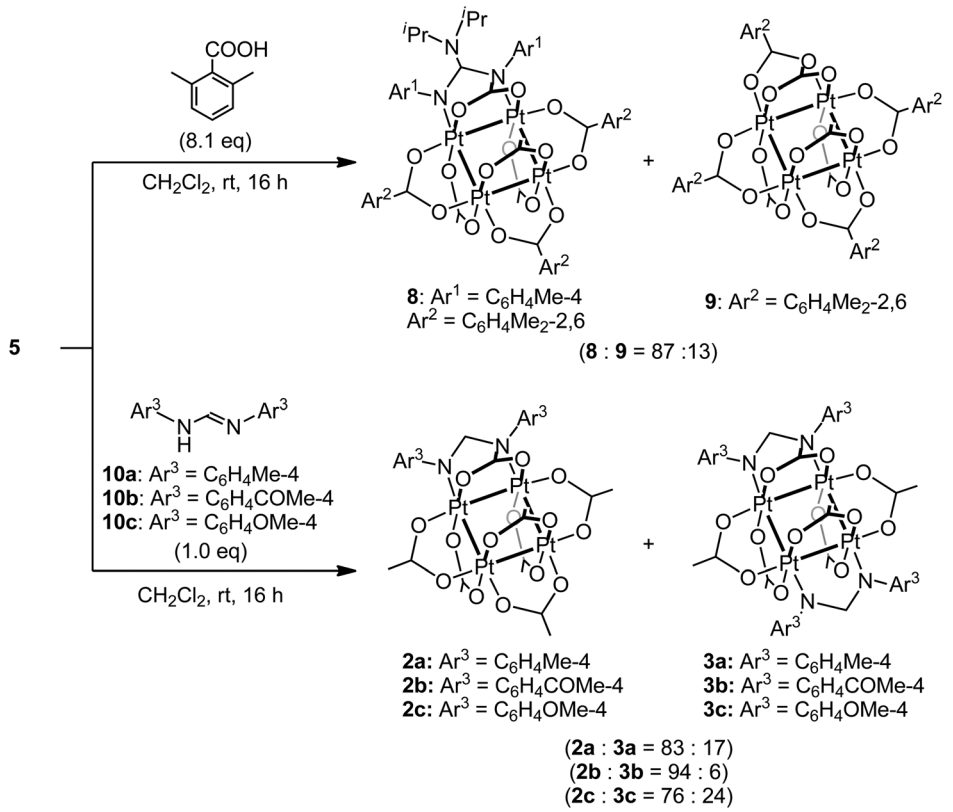


Fig. 1 Molecular structure of complex **5**. Hydrogen atoms and a hexane molecule are omitted for clarity.

N,N′-bis(*p*-acetylphenyl)formamidine (**10b**) afforded the corresponding mono(amidinate) complex **2b** and *trans*-bis(amidinate) complex **3b** in a 94 : 6 ratio, and that with *N,N′*-bis(*p*-anisyl)formamidine (**10c**) gave **2c** and **3c** in a 76 : 24 ratio.

Notably, the reaction of **5** with *N,N′*-bis(*p*-acetylphenyl)formamidine **10b** provided direct information about the mechanism of the substitution reaction of **5** with amidines. Monitoring the reaction of **5** with 1 equiv. of **10b** in $CDCl_3$ by ^{1}H NMR spectroscopy, a mixed ligand guanidinate–amidinate complex, $[Pt_4(\mu\text{-}OCOCH_3)_6(\mu\text{-}(Ar^1N)_2CN^iPr_2)(\mu\text{-}Ar^2NCNAr^2)]$ (**11**: $Ar^1 = C_6H_4Me$-4, $Ar^2 = C_6H_4COMe$-4), was immediately generated based on its ^{1}H NMR spectrum that displayed a new set of signals assignable to acetate ligands at δ 1.59, 1.67, 1.72, and 2.35 ppm in a 2 : 1 : 1 : 2 ratio together with a singlet at δ 2.12 due to free acetic acid, and these transient signals gradually decreased with an increase of the two sets of signals assignable to the known mono(amidinate) complex **2b** and free guanidine **4a** (Fig. 2). This observation clearly indicated that complex **11** was a key intermediate that further reacted with the *in situ*-generated acetic acid to give the mono(amidinate) complex **2** (Scheme 3) through the stepwise substitution reaction mechanism. The formation of **2b** was the consequence of the more labile nature of the guanidinate ligand in the intermediate **11** than that of the amidinate ligand located on the *trans*-side of the Pt_4 core, with the guanidinate ligand acting as a labile group.[26b]

The stepwise and selective substitution reaction of **5** with amidine ligands allowed us to prepare a dimer of the Pt_4 cluster using a linker bearing bis(amidinate) moieties. Complex **5** gradually reacted with a bis(amidine) ligand, $N^4,N^4,N^{4'},N^{4'}$-tetrakis(*p*-(*tert*-butyl)phenyl)-[1,1′-biphenyl]-4,4′-dicarboxamidine (**12**), which was derived from 4,4′-biphenyldicarboxylic acid according to a reported procedure,[30] and a dimer



Scheme 2 Substitution reactions of **5** with 2,6-dimethylbenzoic acid and amidines.

