Notes

O-Alkylation of Sulfinate Anion with a Palladium(II) Trimethylenemethane Intermediate Arising from [Pd{η^3-$CH_2C(CH_2Cl)CH_2$}(η^5-C_5R_5)]

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*Summary: The reaction of [Pd{η^3-$CH_2C(CH_2Cl)CH_2$}(η^5-C_5R_5)] (**1**) with $NaSO_2Ph$ initially affords the kinetically preferred O-alkylated complex [Pd{η^3-$CH_2C(CH_2OS(O)Ph)CH_2$}(η^5-C_5R_5)] (**2**), which is subsequently transformed into the thermodynamically preferred S-alkylated complex [Pd{η^3-$CH_2C(CH_2SO_2Ph)CH_2$}(η^5-C_5R_5)] (**3**) and the bimolecular reaction product [Pd{η^3-$CH_2C(CH_2C_5R_5)CH_2$}(η^5-C_5R_5)] (**4**). These reactions are rationalized by the intermediacy of a cationic trimethylenemethane−palladium complex.*

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Introduction

(η^3-2-(Halomethyl)allyl)metal complexes are precursors to electrophilic trimethylenemethane (TMM)−metal complexes via C−X bond cleavage. They have been shown to possess reactivities such as facile oxidative addition,[1,2] methanolysis,[3−6] and isomerization.[4,6,7] Recently, we reported a novel transformation of [Pd{η^3-$CH_2C(CH_2Cl)CH_2$}(η^5-C_5H_5)] (**1a**) to [Pd{η^3-$CH_2C(CH_2C_5H_5)CH_2$}(Cl)]$_2$ in which a TMM−Pd intermediate is assumed to undergo an intermolecular electrophilic substitution with cyclopentadienyl ligand.[6] In an attempt to gain more insight into the reactivity of such a TMM−Pd intermediate, we examined reactions of **1a** or [Pd{η^3-$CH_2C(CH_2Cl)CH_2$}(η^5-C_5Ph_5)] (**1b**) with the sulfinate anion $PhSO_2^-$. Interest in the use of the sulfinate anion has arisen because this anion is ambident and may undergo alkylation either with the sulfur to yield an S-alkylation product by an S_N2 process[8] or with oxygen to produce an O-alkylation product by an S_N1 process.[9] We report here the formation of O-alkylated complex **2** rather than S-alkylated complex **3** in the reaction of **1** with $NaSO_2Ph$, demonstrating the intermediacy of the discrete TMM−Pd species [Pd{η^3-$CH_2C(CH_2)CH_2$}(η^5-C_5R_5)]$^+$.

Results and Discussion

Treatment of **1a** (1.62×10^{-2} [M]) with excess $NaSO_2Ph$ (10 equiv) in $CDCl_3$ at 25 °C for 23 h resulted in the formation of a mixture of O-alkylated complex **2a** (88%) and S-alkylated complex **3a** (8%) together with **4a** (3%), which is among several products from the spontaneous transformation of **1a**.[6] A slower isomerization of **2a** to **3a** in the solution will be described later.

We failed to isolate **2a** in a pure state, since it isomerized into **3a** in the workup stage of isolation. However, the structure of **2a** was supported by comparing its ^{1}H NMR spectrum with that of the analogous C_5Ph_5 complex **2b**, which was sufficiently more stable with respect to the isomerization to allow isolation (see below). **3a** was synthesized alternatively from the corresponding Cl complex **6**, prepared according to Scheme 1, and TlC_5H_5.

The purple complex **1b** (1.50×10^{-2} M), prepared readily from [Pd{η^3-$CH_2C(CH_2Cl)CH_2$}(Cl)]$_2$ (**7**) and LiC_5Ph_5 in 77% isolated yield, was reacted with excess $NaSO_2Ph$ (10 equiv) in $CDCl_3$ at 25 °C for 72 h to give exclusively the O-alkylated complex **2b** in 88% NMR yield (conversion of **1b** 95%) (Scheme 1). Pure **2b** could be obtained in 62% isolated yield by recrystallization of the crude product with C_6H_6/hexane.

The ^{1}H NMR spectrum of **2b** showed four nonequivalent resonances (δ 2.62, 2.64, 3.48, 3.57) due to syn and anti protons and two doublets (δ 4.01 and 4.55, $J = 11.9$ Hz) due to the diastereotopic protons of the $CH_2OS(O)Ph$ group. Furthermore, it should be noted that the diastereotopic methylene protons were shifted to the lower fields in comparison to those observed for the isomer **3b** (δ 3.75) because of the CH_2-O bonding. The ^{1}H NMR spectrum of **2a** also showed four nonequivalent resonances (δ 2.28, 2.32, 3.46, 3.62) and two doublets (δ 4.00 and 4.36, $J = 11.3$ Hz), similarly to those for **2b**. These data are consistent with their asymmetric structures. The structure of **2b** was also characterized by X-ray diffraction; an ORTEP view is given in Figure 1 along with selected bond lengths and angles. The O atom attached to the S atom was disordered with 67/33

