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Dinuclear Palladium(0) and Platinum(0) Complexes with *p*-Benzoquinone and Norbornene Ligands

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Palladium(0) and platinum(0) precursor complexes, $Pd_2(dba)_3$ and $Pt(dba)_2$, reacted with *p*-benzoquinone (bq) and norbornene (nbe) to afford new dinuclear complexes possessing *p*-benzoquinone as a bridging ligand and norbornene as a monodentate ligand, $Pd_2(bq)_2(nbe)_2$ and $Pt_2(bq)_2(nbe)_2$, respectively. The solid-state structure of the obtained complexes presented the short metal−metal distances similar to predecessors possessing the significant $d^{10}-d^{10}$ bonding interaction. The formations of the previously reported mononuclear *p*-benzoquinone and *p*-naphthoquinone complexes using 1,5-cyclooctadiene in place of norbornene were also unambiguously confirmed by the single-crystal X-ray diffraction studies. The present dinuclear palladium complex proved to be an efficient catalyst precursor for the linear cotrimerization of 1-octene and dimethyl acetylenedicarboxylate. On the other hand, the platinum analogue catalyzed the hydrosilylation of styrene under mild reaction conditions.

Introduction

p-Quinones have received continuous attention in coordination chemistry as redox-active, π-acidic bidentate ligands. A wide range of transition metals form *p*-quinone complexes with other ligand(s) such as CO, cyclopentadienyl, alkenes, and N- or P-donor ligands.[1] Among them, a quinone complex involving only an unactivated alkene as an extra ancillary ligand is of significance as a versatile precursor for other quinone complexes or a homogeneous catalyst, because weakly coordinated alkene ligands are readily replaced by other molecules. Such mixed alkene complexes were, however, confined to those of group 10 elements with cyclic dienes acting as a bidentate ligand, e.g. 1,5-cyclooctadiene, norbornadiene, etc.[2] The only existent examples of a more labile monoalkene ligand are platinum complexes having an ethene ligand as well as phosphine and *p*-quinone ligands.[3]

Previously, one of us (K.I.) reported the synthesis of mixed olefin complexes of palladium(0) possessing both activated alkene(s) (maleic anhydride, dimethyl fumarate, and tetracyanoethylene) and neutral alkene(s) (cyclooctene, norbornene, 1,5-cyclooctadiene, and norbornadiene).[4] Subsequently, one of these mixed olefin complexes, $Pd(ma)_2(nbe)$ (ma = maleic anhydride, nbe = norbornene), was found to effectively catalyze the linear cotrimerization of two molecules of a terminal alkene and dimethyl acetylenedicarboxylate.[5] To extend this chemistry, we commenced the study of palladium(0) complexes of *p*-quinones as activated olefins. Here we report new dinuclear palladium(0) and platinum(0) complexes containing *p*-benzoquinone as a bridging ligand and norbornene as a monodentate unactivated olefin ligand.

Results and Discussion

Synthesis and X-ray Structure Determination of Dinuclear Pd(0) and Pt(0) Complexes Containing a *p*-Quinone Bridging Ligand. A palladium(0) precursor, $Pd_2(dba)_3$ (dba = (*E*,*E*)-dibenzylideneacetone), was treated with *p*-benzoquinone (10 equiv) and norbornene (20 equiv) in acetone at ambient temperature for 30 min (eq 1). The initial purple suspension finally

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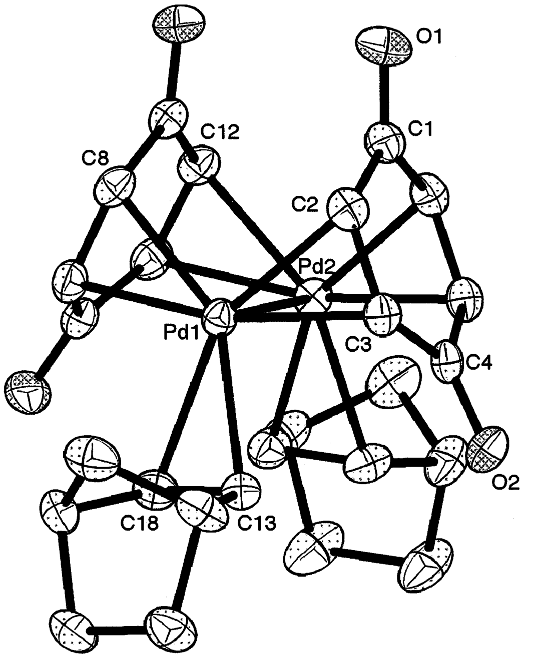
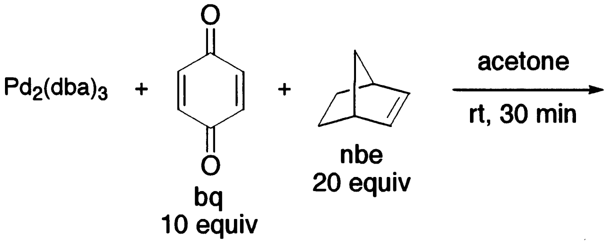