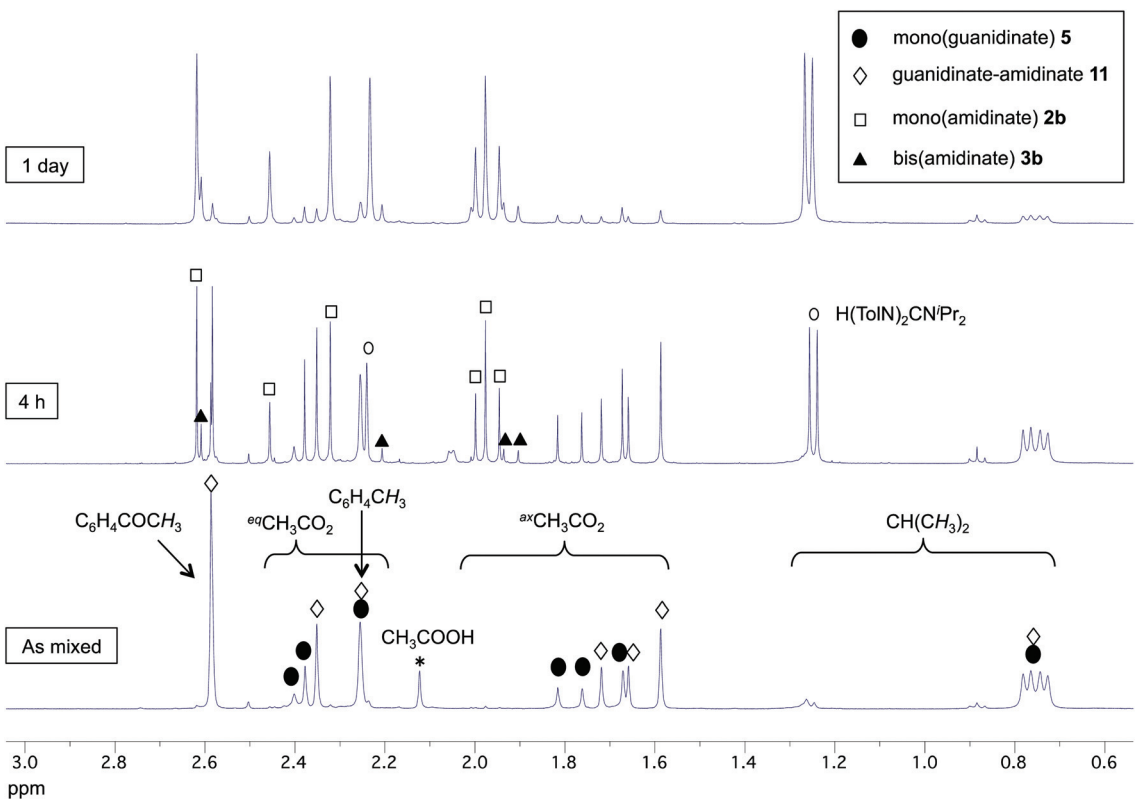
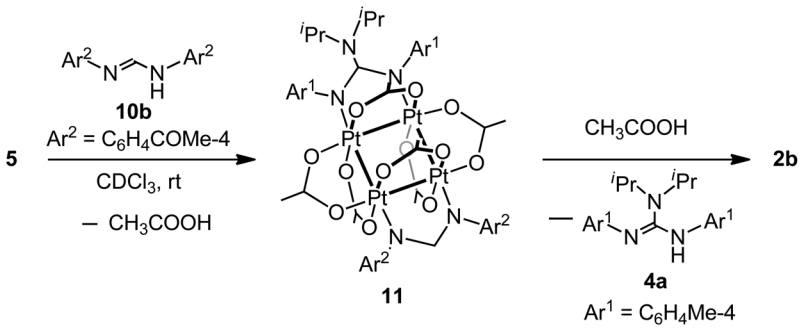


Fig. 2 Reaction of complex **5** with *N*,*N*′-bis(*p*-acetylphenyl)formamidine **10b** in $CDCl_3$ solution monitored by ^1H NMR (400 MHz, 30 °C).



Scheme 3 Mechanism for substitution of guanidinate by amidine.

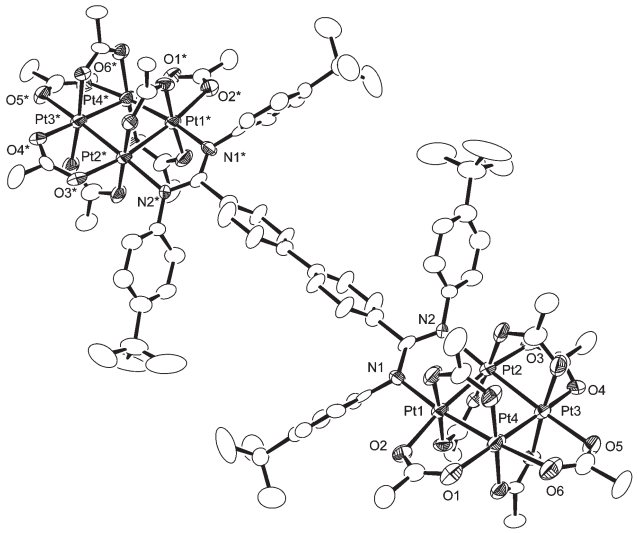
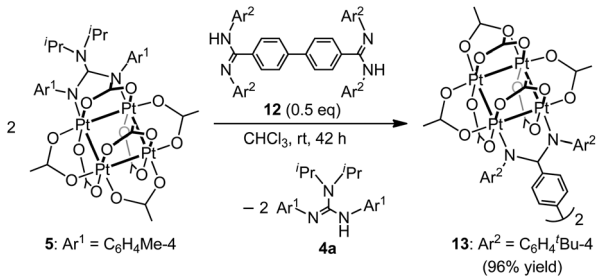


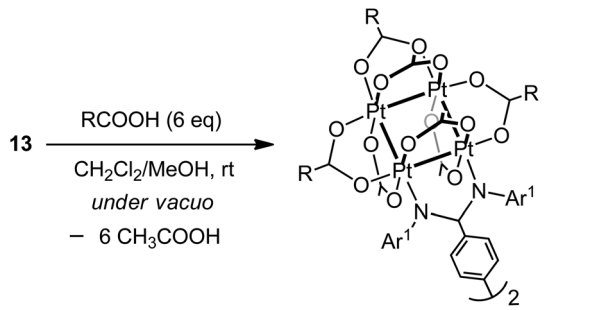
Fig. 3 Molecular structure of complex **13**. Hydrogen atoms, $CHCl_3$ molecules, and an Et_2O molecule are omitted for clarity.

complex $[Pt_4(\mu\text{-}OCOCH_3)_7]_2\text{-}\{\mu\text{-}(ArN)_2C(C_6H_4)_2C(NAr)_2\}$ (**13:** Ar = $C_6H_4{}^tBu$-4) was obtained in 96% yield together with the quantitative dissociation of guanidine **4a** (eqn (1)). The Pt_4 dimer complex **13** was characterized by ^1H, $^{13}C\{^1H\}$ NMR, ESI-MS, combustion analysis, and single crystal X-ray analysis. In the ^1H NMR spectrum of **13**, acetate groups bound to Pt_4 units in **13** were observed as five nonequivalent singlets at δ 1.85, 1.87, 2.02, 2.26, and 2.42 with a 1 : 2 : 1 : 2 : 1 integral ratio, indicating that two Pt_4 cluster units were equivalent in solution and each $[Pt_4(OCOCH_3)_7]^+$ unit had C_s symmetry. The ESI-MS of **13** showed a peak at m/z 3091, which was assignable to $[\mathbf{13}\text{–}OAc]^+$, and its isotopic distribution was in good agreement with the simulated one. Fig. 3 shows the molecular structure of **13**, in which a bis(amidinate) ligand coordinates to the in-plane side of the Pt_4 core, and eventually the two Pt_4 units are connected by the biphenyl linker. Selected geometrical parameters of **13** are listed in Table 1. In the dimer complex **13**, geometries around the Pt_4 core are nearly the same as those of **2a** except for shorter Pt–N distances and a smaller value of the sum (θ) of internal angles of the Pt_4 square. The mean Pt–O^{eq} distance (2.22 Å) of *trans*-positioned acetates is longer than that (2.17 Å) of *cis*-positioned acetates due to the *trans*-influence mediated by the Pt–Pt bond from nitrogen-based bridging ligands, being the same tendency as observed for **2a** and **5**.[26b]



