Metathesis Approach to Linkage of Two Tetraplatinum Cluster Units: Synthesis, Characterization, and Dimerization of $[Pt_4(\mu\text{-}OCOCH_3)_7(\mu\text{-}OCO(CH_2)_nCH{=}CH_2)]$ ($n = 0$–3)

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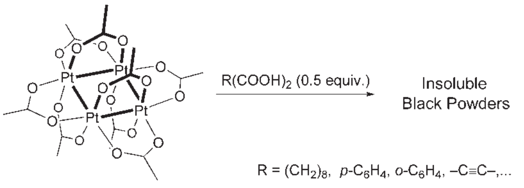
Reaction of $[Pt_4(\mu\text{-}OCOCH_3)_8]$ (**1**) with 1 equiv of acrylic acid led to the selective monosubstitution of one of the four in-plane acetates in **1**, affording $[Pt_4(\mu\text{-}OCOCH_3)_7(\mu\text{-}OCOCH{=}CH_2)]$ (**2a**), whereas treatment with excess amounts of acrylic acid resulted in a full-substitution of four in-plane acetates, yielding $[Pt_4(\mu\text{-}OCOCH_3)_4(\mu\text{-}OCOCH{=}CH_2)_4]$ (**3**). Similarly, monosubstituted heptaacetate complexes $[Pt_4(\mu\text{-}OCOCH_3)_7\{\mu\text{-}OCO(CH)_nCH{=}CH_2\}]$ (**2b**–**2d**: $n = 1$–3) were prepared. Catalytic intermolecular coupling reactions of **2c** and **2d** assisted by Grubbs' catalysts gave the desired dimers $[\{Pt_4(\mu\text{-}OCOCH_3)_7\}_2\{\mu\text{-}OCO(CH_2)_nCH{=}CH(CH_2)_n(\mu\text{-}OCO)\}]$ (**6c**: $n = 2$; **6d**: $n = 3$).

Supramolecular assemblies of metal centers as entities have recently attracted much attention because the molecular architecture is tunable through changing the types of metal fragments and organic linkers as well as the composition ratio between them.[1,2] Although mononuclear units are major building blocks, multinuclear units, especially metal–metal bonded clusters with three or more metal centers, are rarely used.[3–6] We are interested in synthetic approaches to metal–metal bonded multinuclear complexes, such as heteronuclear metal-wires,[7] an infinite zigzag chain,[8] and a Pd_6 bicorn tetrahedron,[9] because these complexes exhibit unique properties, different from those of mononuclear complexes, due to electron transfer through the metal–metal bond and, in some cases, synergistic effects of the plural metal centers.[10]

As part of our continuing studies, we embarked on the construction of a new series of supramolecular arrays composed of a cluster complex, and a tetranuclear platinum octaacetate complex, $[Pt_4(\mu\text{-}OCOCH_3)_8]$ (**1**),[11] was chosen as a suitable building block. In **1**, four platinum atoms lie at the apexes of a square, 2.50 Å per side, and four in-plane acetate ligands are selectively replaced by free carboxylate ions in solution.[12] Thus, we have attempted the syntheses of dicarboxylate-bridged octaplatinum complexes via the dimerization reaction of **1**. However, direct reaction of **1** with half the amount of dicarboxylic acid resulted in failure; careful addition of 0.5 equiv of different kinds of dicarboxylic acids such as sebacic acid and terephthalic acid to **1** induced the precipitation of insoluble black organoplatinum compounds (eq 1).[13,14]

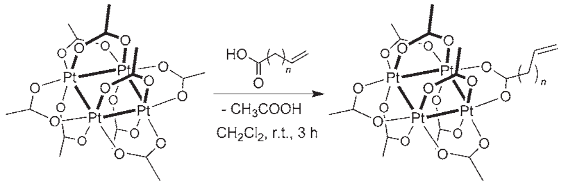


(1)

1

Herein, we report the syntheses of several dimers of the Pt_4 compounds through successive reactions of (a) the selective monosubstitution of one of the four in-plane acetates in **1** by α,ω-alkenyl carboxylic acids, affording $[Pt_4(\mu\text{-}OCOCH_3)_7(\mu\text{-}OCO(CH_2)_nCH{=}CH_2)]$ (**2**), and (b) its intermolecular metathesis coupling reaction mediated by Grubbs' catalysts since alkene metathesis is one of the promising tools to connect two cluster moieties with a $(CH_2)_nCH{=}CH_2$ fragment.[15]