Figure 1. ORTEP diagram of Pd$_2$(bq)$_2$(nbe)$_2$ (**1**). All hydrogen atoms were omitted for clarity. Selected bond distances (Å) and angles (deg): Pd1–Pd2, 2.9399(4); Pd1–C2, 2.221(3); Pd1–C3, 2.180(3); Pd1–C13, 2.315(4); Pd1–C18, 2.339(4); C1–O1, 1.226(5); C1–C2, 1.484(5); C2–C3, 1.402(5); C3–C4, 1.479(5); C4–O2, 1.235(5); C13–C18, 1.360(5); C2–Pd1–C3, 37.14(13); Pd1–C2–C3, 69.8(2), Pd1–C3–C2, 73.0(2); C3–Pd1–C13, 79.45(13), C13–Pd1–C18, 33.97(13); Pd1–C13–C18, 74.0(2); C2–Pd1–Pd2, 84.62(9); C3–Pd1–Pd2, 85.08(9); C13–Pd1–Pd2, 107.48(10); C2–Pd1–C8, 85.70(9).

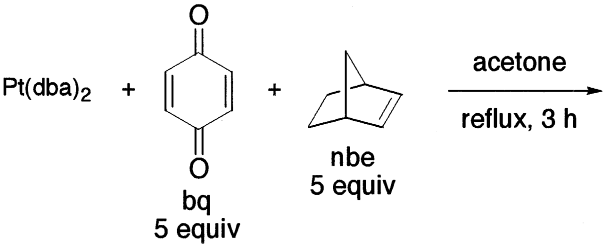


Pd$_2$(bq)$_2$(nbe)$_2$ (1)

92%

turned into a reddish brown homogeneous solution. After concentration of the solution in vacuo, the residual crude complex was recrystallized from acetone/ether to afford dark brown crystals. The presence of coordinated *p*-benzoquinone in the obtained complex **1** is confirmed by its infrared spectrum showing a carbonyl absorption with frequency (1631 cm^{-1}) lower than that of free *p*-benzoquinone (1656 cm^{-1}). The ^{1}H NMR measurement revealed that the quinone and norbornene ligands are present in a 1:1 ratio. In contrast to the known complex Pd(bq)(cod) (bq = *p*-benzoquinone, cod = 1,5-cyclooctadiene),[2d] the vinylic protons of the quinone ligand were observed as a pair of peaks at δ 4.95 and 4.43 ppm (ddd, J = 8.6, 3.6, and 1.2 Hz), indicative of this ligand being unsymmetrically coordinated. The structure of **1** was unambiguously determined by single-crystal X-ray analysis. As shown in Figure 1, **1** is a dinuclear palladium(0) complex containing two pairs of *p*-benzoquinone and norbornene ligands. Each *p*-benzoquinone ligand bridges between the two trigonal palladium(0) centers, and a third coordination site on each metal was occupied by a norbornene molecule, which is coordinated with its exo face. Such a cagelike structure was also found in a recently reported complex, Pd$_2$(bq)$_2$(dafo) (dafo = 4,5-diazafluoren-9-one).[11] Interestingly, the [Pd$_2$(bq)$_2$] unit of **1** is very similar to the diazafluorenone analogue. The Pd–Pd distance of 2.9399(4) Å in **1** is, however, longer than that of Pd$_2$(bq)$_2$(dafo) (2.7747(4) Å). The shorter Pd–Pd separation of the latter might be attributed to the dafo ligand, forming an additional bridge between the palladium centers (vide infra). In addition, the *p*-benzoquinone ligands in **1** come into close proximity to open larger coordination spaces for norbornene, which is more sterically demanding than 4,5-diazafluoren-9-one. As a result, the angles between the upper Pd–C(sp^2, bq) bonds, C2–Pd1–C8 and C6–Pd2–C12, are smaller in **1** (85.70(9) and 92.02(14)°) than in Pd$_2$(bq)$_2$(dafo) (98.74(16)°).