(1)

Because each Pt_4 core of complex **13** has three in-plane acetates, the addition of 6 equiv. of 2,6-dimethylbenzoic acid to the solution of **13** in a mixture of dichloromethane and methanol under reduced pressure gave $[Pt_4(\mu\text{-}OCOCH_3)_4\text{-}(\mu\text{-}OCOC_6H_3Me_2\text{-}2,6)_3]_2\text{-}\{\mu\text{-}(ArN)_2C(C_6H_4)_2C(NAr)_2\}$ (**14:** Ar = $C_6H_4{}^tBu$-4) quantitatively. Similarly, we prepared a 2,4,6-triisopropylbenzoate derivative $[Pt_4(\mu\text{-}OCOCH_3)_4(\mu\text{-}OCOC_6H_2{}^iPr_3\text{-}2,4,6)_3]_2\text{-}\{\mu\text{-}(ArN)_2C(C_6H_4)_2C(NAr)_2\}$ (**15:** Ar = $C_6H_4{}^tBu$-4) and a ferrocenyl derivative $[Pt_4(\mu\text{-}OCOCH_3)_4(\mu\text{-}OCOC_5H_4FeCp)_3]_2\text{-}\{\mu\text{-}(ArN)_2C(C_6H_4)_2C(NAr)_2\}$ (**16:** Ar = $C_6H_4{}^tBu$-4) by a substitution reaction of **13** with 6 equiv. of 2,4,6-triisopropylbenzoic acid and ferrocenecarboxylic acid, respectively. Complexes **14**, **15**, and **16** were characterized by ^1H, $^{13}C\{^1H\}$ NMR, and ESI-MS and combustion analysis for complexes **15** and **16**.



(2)

The electrochemical interaction between the two Pt_4 units was elucidated by the cyclic voltammetry (CV) measurement for complexes **5**, **13**, **14**, **15**, **16** (Fig. 4), and their $E_{1/2}$ values are

Table 1 Selected mean bond distances (Å) and sums of angles (°) in complexes **1**, **2a**, **5**, and **13**

	Pt–Pt	Pt–^{ax}O	Pt–^{eq}O	Pt–N	θ^a	ϕ^b	Ref.
1	2.495	2.002	2.162	—	358.36	—	24*b*
2a	2.512	2.01	2.20 (*cis*), 2.26 (*trans*)	2.17	359.38	359.4, 358.5	26*b*
5	2.505	2.01	2.17 (*cis*), 2.23 (*trans*)	2.11	355.81	354.9, 357.9	This work
13	2.505	2.00	2.17 (*cis*), 2.22 (*trans*)	2.12	357.18	358.3, 359.2	This work

[a] θ = the sum of the internal angles of the Pt_4 square. [b] ϕ = the sum of the angles around the nitrogen atom.

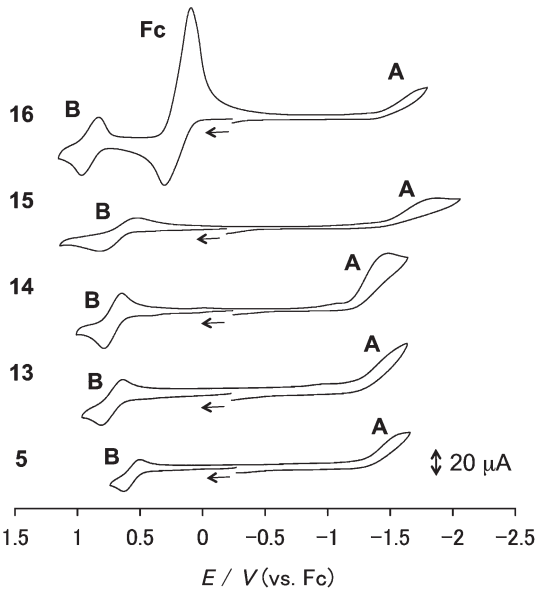


Fig. 4 CVs of **5**, **13**, **14**, **15**, and **16** recorded in 1 mM dichloromethane solution containing 0.1 M of [^{n}Bu$_4$N][PF$_6$] using a scan rate of 100 mV s^{-1}.

Table 2 $E_{1/2}$ (mV *vs.* Fc$^+$/Fc) and ΔE_p (mV) of **2a**, **5**, **13**, **14**, **15**, and **16** determined by CV analysis in 1 mM dichloromethane solution containing 0.1 M of [^{n}Bu$_4$N][PF$_6$]

Complex	**A** (Pt_4^{8+}/Pt_4^{7+})	**Fc** (Fe^{3+}/Fe^{2+})	**B** (Pt_4^{9+}/Pt_4^{8+})	ΔE_p of **B**
2a[26b]	−1470[a]	—[b]	710	100
5	—[c]	—[b]	570	80
13	—[c]	—[b]	720	120
14	−1490[a]	—[b]	720	140
15	−1880[a]	—[b]	690	270
16	—[c]	210	910	130

[a] Irreversible wave: $E_{p.a.}$ value is shown instead of $E_{1/2}$ value. [b] Not observed. [c] Irreversible wave: $E_{p.a.}$ value was not determined from the observed wave.

listed in Table 2. The CV of mono(guanidinate)tetraplatinum complex **5** exhibited an irreversible reduction process **A** assignable to Pt_4^{8+}/Pt_4^{7+} and a reversible oxidation process **B** due to Pt_4^{9+}/Pt_4^{8+}. The $E_{1/2}$ value (570 mV) of process **B** was negatively shifted by 140 mV from that of mono(amidinate)tetraplatinum complex **2a** due to the stronger electron donative nature of the guanidinate ligand. The Pt_4 dimer complexes **13** also showed an irreversible reduction process **A** and a reversible oxidation process **B**, whose $E_{1/2}$ value (720 mV) was comparable to that (710 mV) of mono(amidinate) complex **2a**. Similarly, the CV of complex **14** displayed a reversible oxidation process **B** at $E_{1/2}$ = 720 mV together with an irreversible reduction process **A**. In the CV of complex **15**, an oxidation process of Pt_4 units (**B**) was observed as a broader wave compared with that of **13**. In fact, the difference between the oxidation and reduction peak (ΔE_p) of process **B** was larger (270 mV) for **15** than that (120 mV) for **13**, indicating that electrochemical reversibility of the redox event at the Pt_4 unit in **15** was decreased due to the incorporation of bulky triisopropylphenyl groups on the in-plane sides of the Pt_4 units. The CV of complex **16** displayed an oxidation process labeled as **Fc** assignable to one electron oxidation of six Fc units (Fe^{2+}/Fe^{3+}) along with process **B**. The $E_{1/2}$ value (910 mV) of process **B** was positively shifted by 190 mV from the parent complex **13** due to an electron withdrawing effect of oxidized Fc units. A notable feature of the CV of **16** was the large reduction and oxidation peak current ratio of process **Fc**, which was attributed to the deposition of multiply charged species on the working electrode. Similar phenomena were also observed in other poly ferrocenyl complexes.[31] The electron number in process **B** was assigned to two electrons on the basis of the ratio of oxidation currents of process **B** and process **Fc**. Thus, two Pt_4 units in a Pt_4 dimer complex were oxidized independently without the formation of any intermediate one-electron oxidized species.