Treatment of **1** with an equimolar amount of acrylic acid yielded a monosubstituted Pt_4 complex, $[Pt_4(\mu\text{-}OCOCH_3)_7(\mu\text{-}OCOCH{=}CH_2)]$ (**2a**) (eq 2), in which the introduced acrylate selectively occupied an in-plane coordination site and the terminal C=C double bond was not involved in the coordination to any platinum centers. This procedure was applied to other α,ω-alkenyl carboxylic acids, producing a series of monosubstituted Pt_4 complexes $[Pt_4(\mu\text{-}OCOCH_3)_7\{\mu\text{-}OCO(CH_2)_nCH{=}CH_2\}]$ (**2b**: $n = 1$; **2c**: $n = 2$; **2d**: $n = 3$). In contrast, the reaction of **1** with an equimolar amount of 4-vinyl benzoic acid gave a mixture of the corresponding mono- and disubstituted products. The addition of excess amounts of acrylic acid to **1** led to the complete substitution of four in-plane acetates, the same reaction mode as in the published report using CF_3COOH,[12] to yield a $[Pt_4(\mu\text{-}OCOCH_3)_4(\mu\text{-}OCOCH{=}CH_2)_4]$ (**3**).[16]



(2)

1

2a: $n = 0$ (95%)
2b: $n = 1$ (85%)
2c: $n = 2$ (90%)
2d: $n = 3$ (85%)

In the ^{1}H NMR spectrum of **2d**, the terminal olefinic part of the 5-hexenyl carboxylate was observed as a typical pattern of vinyl protons at δ_H 4.95, 5.08, and 5.86. In addition to the signals assignable to the 5-hexenyl carboxylate, the ^{1}H NMR spectrum of **2d** exhibited three signals attributable to the out-plane acetates at δ 1.98, 2.00, and 2.01, together with two signals of the *in*-plane acetates at δ 2.44 and 2.45 with an intensity ratio of 1:1:2 and 2:1, respectively.[17] Observation of the solvated ion peak of m/z 1347, $[\mathbf{2d} + CH_3CN]^+$, in the ESI-MS spectrum of **2d** strongly supported the monosubstituted structure.

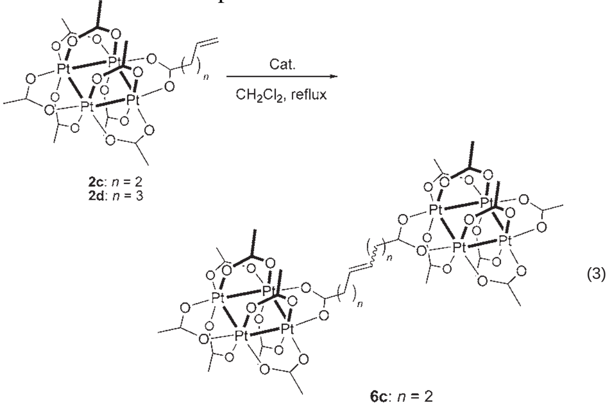
Complexes **2a**–**2d** were treated with catalytic amounts of Grubbs' catalysts, and the results are summarized in Table 1. Intermolecular metathesis reactions of **2c** and **2d** afforded the corresponding octaplatinum clusters $[\{Pt_4(\mu\text{-}OCOCH_3)_7\}_2\{\mu\text{-}OCO(CH_2)_nCH{=}CH(CH_2)_n(\mu\text{-}OCO)\}]$ (**6c**: $n = 2$; **6d**: $n = 3$) (eq 3, Table 1, Entries 5–10). In the metathesis reaction of **2d** with the longest methylene the coupling product reached 95% when 20 mol % of **5** was used as a catalyst over 16 h (Table 1,

Table 1. Catalytic intermolecular coupling reactions mediated by Grubbs' complexes[a]