In a similar manner with **1**, a platinum(0) precursor complex, Pt(dba)$_2$, was treated with *p*-benzoquinone (5 equiv) and norbornene (5 equiv) in refluxing acetone for 3 h to afford the corresponding dinuclear platinum(0) complex **2** in 74% yield (eq 2). The X-ray analysis of **2** showed that the platinum analogue also has a cagelike structure assembled from two pairs of bridging *p*-benzoquinone and monodentate norbornene ligands (Figure 2). The Pt–Pt distance of 2.9667(2) Å is slightly longer than the Pd–Pd distance of 2.9399(4) Å in **1**. On the other hand, the shorter Pt–C(sp^2) bond distances and the longer C(sp^2)–C(sp^2) double-bond lengths in the ligands clearly show that the back-donation from the metal centers to the coordinated olefin moieties is stronger than those in the palladium analogue **1**. The angles between the upper Pt–C(sp^2, bq) bonds, C2–Pt1–C8 and C6–Pt2–C12 (91.11(19) and 90.9(2)°), are once again smaller than the corresponding angle in Pd$_2$(bq)$_2$(dafo) (98.74(16)°).



Pt$_2$(bq)$_2$(nbe)$_2$ (2)

74%

The *structural* similarities among the mixed olefin complexes **1** (M = Pd) and **2** (M = Pt) and the diazafluorenone complex Pd$_2$(bq)$_2$(dafo) are well exemplified by the typical bond distances and angles compiled in Table 1.

X-ray Structural Analysis of Mononuclear Pd(0) Quinone Complexes. The strained monoalkene ligand is quite essential for the assembly of the dinuclear framework. Using cyclooctene instead of norbornene only gave an intractable dark brown powder. In addition, the formation of a mononuclear complex, Pd(bq)(cod) (**3**), using 1,5-cyclooctadiene in place of norbornene was reported by Sakai and co-workers. We

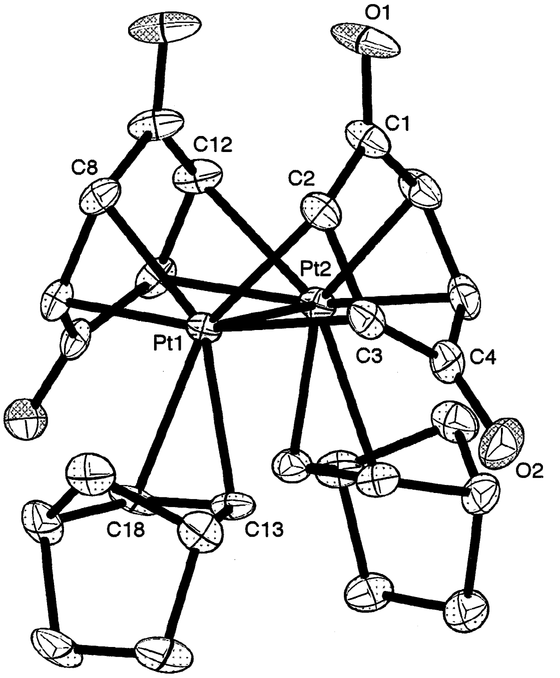
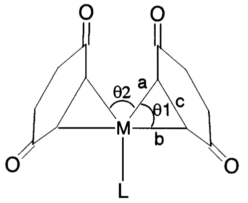


Figure 2. ORTEP diagram of $Pt_2(bq)_2(nbe)_2$ (**2**). All hydrogen atoms were omitted for clarity. Selected bond distances (Å) and angles (deg): Pt1−Pt2, 2.9667(2); Pt1−C2, 2.151(5); Pt1−C3, 2.164(4); Pt1−C13, 2.277(4); Pt1−C18, 2.267(4); C1−O1, 1.224(6); C1−C2, 1.479(7); C2−C3, 1.416(7); C3−C4, 1.487(7); C4−O2, 1.228(6); C13−C18, 1.385(7); C2−Pt1−C3, 38.31(18); Pt1−C2−C3, 71.3(3), Pt1−C3−C2, 70.4(3); C3−Pt1−C13, 78.99(18), C13−Pt1−C18, 35.48(18); Pt1−C13−C18, 71.9(3); C2−Pt1−Pt2, 84.71(13); C3−Pt1−Pt2, 85.13(13); C13−Pt1−Pt2, 105.00(12); C2−Pt1−C8, 91.11(19).