Conclusion

In summary, we successfully prepared the mono(guanidinate)-tetraplatinum complex **5**, in which a guanidinate ligand was selectively substituted by amidine ligands in a unique stepwise substitution sequence through the guanidinate–amidinate Pt_4 complex **11**. The Pt_4 dimer complex **13** was obtained in good yield by treating **5** with 0.5 equiv. of a bis(amidine) linker ligand **12**. In the Pt_4 dimer complex **13**, six in-plane acetate ligands were found to be labile so that further substitution by benzoic acid derivatives and ferrocenecarboxylic acid proceeded while maintaining its dimer structure, giving Pt_4 dimer derivatives **14–16**. The electrochemical measurement revealed the reversible oxidation process of Pt_4 dimer complexes **13–16** due to Pt_4^{9+}/Pt_4^{8+}. In addition, a multielectron oxidation process due to Fe^{3+}/Fe^{2+} of six ferrocenyl units was observed for hexaferrocenyl derivative **16**, but there was no electronic communication between the two Pt_4 centers or the Fc unit.

Experimental section

General procedures

All manipulations involving air- and moisture-sensitive compounds were carried out under argon using standard Schlenk techniques or in an argon-filled glovebox. $[Pt_4(\mu\text{-}OCOCH_3)_8]$ (**1**)[25a] and *N,N′*-bis(aryl)formamidine[32] were prepared according to literature procedures. 2,6-Dimethylbenzoic acid, 2,4,6-triisopropylbenzoic acid, and ferrocenecarboxylic acid were purchased and used as received. Dehydrated hexane, Et_2O, and CH_2Cl_2 were purchased from Kanto Chemical and further purified by passage through activated alumina under positive argon pressure as described by Grubbs *et al.*[33] Dehydrated MeOH, CD_3OD, $CHCl_3$, $CDCl_3$, and DMSO-d_6 were degassed and stored under argon over activated 3 Å (MeOH and CD_3OD) and 4 Å ($CHCl_3$, $CDCl_3$, and DMSO-d_6) molecular sieves. ^1H NMR (400 MHz) and $^{13}C\{^1H\}$ NMR (100 MHz) were measured on Bruker AVANCEIII-400 spectrometers, and all spectra were recorded at 30 °C or 35 °C unless mentioned otherwise and referenced to an internal solvent. Cyclic voltammograms were recorded using an electrochemical analyzer (Model 610D, ALS/CH Instruments) at room temperature in a 0.1 M $[^nBu_4N][PF_6]$ solution in CH_2Cl_2 with a glassy carbon working electrode, a platinum wire auxiliary electrode, a saturated calomel reference electrode (SCE), and a scan rate of 100 mV s^{-1}. Elemental analyses were recorded on a Perkin-Elmer 2400II microanalyzer in the Department of Chemistry, Faculty of Engineering Science, Osaka University. Mass spectrometric data were obtained using ESI or FAB techniques (on a JEOL SX-102 spectrometer) or ESI techniques (on a BRUKER micrOTOF spectrometer). Melting points were measured in sealed tubes and were not corrected.

Preparation of *N,N′*–bis(*p*-tolyl)-*N″*-diisopropylguanidine (4a). To a solution of diisopropylamine (0.950 mL, 6.72 mmol) in THF (10 mL) at −78 °C was dropwise added ^{n}BuLi (1.57 M solution in hexane, 4.30 mL, 6.75 mmol, 1.0 equiv.). After stirring for 1 hour at ambient temperature, this solution was added to a solution of *N,N′*-bis(*p*-tolyl)carbodiimide (1.57 g, 6.78 mmol, 1.0 equiv.) in THF (15 mL) at −78 °C, giving a green suspension. The cold bath was removed and the reaction mixture was stirred at ambient temperature for 14 hours. During this operation, precipitated solids were dissolved and the reaction mixture turned to a green solution. The removal of volatiles under vacuum afforded a yellow-green oil, which was washed with hexane to give the lithium salt of **4a** as a light yellow powder. A mixture of toluene (10 mL) and deionized water (10 mL) was added to this powder, and the resulting suspension was stirred for 30 min, followed by separation of the organic layer using a separating funnel, and the water layer was extracted with toluene (10 mL, twice). A combined toluene solution was washed with deionized water (10 mL), and then dried over anhydrous $MgSO_4$. All volatiles were removed under vacuum, and the resulting red oil was washed with hexane (5 mL, three times). **4a** was obtained as a pale red powder (393 mg, 18%), mp 83–84 °C. ^1H NMR (400 MHz, $CDCl_3$, 30 °C, δ/ppm): 1.30 (d, $^3J_{HH}$ = 6.8 Hz, 12H, N(CH(CH_3)$_2$)$_2$), 2.25 (s, 6H, $C_6H_4CH_3$), 3.85 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, N(C*H*(CH_3)$_2$)$_2$), 5.27 (br s, 1H, NH), 6.77 (d, $^3J_{HH}$ = 8.0 Hz, 4H, ArH), 6.98 (d, $^3J_{HH}$ = 8.0 Hz, 4H, ArH). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 30 °C, δ/ppm): 20.6 ($C_6H_4CH_3$), 21.4 (CH(CH_3)$_2$), 47.4 (*C*H(CH_3)$_2$), 120.6, 129.4, 130.7, 149.4 (ArC), a guanidinate carbon was not detected. HRMS-ESI (*m*/*z*): $[M + H]^+$ calcd for $C_{21}H_{30}N_3$, 324.2434; found, 324.2462.

