Notes

Ring Methyl Activation of 1,2-Dimethyl-3,4-di(*tert*-butyl)cyclobutadiene Complexes of Palladium Giving *exo*-Methylene-η^3-cyclobutenyl Complexes of Palladium

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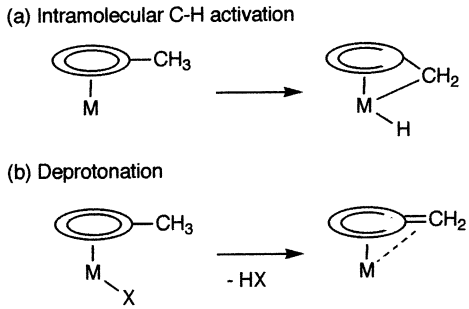
*Summary: We found the first ring methyl activation of an η^4-cyclobutadiene complex. Base-promoted ring methyl activation of the cyclobutadiene-palladium(II) complex $[PdCl_2(\eta^4\text{-}C_4Me_2(^tBu)_2)]_2$ (**2**) in the presence of triethylamine afforded the dinuclear exo-methylene-η^3-cyclobutenyl complex $[PdCl(\eta^3\text{-}C_4(=CH_2)Me(^tBu)_2)]_2$ (**3**) in 81% yield. In the case of pyridine as base, a mixture of **3** and $[C_5H_5NH][PdCl_3(\eta^4\text{-}C_4Me_2(^tBu)_2)]$ (**4**) was obtained. The complex **4** was alternatively derived from the reaction of **2** with 2 equiv of $C_5H_5N{\cdot}HCl$. The ring methyl activation of **2** in the presence of 2,2′-bipyridine and triethylamine followed by treatment with $AgBF_4$ led to the formation of the cationic complex $[Pd(\eta^3\text{-}C_4(=CH_2)Me(^tBu)_2)(bipy)]]BF_4$ (**6**) in 83% yield. The mononuclear exo-methylene-η^3-cyclobutenyl structure of **6** was confirmed by spectral data and a crystallographic study.*

Introduction

Stoichiometric and catalytic transformations of organic compounds involving C−H bond activation by using transition metal complexes have attracted recent interest.[1] Among them, one of the fundamental organometallic reactions is the C−H bond cleavage of the ring methyl groups of cyclopentadienyl and arene ligands bound to transition metals. The pentamethylcyclopentadienyl complexes of early transition metals underwent an intramolecular ring methyl C−H bond activation to preferentially give 1,2,3,4-tetramethylfulvene complexes as depicted in Scheme 1a,[2−4] and in some particular cases, sequential C−H bond activation afforded bis(*exo*-methylene) complexes.[5−8] As shown in Scheme 1b, the pentamethylcyclopentadienyl complexes of late transition metals favored the deprotonation of the ring methyl group of the ligand by using appropriate base as well as dioxygen, resulting in the formation of fulvene complexes or their derivatives involving the alkylation of the ring methyl groups.[9−11] Moreover, the C−H bond activation of the C_6Me_6 ligand bound in an η^6-fashion to Mn[12] and Fe[13−20] was reported to give

Scheme 1. Schematic Drawings of Ring Methyl Activations



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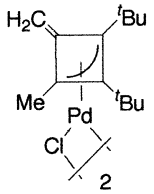
unique *exo*-methylene-η^5-cyclohexadienyl complexes, and that of Ta[21] afforded *exo*-η^1-methylene-η^5-cyclohexadienyl complexes. To the best of our knowledge, no analogous ring methyl activation has been observed in a complex of η^4-cyclobutadiene. The isolobal relation[22] among half-sandwich complexes of general formula (η^n-C_nR_n)ML_x (**1**) (n = 6 for M(0) = group 8 metals, n = 5 for M(I) = group 9 metals, and n = 4 for M(II) = group 10 metals) prompted us to study the ring methyl activation of methyl-substituted cyclobutadiene complexes of group 10 metals. Herein we report the first evidence for such a reaction for η^4-cyclobutadiene complexes of palladium, leading to the formation of unique *exo*-methylene-η^3-cyclobutenyl palladium complexes.