Table 1. Comparison of Average Bond Distances (Å) and Angles (deg) of $Pd_2(bq)_2(nbe)_2$ (1), $Pt_2(bq)_2(nbe)_2$ (2), and $Pd_2(bq)_2(dafo)$



	$Pd_2(bq)_2(nbe)_2$	$Pt_2(bq)_2(nbe)_2$	$Pd_2(bq)_2(dafo)$
M−M	2.9399(4)	2.9667(2)	2.7747(4)
a	2.209	2.165	2.197(4)
b	2.188	2.160	2.153(4)
c	1.393	1.415	1.389
θ1	36.92	38.19	37.41
θ2	88.86	91.01	98.74(16)

further revisited the synthesis of **3**, because its structural data in the solid state were not available to date. In a manner similar to the synthesis of **1**, $Pd_2(dba)_3$ was treated with *p*-benzoquinone (10 equiv) and 1,5-cyclooctadiene (5 equiv) in acetone at ambient temperature for 30 min (eq 3). The ^1H NMR spectrum of the obtained material showed only one singlet peak at δ 5.84 ppm assignable to the *p*-benzoquinone ligand, except for the absorptions of the coordinated 1,5-cyclooctadiene. This fact suggests that the complex has a highly symmetrical structure, in accordance with the original report.[2e] To clearly confirm its structure, a single crystal of **3** was subjected to an X-ray diffraction study. As presented in Figure 3, **3** proved to be a mononuclear Pd(0) complex, in which the tetrahedral palladium center coordinates to both bq and cod ligands in a η^2:η^2 bidentate fashion. Such a coordination mode resembles the known analogues of group 10 elements, Ni(duroquinone)(cod)[2c] and $Pt(2,6\text{-}^tBu_2C_6H_2O_2)(cod)$.[2d] The Pd−C(sp^2) distances for the *p*-benzoquinone ligand ranging from 2.310(9) to 2.387(8) Å are similar to those reported for the latter species (2.268(3)−2.386(3) Å).[2d] The Pd−C(sp^2) distances for the cod ligand ranging from 2.225(9) to 2.254(8) Å are, however, slightly longer than those in the platinum complex (2.154(4)−2.193(4) Å).[2d] These facts show that the back-donation from the metal center to the cod ligand is weaker in the palladium complex. This was also confirmed by the comparison of the C−C double-bond lengths of the cod ligands. The shorter bond lengths were observed for **3** (1.341(16) and 1.375(13) Å for Pd(bq)(cod) vs 1.393(6) and 1.400(6) Å for $Pt(2,6\text{-}^tBuC_6H_2O_2)(cod)$).

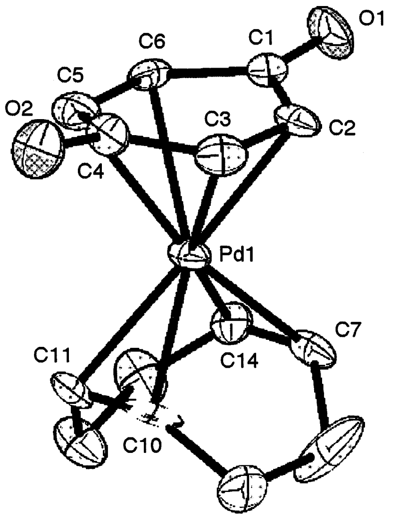
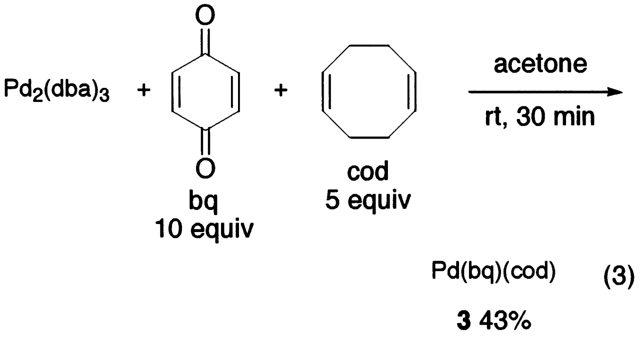