Preparation of $[Pt_4(\mu\text{-}OCOCH_3)_7(\mu\text{-}(TolN)_2CN^iPr_2)]$ (5: Tol = C_6H_4Me-4). The solution of **1** (248 mg, 198 μmol) and **4a** (256 mg, 791 μmol, 4.0 equiv.) in a mixture of CH_2Cl_2 (5 mL) and MeOH (5 mL) was stirred for 16 h at ambient temperature. The resulting deep-red solution was concentrated under vacuum and the residue was washed with a mixture of Et_2O and hexane (5 mL + 5 mL, four times), giving **5** as a reddish-brown powder (200 mg, 67% yield), mp. 179–182 °C (dec.). ^1H NMR (400 MHz, $CDCl_3$, 30 °C, δ/ppm): 0.74 (d, $^3J_{HH}$ = 6.8 Hz, 6H, N(CH(C*H*$_3$)$_2$)$_2$), 0.77 (d, $^3J_{HH}$ = 6.8 Hz, 6H, N(CH-(C*H*$_3$)$_2$)$_2$), 1.67 (s, 6H, $^{ax}CH_3CO_2$), 1.76 (s, 3H, $^{ax}CH_3CO_2$), 1.82 (s, 3H, $^{ax}CH_3CO_2$), 2.25 (s, 6H, $C_6H_4CH_3$), 2.38 (s, 6H, $^{eq}CH_3CO_2$), 2.40 (s, 3H, $^{eq}CH_3CO_2$), 3.91 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, N(C*H*(CH_3)$_2$)$_2$), 4.08 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, N(C*H*-(CH_3)$_2$)$_2$), 7.07 (br d, 4H, $C_6H_4CH_3$), 7.20 (br s, 4H, $C_6H_4CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 35 °C, δ/ppm): 20.9 ($^{ax}CH_3CO_2$), 21.1 ($C_6H_4CH_3$), 21.2 ($^{ax}CH_3CO_2$), 21.9$_9$, 22.0$_3$ (N(CH(*C*H$_3$)$_2$)$_2$), 22.2 ($^{ax}CH_3CO_2$), 22.4, 22.6 ($^{eq}CH_3CO_2$), 52.1, 52.6 (N(*C*H(CH_3)$_2$)$_2$) 128.6, 133.1, 146.3, 168.1 (ArC), 182.5, 186.9, 192.3, 192.5 (CH_3CO_2), one carboxylate carbon (CH_3CO_2) was overlapped with another carbon, and a guanidinate carbon was not detected. MS (ESI positive, CH_3CN, *m*/*z*): 1456 ($[M - CH_3COO]^+$). Elemental analysis calcd (%) for $C_{35}H_{49}N_3O_{14}Pt_4$: C 27.73, H 3.26, N 2.77; found: C 27.79, H 2.99, N 2.80.

Preparation of $N^4,N^{4'}$-bis(*p*-(*tert*-butyl)phenyl)-[1,1′-biphenyl]-4,4′-dicarboxamide. To the mixture of 4,4′-biphenyldicarboxylic acid (1.33 g, 5.50 mmol), triethylamine (2 mL, 0.01 mol, 3 equiv.), *p*-*tert*-butylaniline (1.80 mL, 11.4 mmol, 2.1 equiv.) and *p*-*N*,*N*-dimethylaminopyridine (1.35 g, 11.1 mmol, 2.0 equiv.) in DMF (100 mL) was added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (2.21 g, 11.6 mmol, 2.1 equiv.) at 0 °C, giving a pale red solution. After stirring at ambient temperature for 3 days, the reaction mixture turned to an orange suspension, which was concentrated under reduced pressure. CH_2Cl_2 (50 mL) and H_2O (50 mL) were added to the resulting solid, giving an orange suspension, from which an insoluble white solid was separated by filtration. The white powder was washed with H_2O and then dried under vacuum. The title compound was obtained as a white powder (1.07 g, 39%), mp >300 °C. ^1H NMR (400 MHz, DMSO-d_6, 30 °C, δ/ppm): 1.29 (s, 18H, C(CH_3)$_3$), 7.38 (d, $^3J_{HH}$ = 8.8 Hz, 4H, ArH), 7.72 (d, $^3J_{HH}$ = 8.8 Hz, 4H, ArH), 7.93 (d, $^3J_{HH}$ = 8.6 Hz, 4H, ArH), 8.10 (d, $^3J_{HH}$ = 8.6 Hz, 4H, ArH), 10.25 (s, 2H, CONH). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 30 °C, δ/ppm): 31.2 ($C_6H_4C(CH_3)_3$), 34.0 (C_6H_4C(CH_3)$_3$), 120.2, 125.2, 126.8, 128.4, 134.3, 136.5, 141.9, 146.0 (ArC), 164.8 (CONH). HRMS-FAB (*m*/*z*): $[M + H]^+$ calcd for $C_{34}H_{37}N_2O_2$, 505.2855; found, 505.2883.

Preparation of $N^4,N^4,N^{4'},N^{4'}$-tetrakis(*p*-(*tert*-butyl)phenyl)-[1,1′-biphenyl]-4,4′-dicarboxamidine (12). An 80 mL Schlenk tube charged with $N^4,N^{4'}$-bis(*p*-(*tert*-butyl)phenyl)-[1,1′-biphenyl]-4,4′-dicarboxamide (492 mg, 975 μmol) and $SOCl_2$ (10 mL) was heated at 60 °C for 6 h. After removal of volatile compounds *in vacuo*, the resulting yellow solid was treated with *p*-*tert*-butylaniline (0.320 mL, 2.01 mmol, 2.1 equiv.) in toluene (50 mL). The reaction mixture was refluxed for 17 h. After cooling, saturated Na_2CO_3 aq. (20 mL) was added to the yellow suspension. The yellow solid was separated by filtration and washed with $CHCl_3$. **12** was obtained as a yellow powder (140 mg, 19%), mp 168–171 °C. ^{1}H NMR (400 MHz, CD_3OD, 60 °C, δ/ppm): 1.28 (br s, 36H, $C(CH_3)_3$), 7.20 (br d, 8H, ArH), 7.39 (br d, 8H, ArH), 7.90 (br s, 8H, ArH). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3OD, 60 °C, δ/ppm): 31.6 ($C(CH_3)_3$), 35.5 ($C(CH_3)_3$), 125.8, 127.5, 128.9, 130.2, 132.0, 134.2, 145.4, 152.9 (ArC), 163.2 (N*C*RN). HRMS-ESI (*m*/*z*): $[M + H]^+$ calcd for $C_{54}H_{63}N_4$, 767.5047; found, 767.5056.

Preparation of $[Pt_4(\mu\text{-}OCOCH_3)_7]_2$-{μ-(ArN)$_2$C(C$_6H_4$)$_2$C(NAr)$_2$} (13: Ar = C$_6H_4$^{t}Bu-4). The mixture of **5** (92.4 mg, 609 μmol) and **12** (23.5 mg, 30.6 μmol, 0.50 equiv.) in $CHCl_3$ (5 mL) was stirred for 42 hours at ambient temperature. After the removal of volatile compounds under reduced pressure, the resulting dark-red powders were washed with MeOH (5 mL, twice). Complex **13** was obtained as a brown powder (92.2 mg, 96%), mp 190–193 °C (dec.). ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C, δ/ppm): 1.17 (s, 36H, $-C_6H_4C(CH_3)_3$), 1.85 (s, 6H, $^{ax}CH_3CO_2$), 1.87 (s, 12H, $^{ax}CH_3CO_2$), 2.02 (s, 6H, $^{ax}CH_3CO_2$), 2.26 (s, 12H, $^{eq}CH_3CO_2$), 2.42 (s, 6H, $^{eq}CH_3CO_2$), 6.91 (d like, 12H, $C_6H_4C(CH_3)_3$ + $(C_6H_4)_2$), 7.02 (d like, 12H, $C_6H_4C(CH_3)_3$ + $(C_6H_4)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 30 °C, δ/ppm): 21.2, 21.3, 21.6 ($^{ax}CH_3CO_2$), 22.2, 22.7 ($^{eq}CH_3CO_2$), 31.3 ($C(CH_3)_3$), 34.3 ($C(CH_3)_3$), 124.6, 125.3, 127.6, 130.8, 133.1, 139.4, 144.7, 146.4 (ArC), 171.9 (N*C*RN), 183.8, 186.7 ($^{eq}CH_3CO_2$), 192.3, 192.5, 193.0 ($^{ax}CH_3CO_2$). MS (ESI positive, CH_3CN, *m*/*z*): 3150 ($[M]^+$), 3091 ($[M - CH_3COO]^+$). Anal. calcd for $C_{82}H_{102}N_4O_{28}Pt_8$: C 31.24, H 3.26, N 1.78; found: C 31.22, H 3.48, N 1.89.