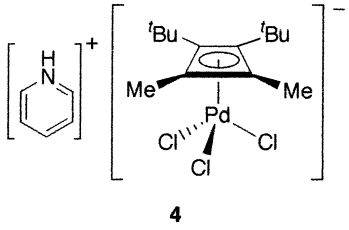
Results and Discussion

We found that base-promoted ring methyl activation of a cyclobutadiene-palladium complex, $[PdCl_2(\eta^4\text{-}C_4Me_2(^tBu)_2)]_2$ (**2**), which was prepared according to the method reported by Maitlis et al.,[23] proceeded smoothly. A mixture of the complex **2** and 2 equiv of triethylamine in dichloromethane at room temperature over a period of 1 h reacted to give a pale yellow solution, from which was isolated a dinuclear complex, $[PdCl(\eta^3\text{-}C_4(=CH_2)\text{-}Me(^tBu)_2)]_2$ (**3**), as a yellow solid in 81% yield. The spectral data are consistent with an *exo*-methylene-η^3-cyclobutenyl structure of **3**, which was a product of deprotonation from one of the two methyl groups of **2**. The ^1H NMR spectrum of **3** in $CDCl_3$ displayed two singlets at δ 1.32 and 1.43 due to two *tert*-butyl groups and one singlet at δ 1.47 due to a methyl group in an exact integral ratio. At lower field, exocyclic methylene protons appeared at δ 3.63 and 3.70. In the ^{13}C NMR spectrum of **3**, the triplet signal centered at δ 78.7 with a coupling constant of 162 Hz was assignable to the *exo*-methylene carbon. The FAB-mass spectrum of **3** gave its parent peak.



3

Reaction of **2** with bases such as NaOMe or KOH resulted in the precipitation of palladium black, in contrast to the alkoxylation of the ring methyl group in Cp*Ir complexes.[11h,i] In the reaction with pyridine, we obtained complex **3** together with an unexpected complex, $[C_5H_5NH][PdCl_3(\eta^4\text{-}C_4Me_2(^tBu)_2)]$ (**4**), which was a product of the reaction of **2** with pyridine·HCl. Separation of these two complexes by crystallization has been a failure, but we were able to isolate **4** in 77% yield by treating **2** with 2 equiv of C_5H_5N·HCl in dichloromethane. The structure of complex **4** was established by X-ray analysis.[24]



4

No ring methyl activation occurred in the reaction of **2** with 2,2′-bipyridine in dichloromethane; however, a cationic cyclobutadiene complex $[PdCl(\eta^4\text{-}C_4Me_2(^tBu)_2)\text{-}(bipy)]Cl$ (**5**) was obtained in 85% yield. On the other hand, addition of NEt_3 caused the ring methyl activation, giving the cationic complex **6** in 83% yield after treating with $AgBF_4$. The coordination of bipy lowered the number of Cl atoms coordinating to the palladium atom to increase the acidity of the methyl group. A similar η^3-pentatolylcyclobutenyl palladium complex, [Pd(1−3-η-1,2,3,4,4-penta(tolyl)cyclobutenyl)(bipy)]PF_6 (**7**), was prepared by the reaction of $B(C_6H_4Me\text{-}p)_4$ to the

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(24) The crystal structure of **4** is shown in the Supporting Information.

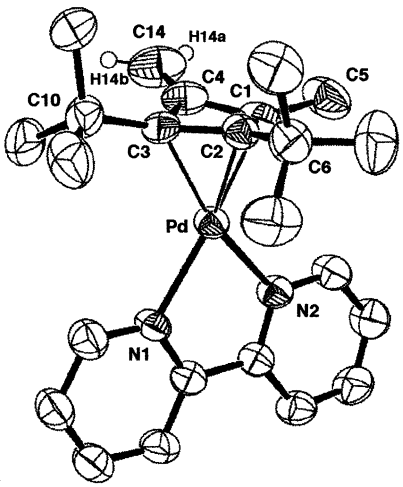
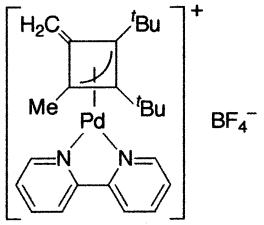


Figure 1. Molecular structure of **6** with numbering scheme. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 6