Figure 3. ORTEP diagram of Pd(bq)(cod) (**3**). All hydrogen atoms were omitted for clarity. Selected bond distances (Å) and angles (deg): Pd1−C2, 2.323(9); Pd1−C3, 2.367(8); Pd1−C5, 2.387(8); Pd1−C6, 2.310(9); Pd1−C7, 2.254(8); Pd1−C10, 2.225(9); Pd1−C11, 2.242(8); Pd1−C14, 2.235(7), C1−O1, 1.280(16); C1−C2, 1.429(13), C2−C3, 1.373(5); C3−C4, 1.505(10); C4−O2, 1.210(14), C7−C14, 1.341(16); C2−Pd1−C3, 34.02(14), Pd1−C2−C3, 74.7(6); Pd1−C3−C2, 71.2(7); C5−Pd1−C6, 33.96(14); Pd1−C5−C6, 69.9(7), Pd1−C6−C5, 76.1(7); C2−Pd1−C6, 63.7(3); C3−Pd1−C5, 63.6(3).



In contrast to 1,5-cyclooctadiene, a similar bidentate diene, norbornadiene, again resulted in the formation of an intractable dark brown powder. In addition to *p*-benzoquinone, *p*-naphthoquinone also formed a mono-

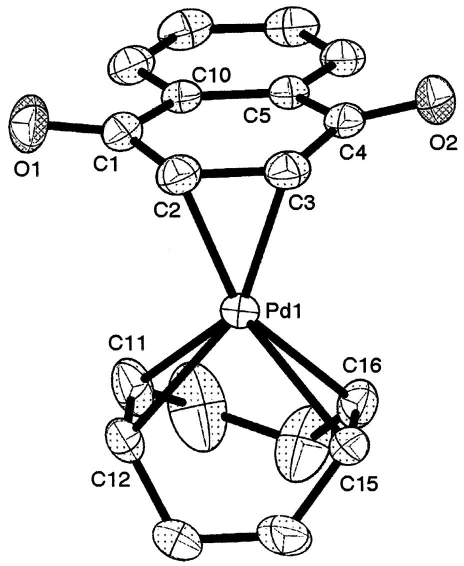
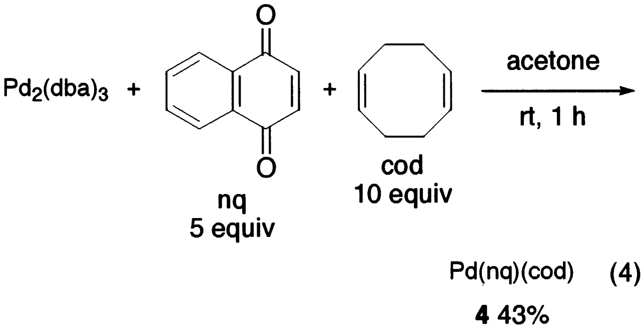


Figure 4. ORTEP diagram of Pd(nq)(cod) (**4**). All hydrogen atoms were omitted for clarity. Selected bond distances (Å) and angles (deg): Pd1–C2, 2.106(2); Pd1–C3, 2.129(2); Pd1–C11, 2.264(3); Pd1–C12, 2.306(2); Pd1–C15, 2.291(2); Pd1–C16, 2.300(2); C1–O1, 1.229(3); C1–C2, 1.458(3), C2–C3, 1.424(3); C3–C4, 1.457(3); C4–O2, 1.231(3), C5–C10, 1.406(3); C11–C12, 1.353(4); C15–C16, 1.346(4); C2–Pd1–C3, 39.30(9), Pd1–C2–C3, 71.22(13); Pd1–C3–C2, 69.48(13).

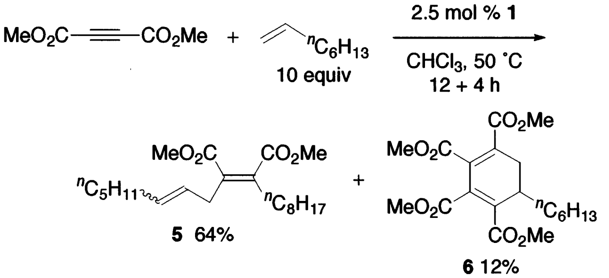
nuclear palladium complex with 1,5-cyclooctadiene. The reaction of $Pd_2(dba)_3$ with *p*-naphthoquinone (nq, 5 equiv) and 1,5-cyclooctadiene (10 equiv) in acetone at ambient temperature for 1 h afforded a known complex, Pd(nq)(cod) (**4**),[2e] in 43% yield (eq 4). The single-crystal