Preparation of $[Pt_4(\mu\text{-}OCOCH_3)_4(\mu\text{-}OCOC_6H_3Me_2\text{-}2,6)_3]_2$-{μ-(ArN)$_2$C(C$_6H_4$)$_2$C(NAr)$_2$} (14: Ar = C$_6H_4$^{t}Bu-4), $[Pt_4(\mu\text{-}OCOCH_3)_4(\mu\text{-}OCOC_6H_2{}^iPr_3\text{-}2,4,6)_3]_2$-{μ-(ArN)$_2$C(C$_6H_4$)$_2$C(NAr)$_2$} (15: Ar = C$_6H_4$^{t}Bu-4), and $[Pt_4(\mu\text{-}OCOCH_3)_4(\mu\text{-}OCOC_5H_4FeCp)_3]_2$-{μ-(ArN)$_2$C(C$_6H_4$)$_2$C(NAr)$_2$} (16: Ar = C$_6H_4$^{t}Bu-4). The mixture of **13** (30.8 mg, 609 μmol) and 2,6-dimethylbenzoic acid (9.2 mg, 59 μmol, 6.1 equiv.) in a mixture of CH_2Cl_2 (5 mL) and MeOH (3 mL) was stirred for 6 hours at ambient temperature under partially reduced pressure. During this operation, a mixture of $CHCl_3$ (5 mL) and MeOH (5 mL) was repeatedly added before all volatiles were removed. The removal of all volatiles afforded dark red solids, which were washed with Et_2O. **14** was obtained as a brown powder (37.6 mg, quant.), mp 184–187 °C (dec.). ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C, δ/ppm): 1.09 (s, 36H, $C_6H_4C(CH_3)_3$), 1.91 (s, 6H, $^{ax}CH_3CO_2$), 1.93 (s, 12H, $^{ax}CH_3CO_2$), 2.07 (s, 6H, $^{ax}CH_3CO_2$), 2.13 (s, 24H, $C_6H_3(CH_3)_2$), 2.36 (s, 12H, $C_6H_3(CH_3)_2$), 6.87–6.95 (m, 32H, ArH), 7.01–7.06 (m, 10H, ArH). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 30 °C, δ/ppm): 19.5, 20.0 ($C_6H_3(CH_3)_2$), 21.0, 21.4 ($^{ax}CH_3CO_2$), 31.2 ($C(CH_3)_3$), 34.2 ($C(CH_3)_3$), 124.7, 125.3, 126.9, 127.0, 127.4, 127.6, 128.0, 130.7, 132.8, 133.9, 134.9, 135.1, 137.4, 139.2, 144.9, 146.3 (ArC), 172.0 (N*C*RN), 181.7, 184.2 ($^{eq}ArCO_2$), 192.2, 192.4, 192.9 ($^{ax}CH_3CO_2$), one methyl carbon ($^{ax}CH_3CO_2$) was overlapped with another carbon.

Complexes **15** and **16** were prepared in a similar manner. **15**: a dark red powder (63% yield), mp 206–210 °C (dec.). ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C, δ/ppm): 0.98 (s, 36H, $-C_6H_4C(CH_3)_3$), 1.13 (br d, $^3J_{HH}$ = 6.8 Hz, 48H, $-C_6H_2(CH(CH_3)_2)_3$), 1.18 (d, $^3J_{HH}$ = 6.8 Hz, 12H, $-C_6H_2(CH(CH_3)_2)_3$), 1.19 (d, $^3J_{HH}$ = 6.8 Hz, 24H, $-C_6H_2(CH(CH_3)_2)_3$), 1.22 (d, $^3J_{HH}$ = 6.8 Hz, 24H, $-C_6H_2(CH(CH_3)_2)_3$), 1.85 (s, 6H, $^{ax}CH_3CO_2$), 1.88 (s, 12H, $^{ax}CH_3CO_2$), 2.00 (s, 6H, $^{ax}CH_3CO_2$), 2.82 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, $C_6H_2(CH(CH_3)_2)_3$), 2.84 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, $C_6H_2(CH(CH_3)_2)_3$), 2.96 (br s, 8H, $C_6H_2(CH(CH_3)_2)_3$), 3.15 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, $C_6H_2(CH(CH_3)_2)_3$), 6.83 (d, $^3J_{HH}$ = 8.8 Hz, 8H, $C_6H_4C(CH_3)_3$), 6.86 (d, $^3J_{HH}$ = 8.8 Hz, 8H, $C_6H_4C(CH_3)_3$), 6.87 (s, 12H, $C_6H_2(CH(CH_3)_2)_3$), 6.97 (d, $^3J_{HH}$ = 8.8 Hz, 4H, $(C_6H_4)_2$), 7.08–7.14 (m, 4H, $(C_6H_4)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 30 °C, δ/ppm): 20.5_6, 20.6_2, 21.2 ($^{ax}CH_3CO_2$), 24.0_5, 24.0_6, 24.1, 24.2 ($CH(CH_3)_2$), 30.8 ($CH(CH_3)_2$), 31.1 ($C(CH_3)_3$), 34.3_7, 34.4_0 ($CH(CH_3)_2$), 34.1 ($C(CH_3)_3$), 119.8, 119.9, 124.6, 125.4, 127.4, 130.9, 133.1, 134.1, 139.2, 143.4, 143.7, 144.8, 145.9, 147.9, 148.1 (ArC), 171.2 (N*C*RN), 182.7, 185.5 ($^{eq}ArCO_2$), 191.8, 191.9, 192.6 ($^{ax}CH_3CO_2$), one isopropyl carbon (*C*H-$(CH_3)_2$) and one aryl carbon were overlapped with another carbon. MS (ESI positive, CH_3CN, *m*/*z*): 4304 ($[M + Na]^+$), 4032 ($[M - O_2CC_6H_2{}^iPr_3]^+$). Elemental analysis calcd (%) for $C_{166}H_{222}N_4O_{28}Pt_8$: C 46.56, H 5.23, N 1.31; found: C 46.18, H 5.23, N 1.33.