Pd−C(1)	2.142(5)
Pd−C(2)	2.166(4)
Pd−C(3)	2.171(4)
Pd−C(4)	2.404(5)
Pd−N(1)	2.179(4)
Pd−N(2)	2.129(4)
C(1)−C(2)	1.432(7)
C(1)−C(4)	1.489(8)
C(2)−C(3)	1.457(6)
C(3)−C(4)	1.505(7)
C(1)−C(5)	1.498(7)
C(3)−C(10)	1.500(7)
C(4)−C(14)	1.331(8)
N(2)−Pd−N(1)	76.86(16)
C(2)−C(1)−C(4)	90.3(4)
C(1)−C(2)−C(3)	91.4(4)
C(2)−C(3)−C(4)	88.7(4)
C(1)−C(4)−C(3)	87.4(4)

tetra(tolyl)cyclobutadiene complex of palladium.[25] The *exo*-methylene-η^3-cyclobutenyl structure of **6**, essentially the same as **3**, was confirmed by spectral data and a crystallographic study. The cationic part of **6** was observed as a parent ion peak in its FAB-mass spectrum. The presence of two *tert*-butyl groups and one methyl group in **6** was evident from three singlet signals in a 3:3:1 ratio, and two doublets (δ 3.95 and 4.02) with a coupling constant of 1.6 Hz were assigned to the exocyclic methylene protons. In the ^{13}C NMR spectrum, the most informative datum was the signal due to the methylene carbon appearing at δ 85.3, whose J_{C-H} coupling constant (162 Hz) was typical of an sp^2 carbon. Figure 1 shows the molecular structure of **6**, and its selected bond distances and angles are summarized in Table 1. The bond distances within the C(1)−(2)−C(3) moiety [C(1)−C(2) = 1.432(7) Å and C(2)−C(3) = 1.457(6) Å] and the bond distances of Pd−C(1) [2.142(5) Å], Pd−C(2) [2.166(4) Å], and Pd−C(3) [2.171(4) Å] are comparable to those found for cyclic-η^3-allyl palladium complexes.[26−29] In contrast, the longer distance of Pd−C(4) [2.404(5) Å] clearly indicates that the exocyclic methylene moiety is uncoordinated to the palladium atom, as further supported by the C=C double bond distance of C(4)−C(14) [1.331(8) Å], being shorter by 0.167 Å than the single bond distance of C(1)−C(5) [1.498(7) Å]. The four-membered ring is not planar and the ring carbon C(4) is slightly bent away from the metal: the dihedral angle of the least-squares planes [C(1), C(2), and C(3)] and [C(1), C(3), and C(4)] is 15.9(5)°.



6

In conclusion, base-induced ring methyl activation was observed for half-metallocene type η^4-butadiene complexes of palladium, which is the first ring methyl activation of the η^4-cyclobutadiene complex. We have thus synthesized and characterized two palladium complexes, [PdCl(η^3-C$_4$(=CH$_2$)Me(^{t}Bu)$_2$)]$_2$ (**3**) and [Pd(η^3-C$_4$(=CH$_2$)Me(^{t}Bu)$_2$)(bipy)]]BF$_4$ (**6**), whose *exo*-methylene-η^3-cyclobutenyl structure was confirmed by spectral data and a crystallographic study for the complex **6**.

Experimental Section

General Procedures. All manipulations involving air- and moisture-sensitive organometallic compounds were carried out using standard Schlenk techniques under argon. THF, ether, hexane, and toluene were dried and deoxygenated by distillation over sodium benzophenone ketyl under argon. Methanol was refluxed over magnesium methoxide and then distilled under argon. Chloroform-d_1 was distilled and degassed by trap-to-trap after drying over calcium hydride. Triethylamine was purchased from Nakalai Tesque and distilled over calcium hydride. Complex **2** was prepared according to the literature procedure.[23]

^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz), and ^{19}F NMR (280 MHz) were measured on a Varian-Mercury300. Assignments for ^{1}H and ^{13}C NMR for some of the complexes were aided by 2D ^{1}H−^{1}H COSY and 2D ^{1}H−^{13}C COSY spectra, respectively. IR spectra were recorded by the use of a Jasco FT/IR-230. Mass spectrometric data were obtained using FAB techniques on a JEOL SX-102 spectrometer. ESI-mass spectra were taken on a PE-Sciex API-III plus spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 microanalyzer in the Department of Chemistry, Faculty of Engineering Science, Osaka University. All melting points were measured in sealed tubes and were not corrected.