(4)

X-ray analysis of **4** revealed that *p*-naphthoquinone is involved as a η^2 ligand (Figure 4). The Pd–C(sp^2) bond distances for the *p*-naphthoquinone ligand (2.106(2) and 2.129(2) Å) are much shorter than those for the *p*-benzoquinone ligand in **2**. The coordinated C2–C3 double-bond length of 1.424(3) Å is also much longer compared to that in **2**, whereas the C5–C10 double-bond length of 1.406(3) Å is quite similar to that of free benzene (1.41 Å). Such a change in coordination mode from η^4 coordination for *p*-benzoquinone to η^2 coordination for *p*-naphthoquinone was also confirmed by X-ray analyses of other palladium quinone complexes.[1l,m] On the other hand, the η^4 coordination of *p*-naphthoquinone ligands was reported for pentamethylcyclopentadienyl cobalt complexes.[6]

Catalytic Activity of Dinuclear Palladium(0) and Platinum(0) *p*-Benzoquinone Complexes. Dinuclear palladium and platinum complexes with a short M(0)–M(0) distance are very rare.[1l,7,8] Such a d^{10}–d^{10} interaction is expected to have no metal–metal σ-bond, but there is some bonding interaction.[9] In the mixed olefin palladium complex **1**, the Pd–Pd distance of 2.9399(4) Å is substantially shorter than the nonbonding Pd–Pd distance of the relevant dba-bridged dinuclear complex $Pd_2(dba)_3 \cdot CHCl_3$ (3.245(2) Å)[1e] and rather closer to those found in known examples possessing significant bonding interactions, $Pd_2(dppm)_3$ (2.959(2) Å, dppm = bis(diphenylphosphino)methane),[7c] $Pd_2(dcpe)_2$ (2.7611(5) Å, dcpe = 1,2-bis(dicyclohexylphosphino)ethane),[7d] $Pd_2(dcpm)_2$ (2.8582(6) Å, dcpm = bis(dicyclohexylphosphino)methane),[7e] and the aforementioned $Pd_2(bq)_2(dafo)$ (2.7747(4) Å).[11] In addition, one of the most significant features of these dinuclear complexes is that they can be attractive precursors of the corresponding mononuclear fragment and, hence, a highly reactive catalyst.[7,8] In fact, the FAB-mass spectrum of **1** showed the peak of the half-fragment Pd(bq)(nbe) at *m/z* 307 instead of the expected molecular ion peak, indicative of a coordinatively unsaturated Pd(0) entity being readily produced. On the basis of these facts, we applied **1** to the catalytic reaction of 1-octene and DMAD (eq 5). Whereas the reactions of DMAD with



(5)

unactivated alkenes usually produce cocyclotrimerization adducts such as **6**,[10] the mixed olefin complex $Pd(ma)_2(nbe)$ relevant to **1** was reported to predominantly catalyze unusual linear cotrimerization.[4] A solution of DMAD in $CHCl_3$ was added over 12 h to a solution of 1-octene (10 equiv) and **1** (0.025 equiv, 5 mol % Pd) in

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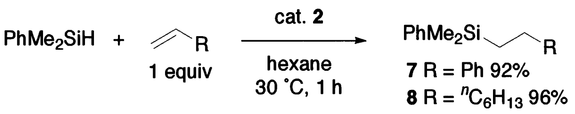
$CHCl_3$ at 50 °C, and the reaction mixture was further stirred for 4 h to selectively afford the expected product **5** in 64% isolated yield together with **6** in 12% yield. On the other hand, the mononuclear complex **3** exhibited no catalytic activity under the same conditions. These results clearly showed that the dinuclear complex **1** is an excellent precursor of a catalytically active [Pd(bq)] fragment.