16: an orange powder (90% yield), mp 192–196 °C (dec.). ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C, δ/ppm): 1.33 (s, 36H, $-C_6H_4C(CH_3)_3$), 1.94 (s, 6H, $^{ax}CH_3CO_2$), 2.04 (s, 12H, $^{ax}CH_3CO_2$), 2.13 (s, 6H, $^{ax}CH_3CO_2$), 4.08 (s, 20H, CpH), 4.22 (br s, 4H, C_5H_4), 4.24 (br s, 4H, C_5H_4), 4.26 (s, 10H, CpH), 4.36 (br s, 4H, C_5H_4), 4.57 (br s, 4H, C_5H_4), 4.81 (br s, 4H, C_5H_4), 5.17 (br s, 4H, C_5H_4), 7.02 (br d, $^3J_{HH}$ = 8.4 Hz, 16H, $C_6H_4C(CH_3)_3$, +$(C_6H_4)_2$), 7.22 (d, $^3J_{HH}$ = 8.4 Hz, 8H, $C_6H_4C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 30 °C, δ/ppm): 21.6, 21.7, 21.9 ($^{ax}CH_3CO_2$), 31.5 ($C(CH_3)_3$), 34.4 ($C(CH_3)_3$), 70.0, 70.1 (CpC), 70.5_8, 70.6_0, 70.7, 70.9, 71.6, 71.8, 72.3, 73.9 (C_5H_4), 124.8, 125.2, 127.9, 130.3, 132.7, 139.2, 144.9, 146.2 (ArC), 171.6 (N*C*RN), 182.8, 185.2 ($FcCO_2$), 192.0, 192.2, 193.0 ($^{ax}CH_3CO_2$). MS (ESI positive, CH_3CN, *m*/*z*): 4172 ($[M]^+$), 3942 ($[M - O_2CC_5H_4FeCp]^+$). Elemental analysis calcd (%) for $C_{136}H_{138}Fe_6N_4O_{28}Pt_8$: C 39.15, H 3.33, N 1.34; found: C 39.16, H 2.89, N 1.49.

X-ray crystallographic analysis

A crystal of **5** (red, block) was grown in the saturated diethyl ether–hexane mixed solution, and a crystal of **13** (red, platelet) was obtained *via* diffusion of diethyl ether into the chloroform solution. Both crystals were mounted on the CryoLoop (Hampton ReseArCh Corp.) with a layer of mineral oil and placed in a nitrogen stream. Complexes **5** and **13** were measured with a Rigaku RAXIS-RAPID Imaging Plate equipped

with a sealed tube X-ray generator (50 kV, 40 mA) with graphite monochromated Mo-Kα (0.71075 Å) radiation in a nitrogen stream at 113(1) K. The unit cell parameters and the orientation matrix for data collection were determined by the least-squares refinement with the setting angles, which are listed in Table S1.† The structures of the two complexes were solved by direct methods on SIR97,[34] after being refined on F^2 by full-matrix least-squares methods using SHELXL-97.[35] Measured nonequivalent reflections with $I > 2.0\sigma(I)$ were used for the structure determination. The hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\Sigma w(F_o^2 - F_c^2)]$ ($w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$), where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$ with $\sigma^2(F_o^2)$ from counting statistics. The functions R_1 and wR_2 were $(\Sigma||F_o| - |F_c||)/\Sigma|F_o|$ and $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^4)]^{1/2}$, respectively. R values of **13** were relatively high because the crystal of **13** contained disordered solvent molecules. Refinement of these molecules was unsuccessful. The ORTEP-3 program was used to draw two molecules.[36] CCDC-901346 (**5**) and 910750 (**13**) contain the supplementary crystallographic data for this paper.