Entry	Substrate	[Substrate] /mmol L^{-1}	Cat. (S/C /mol %)[b]	Time /h	Product (Conv./%)[c]
1	**2a**	5.0	**4** (3.0)	20	N. R.
2	**2a**	5.0	**5** (3.0)	16	N. R.
3	**2b**	5.0	**4** (3.0)	20	N. R.
4	**2b**	5.0	**5** (4.0)	16	N. R.
5	**2c**	7.0	**5** (3.0)	16	**6c** (15)
6	**2d**	4.0	**4** (3.0)	16	**6d** (60)
7	**2d**	7.0	**4** (3.0)	67	**6d** (75)
8	**2d**	6.0	**4** (20.0)	63	**6d** (85)
9	**2d**	8.0	**5** (4.0)	16	**6d** (35)
10	**2d**	6.0	**5** (20.0)	16	**6d** (95)[d]

[a]General conditions: in CH_2Cl_2, reflux. [b]**4**: $(PCy_3)_2(Cl)_2Ru{=}CHPh$, **5**: $(NHC)(PCy_3)(Cl)_2Ru{=}CHPh$, NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene). [c]Conversions were determined by ^1H NMR spectroscopy. [d]Grubbs' catalysts could not be separated from the reaction mixture.

Entry 10). The coupling reaction of either **2a** or **2b** under the same conditions, however, did not produce the prospective products, probably because of the steric hindrance between the platinum cluster and the catalyst or between the platinum cluster and the ruthenium–carbene species derived from **2**.



2c: $n = 2$
2d: $n = 3$

6c: $n = 2$
6d: $n = 3$

(3)

The octaplatinum clusters **6c** and **6d** were characterized on the basis of ESI-MS and NMR spectroscopies. The ESI-MS spectrum of **6d** showed ion peaks at m/z 2584 and 2525 assignable to $[\mathbf{6d}]^+$ and $[\mathbf{6d} - CH_3COO]^+$, respectively, and the ^1H NMR specdtrum of **6d** displayed the signals in the olefinic region due to internal (E)- and (Z)-CH=CH moieties of the product, the E/Z isomers, in a ratio of 55:45 without relying on catalyst variation.

In conclusion, successful synthesis of the octaplatinum cluster was achieved by the selective monosubstituted reaction of the in-plane acetates of $[Pt_4(\mu\text{-}OCOCH_3)_8]$ (**1**) by α,ω-alkenyl carboxylic acids, yielding $[Pt_4(\mu\text{-}OCOCH_3)_7\{\mu\text{-}OCO(CH)_n\text{-}CH{=}CH_2\}]$ (**2a**–**2d**), and metathesis coupling reaction of **2c** ($n = 2$) and **2d** ($n = 3$) using Grubbs' carbene complexes, leading to the well-designed Pt_4 cluster arrays. Extension of such a site-selective replacement of **1** for constructing Pt_4-based assemblies is now in progress in our laboratory.

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References and Notes

1 J.-M. Lehn, *Supramolecular Chemistry: Consepts and Perspectives*, VCH, New York, **1995**.

2 a) C. A. Schalley, A. Lützen, M. Albrecht, *Chem. Eur. J.* **2004**, *10*, 1072. b) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705. c) S. R. Seidel, P. J. Stang, *Acc. Chem. Res.* **2002**, *35*, 972. d) O. R. Evans, W. Lin, *Acc. Chem. Res.* **2002**, *35*, 511. e) B. J. Holliday, C. A. Mirkin, *Angew. Chem., Int. Ed.* **2001**, *40*, 2022. f) F. A. Cotton, C. Lin, C. A. Murillo, *Acc. Chem. Res.* **2001**, *34*, 759. g) S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853. h) J. A. R. Navarro, B. Lippert, *Coord. Chem. Rev.* **1999**, *185–186*, 653. i) M. Fujita, *Chem. Soc. Rev.* **1998**, *27*, 417. j) C. J. Jones, *Chem. Soc. Rev.* **1998**, *27*, 289.