Similarly, there is some bonding interaction in the platinum analogue **2**. The Pt−Pt distance of 2.9667(2) Å in **2** is intermediate between that of the triply bridged $Pt_2(dppm)_3$ (3.0225(3) Å)[8d] and those of the unbridged or doubly bridged examples $Pt_2(dtbpe)_2$ (2.765(1) Å, dtbpe = 1,2-bis(di-*tert*-butylphosphino)ethane)[8a] and $Pt_2(dtbpm)_2$ (2.7948(11) Å, dtbpm = bis(di-*tert*-butylphosphino)methane).[8f] In striking contrast to **1**, the FAB-mass spectrum of **2** showed the molecular ion peak MH^+ at *m/z* 795, indicative of **2** having a more stable dinuclear framework than **1**. Apart from the stability of its dinuclear structure, the present *p*-benzoquinone platinum complex **2** exhibits a favorable catalytic activity toward the hydrosilylation of terminal alkenes (eq 6).[11] In the presence of 0.025 mol % of **2** (0.05 mol % of Pt atom), dimethylphenylsilane was reacted with styrene in hexane at 30 °C for 1 h to furnish the desirable hydrosilylation product **7** in 92% yield. In a similar manner, 0.5 mol % of **2** (1 mol % of Pt atom) catalyzed the reaction of dimethylphenylsilane and 1-octene to give the hydrosilylation product **8** in 96% yield.



(6)

Conclusion

In conclusion, we successfully obtained new dinuclear palladium(0) and platinum(0) complexes containing *p*-benzoquinone as a bridging ligand and norbornene as a monodentate ligand in good yield from readily available starting materials. The single-crystal X-ray analysis revealed that these complexes have short metal−metal distances similar to those of previously reported complexes possessing the significant $d^{10}-d^{10}$ bonding interaction.

The combination of *p*-benzoquinone and norbornene is essential for the assembly of such dinuclear frameworks. The formations of the predecessor mononuclear complexes from 1,5-cyclooctadiene together with *p*-benzoquinone or *p*-naphthoquinone were unambiguously confirmed by the single-crystal X-ray diffraction studies.

The present dinuclear palladium complex is less sensitive toward air and moisture and proved to be an efficient catalyst precursor for the linear cotrimerization of 1-octene and dimethyl acetylenedicarboxylate. On the other hand, the platinum analogue catalyzed the hydrosilylation of terminal alkenes under mild reaction conditions.

Experimental Section

General Considerations. ^1H and ^{13}C NMR spectra were obtained for samples in $CDCl_3$ solution. Elemental analyses were performed by the Microanalytical Center of Kyoto University. Melting points were obtained in capillary tubes and are uncorrected. Acetone was distilled from $CaSO_4$ and degassed. Mononuclear complexes **3** and **4** were reported in ref 2e.

Synthetic Procedure and Analytical Data for 1. A solution of $Pd_2(dba)_3 \cdot CHCl_3$ (165.6 mg, 0.160 mmol), *p*-benzoquinone (177.3 mg, 1.64 mmol), and norbornene (308.8 mg, 3.28 mmol) in dry, degassed acetone (10 mL) was stirred at ambient temperature for 30 min. The resultant reddish brown solution was concentrated to 1 mL in vacuo, diluted with degassed ether (30 mL), and cooled to ca. −15 °C overnight. The dark red crystals obtained were collected on a glass frit and dried under vacuum. The yield was 90.4 mg (92%): mp 98 °C dec; IR (Nujol) 1631, 1288 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ −0.25 (2 H, d, *J* = 9.5 Hz), 0.44 (2 H, d, *J* = 9.5 Hz), 1.21 (4 H, m), 1.61 (4 H, m), 2.95 (4 H, s), 4.43 (4 H, ddd, *J* = 8.6, 3.6, 1.2 Hz), 4.78 (4 H, s), 4.95 (4 H, ddd, *J* = 8.6, 3.6, 1.2 Hz); MS (FAB) *m/z* 307 [Pd(bq)(nbe) − H^+]. Anal. Calcd for $C_{26}H_{28}O_4Pd_2$: C, 50.58; H, 4.57. Found: C, 50.86; H, 4.85.