References

1 J.-M. Lehn, *Supramolecular Chemistry, Concepts and Perspectives*, Wiley-VCH, Weinheim, 1995.
2 R. S. Forgan, J.-P. Sauvage and J. F. Stoddart, *Chem. Rev.*, 2011, **111**, 5434–5464.
3 (*a*) Y. Inokuma, M. Kawano and M. Fujita, *Nat. Chem.*, 2011, **3**, 349–358; (*b*) M. Yoshizawa, J. K. Klosterman and M. Fujita, *Angew. Chem., Int. Ed.*, 2009, **48**, 3418–3438; (*c*) M. Kawano and M. Fujita, *Coord. Chem. Rev.*, 2007, **251**, 2592–2605; (*d*) M. Fujita, M. Tominaga, A. Hori and B. Therrien, *Acc. Chem. Res.*, 2005, **38**, 371–380; (*e*) M. Fujita, *Acc. Chem. Res.*, 1999, **32**, 53–61.
4 (*a*) R. Chakrabarty, P. S. Mukherjee and P. J. Stang, *Chem. Rev.*, 2011, **111**, 6810–6918; (*b*) B. H. Northrop, Y.-R. Zheng, K.-W. Chi and P. J. Stang, *Acc. Chem. Res.*, 2009, **42**, 1554–1563; (*c*) S. R. Seidel and P. J. Stang, *Acc. Chem. Res.*, 2002, **35**, 972–983; (*d*) S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853–908; (*e*) P. J. Stang and B. Olenyuk, *Acc. Chem. Res.*, 1997, **30**, 502–518.
5 (*a*) F. Hof, S. L. Craig, C. Nuckolls and J. Rebek Jr., *Angew. Chem., Int. Ed.*, 2002, **41**, 1488–1508; (*b*) M. M. Conn and J. Rebek Jr., *Chem. Rev.*, 1997, **97**, 1647–1668.
6 (*a*) D. Fiedler, D. H. Leung, R. G. Bergman and K. N. Raymond, *Acc. Chem. Res.*, 2005, **38**, 349–358; (*b*) D. L. Caulder and K. N. Raymond, *Acc. Chem. Res.*, 1999, **32**, 975–982.
7 C. J. Jones, *Chem. Soc. Rev.*, 1998, **27**, 289–299.
8 D. J. Tranchemontagne, Z. Ni, M. O'Keeffe and O. M. Yaghi, *Angew. Chem., Int. Ed.*, 2008, **47**, 2–14.
9 F. A. Cotton, C. Lin and C. A. Murillo, *Acc. Chem. Res.*, 2001, **34**, 759–771.
10 M. W. Cooke and G. S. Hanan, *Chem. Soc. Rev.*, 2007, **36**, 1466–1476.
11 M. Köberl, M. Cokoja, W. A. Herrmann and F. E. Kühn, *Dalton Trans.*, 2011, **40**, 6834–6859.
12 (*a*) R. H. Cayton and M. H. Chisholm, *J. Am. Chem. Soc.*, 1989, **111**, 8921–8923; (*b*) R. H. Cayton, M. H. Chisholm, J. C. Huffman and E. B. Lobkovsky, *J. Am. Chem. Soc.*, 1991, **113**, 8709–8724; (*c*) R. H. Cayton, M. H. Chisholm, J. C. Huffman and E. B. Lobkovsky, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 862–864.
13 M. Köberl, M. Cokoja, B. Bechlars, E. Herdtweck and F. E. Kühn, *Dalton Trans.*, 2011, **40**, 11490–11496.
14 (*a*) H. Kido, H. Nagino and T. Ito, *Chem. Lett.*, 1996, 745–746; (*b*) T. Ito, T. Hamaguchi, H. Nagino, T. Yamaguchi, J. Washington and C. P. Kubiak, *Science*, 1997, **277**, 660–663; (*c*) T. Ito, T. Hamaguchi, H. Nagino, T. Yamaguchi, H. Kido, I. S. Zavarine, T. Richmond, J. Washington and C. P. Kubiak, *J. Am. Chem. Soc.*, 1999, **121**, 4625–4632.
15 H. D. Selby, B. K. Roland and Z. Zheng, *Acc. Chem. Res.*, 2003, **36**, 933–944.
16 (*a*) Z. Zheng, J. R. Long and R. H. Holm, *J. Am. Chem. Soc.*, 1997, **119**, 2163–2171; (*b*) Z. Zheng and R. H. Holm, *Inorg. Chem.*, 1997, **36**, 5173–5178; (*c*) Z. Zheng, T. G. Gray and R. H. Holm, *Inorg. Chem.*, 1999, **38**, 4888–4895.
17 P. Braunstein, L. A. Oro and P. R. Raithby, *Metal Clusters in Chemisty*, Wiley-VCH, Weinheim, 1999.
18 R. Bagai and G. Christou, *Chem. Soc. Rev.*, 2009, **38**, 1011–1026.
19 P. Venkateswara Rao and R. H. Holm, *Chem. Rev.*, 2004, **104**, 527–559.
20 R. D. Adams, *J. Organomet. Chem.*, 2000, **600**, 1–6.
21 H. Suzuki, *Eur. J. Inorg. Chem.*, 2002, 1009–1023.
22 P. D. Harvey, Y. Mugnier, D. Lucas, D. Evrard, F. Lemaitre and A. Vallat, *J. Cluster Sci.*, 2004, **15**, 63–90.
23 T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Hefer and G. Wilkinson, *J. Chem. Soc., Chem. Commun.*, 1965, 3632–3640.
24 (*a*) M. A. A. F. DE, C. T. Carrondo and A. C. Skapski, *J. Chem. Soc., Chem. Commun.*, 1976, 410–411; (*b*) M. A. A. F. DE, C. T. Carrondo and A. C. Skapski, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1978, **34**, 1857–1862; (*c*) M. A. A. F. DE, C. T. Carrondo and A. C. Skapski, *Acta Crystallor., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1978, **34**, 3576–3581.
25 (*a*) T. Yamaguchi, Y. Sasaki, A. Nagasawa, T. Ito, N. Koga and K. Morokuma, *Inorg. Chem.*, 1989, **28**, 4311–4312; (*b*) T. Yamaguchi, Y. Sasaki and T. Ito, *J. Am. Chem. Soc.*, 1990, **112**, 4038–4040; (*c*) T. Yamaguchi, T. Ueno and T. Ito, *Inorg. Chem.*, 1993, **32**, 4996–4997; (*d*) T. Yamaguchi, K. Abe and T. Ito, *Inorg. Chem.*, 1994, **33**, 2689–2691; (*e*) T. Yamaguchi, A. Shibata and T. Ito, *J. Chem. Soc., Dalton Trans.*, 1996, 4031–4032; (*f*) T. Yamaguchi, H. Saito, T. Maki and T. Ito, *J. Am. Chem. Soc.*, 1999, **121**, 10738–10742; (*g*) T. Yamaguchi, A. Shibata and T. Ito, *Chem.–Eur. J.*, 2001, **7**, 5409–5418.

26 (*a*) M. Ohashi, A. Yagyu, T. Yamagata and K. Mashima, *Chem. Commun.*, 2007, 3103–3105; (*b*) S. Tanaka, A. Yagyu, M. Kikugawa, M. Ohashi, T. Yamagata and K. Mashima, *Chem.–Eur. J.*, 2011, **17**, 3693–3709.
27 S. Tanaka and K. Mashima, *Inorg. Chem.*, 2011, **50**, 11384–11393.
28 D. A. Lutterman, N. N. Degtyareva, D. H. Johnston, J. C. Gallucci, J. L. Eglin and C. Turro, *Inorg. Chem.*, 2005, **44**, 5388–5396.
29 (*a*) F. A. Cotton, N. E. Gruhn, J. Gu, P. Huang, D. L. Lichtenberger, C. A. Murillo, L. O. Van Dorn and C. C. Wilkinson, *Science*, 2002, **298**, 1971–1974; (*b*) F. A. Cotton, J. P. Donahue, D. L. Lichtenberger, C. A. Murillo and D. Villagrán, *J. Am. Chem. Soc.*, 2005, **127**, 10808–10809; (*c*) K. Holman, S. Robinson, A. Sahajpal and J. Steed, *J. Chem. Soc., Dalton Trans.*, 1999, 15–18; (*d*) F. A. Cotton, J. Gu, C. A. Murillo and D. J. Timmons, *J. Am. Chem. Soc.*, 1998, **120**, 13280–13281; (*e*) J. F. Berry, E. Bothe, F. A. Cotton, S. A. Ibragimov, C. A. Murillo, D. Villagrán and X. Wang, *Inorg. Chem.*, 2006, **45**, 4396–4406; (*f*) R. Clérac, F. A. Cotton, L. M. Daniels, J. P. Donahue, C. A. Murillo and D. J. Timmons, *Inorg. Chem.*, 2000, **39**, 2581–2584; (*g*) G. J. Chuang, W. Wang, E. Lee and T. Ritter, *J. Am. Chem. Soc.*, 2011, **133**, 1760–1762.
30 (*a*) M. R. Detty and G. P. Wood, *J. Org. Chem.*, 1980, **45**, 80–89; (*b*) A. J. Hill and J. V. Johnson, *J. Am. Chem. Soc.*, 1954, **76**, 920–922.
31 M. W. Cooke, T. S. Cameron, K. N. Robertson, J. C. Swarts and M. A. S. Aquino, *Organometallics*, 2002, **21**, 5962–5971.
32 C. Lin, J. D. Protasiewicz, E. T. Smith and T. Ren, *Inorg. Chem.*, 1995, **35**, 6422–6428.
33 A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, 1996, **15**, 1518.
34 A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115–119.
35 G. M. Sheldrick, *Programs for Crystal Structure Analysis (Release 97–2)*, University of Göttingen, Germany, 1997.
36 L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565.