Preparation of 3. To a solution of **2** (60.3 mg, 81.6 μmol) in dichloromethane (5 mL) was added NEt$_3$ (0.025 mL, 0.18 mmol) via syringe. The reaction mixture was stirred for 1 h at room temperature. All volatiles were removed under reduced pressure. The residual was dissolved in dichloromethane (5 mL), and then the solution was washed with water (twice, 7.5 mL each) to separate ammonium salts. After drying over MgSO$_4$, all volatiles were removed under reduced pres-

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sure. The residual was dissolved in dichloromethane (1 mL), and then hexane (15 mL) was added to precipitate the product as a yellow powder (44.2 mg, 81% yield), mp 155−158 °C (decomp). ^{1}H NMR (300 MHz, $CDCl_3$, 35 °C): δ 1.32 (s, 9H, C(CH_3)$_3$), 1.43 (s, 9H, C(CH_3)$_3$), 1.47 (s, 3H, CH_3), 3.63 (s, 1H, CH_2), 3.70 (s, 1H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, 35 °C): δ 11.7 (q, $^1J_{C-H}$ = 129 Hz, CH_3), 28.6 (q, $^1J_{C-H}$ = 127 Hz, C(CH_3)$_3$), 30.7 (q, $^1J_{C-H}$ = 127 Hz, C(CH_3)$_3$), 33.2 (s, C(CH_3)$_3$), 33.7 (s, C(CH_3)$_3$), 78.7 (t, $^1J_{C-H}$ = 162 Hz, CH_2), 95.0 (s, C_4-(CH_2)Me(^{t}Bu)$_2$), 106.4 (s, C_4(CH_2)Me(^{t}Bu)$_2$), 133.5 (s, C_4(CH_2)-Me(^{t}Bu)$_2$), 138.4 (s, C_4(CH_2)Me(^{t}Bu)$_2$). IR (KBr): ν(C═C)/cm^{-1} 1655 (m). FAB-MS (*m*/*z*): 666 (M^+), 262 (M^+ − Cl).

Preparation of 4. To a solution of **2** (489 mg, 0.662 mmol) in dichloromethane (7.5 mL) was added pyridinium chloride (160 mg, 1.38 mmol). The reaction mixture was stirred for 9.5 h, and then ether (20 mL) was added to precipitate complex **4** as a yellow powder (493 mg, 77% yield), mp 197−200 °C (decomp). ^{1}H NMR (300 MHz, $CDCl_3$, 35 °C): δ 1.46 (s, 18H, C(CH_3)$_3$), 1.96 (s, 6H, CH_3), 7.86 (m, 2H, *m*-C_5H_6N), 8.37 (m, 1H, *p*-C_5H_6N), 9.07 (m, 2H, *o*-C_5H_6N). ^{13}C NMR (75 MHz, $CDCl_3$, 35 °C): δ 12.0 (q, $^1J_{C-H}$ = 131 Hz, CH_3), 29.5 (q, $^1J_{C-H}$ = 128 Hz, C(CH_3)$_3$), 33.6 (s, C(CH_3)$_3$), 117.9 (s, C_4Me_2-^{t}Bu$_2$), 118.7 (s, $C_4Me_2{}^t$Bu$_2$), 126.4 (d, $^1J_{C-H}$ = 172 Hz, *m*-C_5H_6N), 126.4 (d, $^1J_{C-H}$ = 189 Hz, *o*-C_5H_6N), 145.5 (d, $^1J_{C-H}$ = 168 Hz, *p*-C_5H_6N). IR (Nujol): ν (N−H)/cm^{-1} 3430 (m), 3430 (m). ESI-MS (*m*/*z*): 369 [($PdCl_3C_4{}^t$Bu$_2$Me$_2$) − Cl]. Anal. Calcd for $C_{19}H_{30}$-NCl_3Pd: C, 47.03; H, 6.23; N, 2.89. Found: C, 46.63; H, 6.37; N, 3.23.

Preparation of 5. 2,2′-Bipyridine (25.6 mg, 0.016 mmol) and **2** (48.3 mg, 0.0065 mmol) were dissolved in dichloromethane (7.5 mL). The reaction mixture was stirred for 18 h at room temperature. All volatiles were removed under reduced pressure. The residual was washed with hexane (twice, 7.5 mL each) and then dried in vacuo to give the product as a yellow powder (58.8 g, 85% yield), mp 75−79 °C (decomp). ^{1}H NMR (300 MHz, $CDCl_3$, 35 °C): δ 1.47 (s, 18H, C(CH_3)$_3$), 1.76 (s, 6H, CH_3), 7.56 (m, 2H, $C_{10}H_8N_2$), 8.10 (m, 2H, $C_{10}H_8N_2$), 8.82 (m, 4H, $C_{10}H_8N_2$). FAB-MS (*m*/*z*): 489 (M^+ − Cl^-), 453 (M^+ − 2Cl^-).