3 R. H. Cayton, M. H. Chisholm, J. C. Huffman, E. B. Lobkovsky, *J. Am. Chem. Soc.* **1991**, *113*, 8709.

4 Recent papers: a) F. A. Cotton, Z. Li, C. Y. Liu, C. A. Murillo, D. Villagrán, *Inorg. Chem.* **2006**, *45*, 767. b) F. A. Cotton, C. A. Murillo, S.-E. Stiriba, X. Wang, R. Yu, *Inorg. Chem.* **2005**, *44*, 8223. c) F. A. Cotton, C. A. Murillo, R. Yu, *Inorg. Chem.* **2005**, *44*, 8211. d) F. A. Cotton, J. P. Donahue, C. A. Murillo, R. Yu, *Inorg. Chem. Acta* **2005**, *358*, 1373.

5 Recent papers: a) Z. Ni, A. Yassar, T. Antoun, O. M. Yaghi, *J. Am. Chem. Soc.* **2005**, *127*, 12752. b) A. C. Sudik, A. R. Millward, N. W. Ockwig, A. P. Cote, J. Kim, O. M. Yaghi, *J. Am. Chem. Soc.* **2005**, *127*, 7110. c) A. C. Sudik, A. P. Cote, O. M. Yaghi, *Inorg. Chem.* **2005**, *44*, 2998. d) N. W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2005**, *38*, 176.

6 B. Kesanli, Y. Cui, M. R. Smith, E. W. Bittner, B. C. Bockrath, W. Lin, *Angew. Chem., Int. Ed.* **2005**, *44*, 72.

7 a) T. Rüffer, M. Ohashi, A. Shima, H. Mizomoto, Y. Kaneda, K. Mashima, *J. Am. Chem. Soc.* **2004**, *126*, 12244. b) K. Mashima, H. Nakano, A. Nakamura, *J. Am. Chem. Soc.* **1993**, *115*, 11632. c) K. Mashima, H. Nakano, A. Nakamura, *J. Am. Chem. Soc.* **1996**, *118*, 9083. d) K. Mashima, M. Tanaka, K. Tani, A. Nakamura, W. Mori, S. Takeda, K. Yamaguchi, *J. Am. Chem. Soc.* **1998**, *120*, 12151.

8 J.-J. Yi, T. Miyabayashi, M. Ohashi, T. Yamagata, K. Mashima, *Inorg. Chem.* **2004**, *43*, 6596.

9 M. Ohashi, J.-J. Yi, D. Shimizu, T. Yamagata, T. Ohshima, K. Mashima, *J. Organomet. Chem.* **2006**, *691*, 2457.

10 a) F. A. Cotton, R. A. Walton, *Multiple Bonds between Metal Atoms*, 2nd ed., Clarendon Press, Oxford, U. K., **1993**. b) R. D. Adams, F. A. Cotton, *Catalysis by Di- and Polynuclear Metal Cluster Complexes*, Wiley-VCH, New York, **1998**. c) *Metal Clusters in Catalysis*, ed. by B. C. Gates, L. Guzci, V. H. Knozinger, Elsevier, Amsterdam, **1986**.

11 M. A. A. F. de C. T. Carrondo, A. C. Skapski, *J. Chem. Soc., Chem. Commun.* **1976**, 410.

12 T. Yamaguchi, Y. Sasaki, A. Nagasawa, T. Ito, N. Koga, K. Morokuma, *Inorg. Chem.* **1989**, *28*, 4311, and references therein.

13 On the basis of the combustion analysis (C: 15.44, H: 1.69 for the reaction product with a half amount of acetylenedicarboxylic acid), though poor solubility hindered further characterization, we considered the black products to be insoluble organoplatinum compounds.

14 The complete substitution of all the four in-plane acetates in **1** by dicarboxylic acids was confirmed by the reaction of **1** with excess amounts of o-phthalic acid to afford $[Pt_4(\mu\text{-}OCOCH_3)_4\text{-}(\mu\text{-}OCOC_6H_4COOH)_4]$ (**7**), which is completely different from the insoluble black products. Spectral data as well as molecular structure of **7** were deposited in Supporting Information. This is also available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

15 For example: T. Shima, F. Hampel, J. A. Gladysz, *Angew. Chem., Int. Ed.* **2004**, *43*, 5537.

16 Spectral data as well as crystallographic data of **3** were deposited in Supporting Information.

17 Complexes **2a**–**2c** exhibited the characteristic ^1H NMR spectra that are quite similar to that of **2d**. See Supporting Information.

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