Synthetic Procedure and Analytical Data for 2. A solution of $Pt(dba)_2$ (199.2 mg, 0.30 mmol), *p*-benzoquinone (162.2 mg, 1.50 mmol), and norbornene (141.2 mg, 1.50 mmol) in dry, degassed acetone (20 mL) was refluxed for 3 h. The resultant reddish brown solution was concentrated to 1 mL in vacuo, diluted with degassed ether (30 mL), and cooled to ca. −15 °C overnight. The dark red crystals obtained were collected on a glass frit and dried under vacuum. The yield was 88.6 mg (74%): mp 171 °C dec; IR (Nujol) 1653, 1290 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ −0.37 (2 H, d, *J* = 9.6 Hz), 0.12 (2 H, d, *J* = 9.6 Hz), 1.20 (4 H, m), 1.65 (4 H, m), 2.87 (4 H, s), 3.68 (4 H, d, *J* = 8.0 Hz), 4.35 (4 H, d, *J* = 8.0 Hz), 4.53 (4 H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.68 (t, *J* = 21 Hz), 39.95, 43.63, 59.96 (t, *J* = 98 Hz), 64.24 (t, *J* = 74 Hz), 96.23 (t, *J* = 70 Hz), 190.61, 195.78; MS (FAB) *m/z* 795 [MH^+, 25] 701 [$Pt_2(bq)_2(nbe)H^+$, 33], 686 [$Pt_2(bq)(nbe)_2$, 100], 607 [$Pt_2(bq)_2H^+$, 60]. Anal. Calcd for $C_{26}H_{28}O_4Pt_2$: C, 39.30; H, 3.55. Found: C, 39.58; H, 3.43.

Crystallographic Structural Determination of 1−4. Single crystals of **1**−**4** suitable for X-ray analysis were obtained by recrystallization from acetone/ether. A crystal of dimensions 0.1 × 0.7 × 0.8 mm (**1**), 0.5 × 0.5 × 0.7 mm (**2**·(acetone)), 0.2 × 0.5 × 0.8 mm (**3**), or 0.3 × 0.3 × 0.8 mm (**4**) was mounted on a quartz fiber, and diffraction data were collected in the θ range of 1.75−29.13° for **1**, 1.94−29.10° for **2**·(acetone), 2.53−29.14° for **3**, and 2.32−29.15° for **4**, respectively, at 173 K on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). An absorption correction was made using SADABS. The structure was solved by direct methods and refined by full-matrix least squares on F^2 by using SHELXTL. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions. Final refinement details are compiled in Tables S1-1, S2-1, S3-1, and S4-1 (see the Supporting Information).

Catalytic Linear Cotrimerization of Dimethyl Acetylenedicarboxylate and 1-Octene using $Pd_2(bq)_2(nbe)_2$ (1). To a solution of 1-octene (1.75 mL, 11.2 mmol) and $Pd_2(bq)_2(nbe)_2$ (**1**; 15.5 mg, 0.025 mmol) in dry, degassed $CHCl_3$ (4 mL) was added a solution of DMAD (142 mg, 1 mmol) in $CHCl_3$ (2 mL) over 12 h by syringe pump at 50 °C. The reaction mixture was further stirred at 50 °C for 4 h. The resultant brownish mixture was concentrated in vacuo, and the residue was purified by silica gel column chromatography (hexane−AcOEt, 25:1) to afford the linear product **5** (234.5 mg, 64%) as a colorless oil. Further elution gave the cyclic product **6** (48.7 mg, 12%) as a colorless oil.

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[11] For hydrosilylation of trimethylvinylsilane catalyzed by platinum complexes with *p*-quinone ligands, see: Steffanut, P.; Osborn, J. A.; DeCian, A.; Fisher, J. *Chem. Eur. J.* **1998**, *4*, 2008−2017.

Catalytic Hydrosilylation of Terminal Alkene with Dimethylphenylsilane using $Pt_2(bq)_2(nbe)_2$ (2). A solution of dimethylphenylsilane (153 μL, 1.0 mmol) and styrene (104.2 mg, 1.0 mmol) was treated with $Pt_2(bq)_2(nbe)_2$ (**2**; 0.2 mg, 0.00025 mmol) in dry, degassed hexane (10 mL) at 30 °C for 1 h. The solvent was evaporated, and the crude product was purified by silica gel column chromatography (hexane) to afford the hydrosilylation product **7** (221.2 mg, 92%) as a colorless oil.

Similarly, dimethylphenylsilane (153 μL, 1.0 mmol) and 1-octene (156.9 mg, 1.0 mmol) was treated with $Pt_2(bq)_2(nbe)_2$ (**2**; 4.0 mg, 0.005 mmol) to afford **8** (238.1 mg, 96%) as a colorless oil.

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Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters and figures containing the atom-numbering schemes for **1**, **2**·(acetone), **3**, and **4**; data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org. The supplementary crystallographic data for this paper (CCDC 186622 (**1**), CCDC 200852 (**2**·(acetone)), CCDC 186623 (**3**), and CCDC 200853 (**4**)) can also be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.; fax +44 1223 336033 or e-mail deposit@ccdc.cam.ac.uk).

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