Preparation of 6. Complex **2** (253 mg, 0.342 mmol) and 2,2′-bipyridine (113 mg, 0.721 mmol) were dissolved in dichloromethane (7.5 mL), followed by addition of NEt_3 (0.10 mL, 0.72 mmol). To the solution was added $AgBF_4$ (145 mg, 0.737 mmol). The reaction mixture was stirred overnight at room temperature in the dark. The precipitated AgCl was removed by centrifugation. The supernatant solution was concentrated under reduced pressure to remove all volatiles. The residual was dissolved in dichloromethane (8 mL), and then the solution was washed with water (twice, 15 mL each) to separate ammonium salts. After drying over $MgSO_4$, all volatiles were removed under reduced pressure. Recrystallization of the resulting solid from a mixture of dichloromethane and hexane at room temperature afforded **6** as a yellow powder (307 mg, 83% yield), mp 187−191 °C (decomp). ^{1}H NMR (300 MHz, $CDCl_3$, 35 °C): δ 1.36 (s, 9H, C(CH_3)$_3$), 1.52 (s, 9H, C(CH_3)$_3$), 1.76 (s, 3H, CH_3), 3.95 (d, $^2J_{H-H}$ = 1.6 Hz, 1H, CH_2), 4.02 (d, 1H, CH_2), 7.72 (m, 2H, $C_{10}H_8N_2$), 8.26 (m, 2H, $C_{10}H_8N_2$), 8.65 (m, 2H, $C_{10}H_8N_2$), 8.8−9.0 (m, 2H, $C_{10}H_8N_2$). ^{13}C NMR (75 MHz, $CDCl_3$, 35 °C): δ 11.7 (q, $^1J_{C-H}$ = 129 Hz, CH_3), 29.5 (q, $^1J_{C-H}$ = 124 Hz, C(CH_3)$_3$), 30.5 (q, $^1J_{C-H}$ = 124 Hz, C(CH_3)$_3$), 33.5 (s, C(CH_3)$_3$), 33.6 (s, C(CH_3)$_3$), 53.4 (s, C_4(CH_2)Me(^{t}Bu)$_2$), 85.3 (t, $^1J_{C-H}$ = 162 Hz, CH_2), 92.8 (s, C_4(CH_2)Me(^{t}Bu)$_2$), 108.7 (s, C_4(CH_2)Me(^{t}Bu)$_2$), 124.3 (d, $^1J_{C-H}$ = 168 Hz, $C_{10}H_8N_2$), 127.4 (d, $^1J_{C-H}$ = 168 Hz, $C_{10}H_8N_2$), 134.1 (s, C_4(CH_2)Me(^{t}Bu)$_2$), 141.1 (d, $^1J_{C-H}$ = 168 Hz, $C_{10}H_8N_2$), 141.2 (d, $^1J_{C-H}$ = 168 Hz, $C_{10}H_8N_2$), 154.1 (s, $C_{10}H_8N_2$). IR (KBr): ν (BF_4)/cm^{-1} 1084 (s), ν (C═C)/cm^{-1} 1654 (m). FAB-MS (*m*/*z*): 453 (M^+ − BF_4^-), 262 (M^+ − BF_4^- − C_4(CH_2)Me(^{t}Bu)$_2$). Anal. Calcd for $C_{24}H_{31}N_2BF_4$-$Pd(H_2O)$: C, 51.78; H, 5.61; N, 5.03. Found: C, 51.41; H, 5.55; N, 4.95.

Crystallographic Data Collections and Structure Determination of Data Collection. Crystals of **6** suitable for X-ray diffraction studies were sealed in glass capillaries under argon atmosphere and then mounted on a Rigaku AFC-7R four-circle diffractomerter for data collection using Mo Kα (graphite monochromated, λ = 0.71069) radiation. The unit cell parameters and the orientation matrix were determined by a least-squares fit to 2θ values of 25 strong reflections for **6**. Three standard reflections were chosen and monitored every 150 reflections. An empirical absorption correction was applied on the basis of azimuthal scans, and the data were corrected for Lorentz and polarization effects.

The structure of complex **6** was solved by direct methods (SIR-97)[30] and refined on F^2 by full-matrix least-squares methods (SHELXL97).[31] Details are summarized in the Supporting Information. All calculations of least-squares refinements were performed with SHELXL97 programs on a Silicon Graphics Inc. Origin 3400 computer at the Research Center for Structural Biology Institute for Protein Research, Osaka University.

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Supporting Information Available: Tables giving crystallographic data for complexes **4** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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