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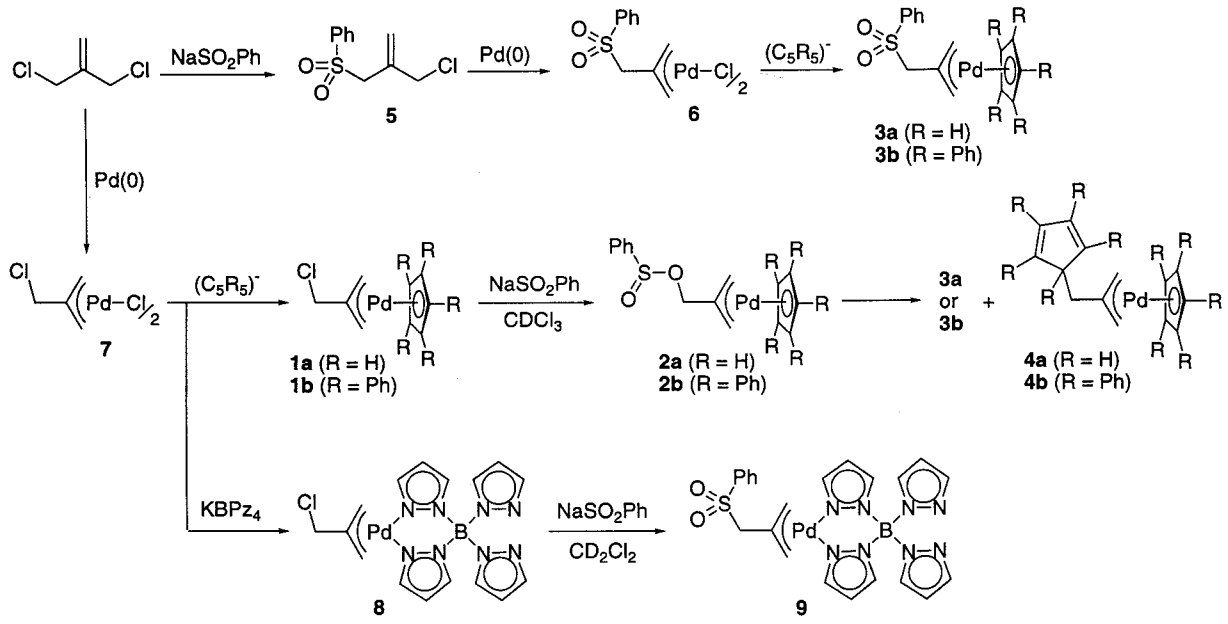
Scheme 1



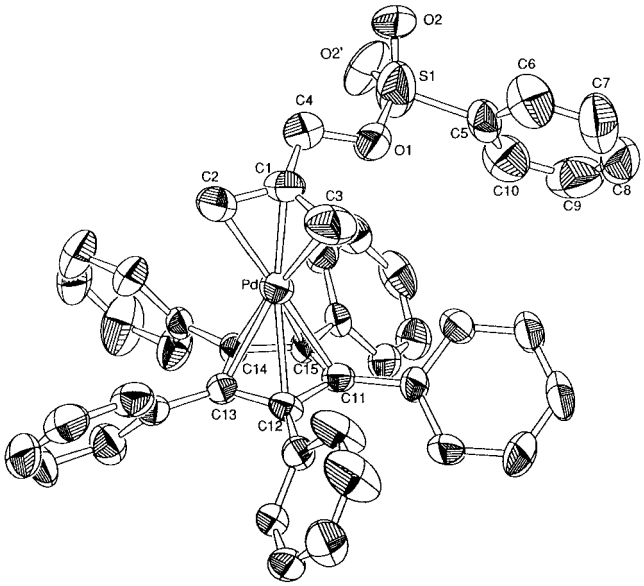


Figure 1. ORTEP drawing of complex **2b** with thermal ellipsoids at 50% probability levels (all hydrogen atoms are omitted for clarity). Note that O2 is disordered. Selected bond lengths (Å) and angles (deg): Pd−Cl, 2.068(9); Pd−C2, 2.15(1); Pd−C3, 2.14(1); Pd−C11, 2.315(8); Pd−C12, 2.294(8); Pd−C13, 2.309(8); Pd−C14, 2.346(8), Pd−C15, 2.443(8); S1−O1, 1.619(7); S1−O2, 1.31(1); S1−O2′, 1.22(2); S1−C5, 1.81(1); O1−C4, 1.44(1); C1−C2, 1.40(1); C1−C3, 1.37(1); C1−C4, 1.49(1); O1−S1−O2, 117.0(7); O1−S1−O2′, 132(1); O1−S1−C5, 92.9(4), O2−S1−O2′, 80(1); O2−S1−C5, 110.9(7); O2′−S1−C5, 123(1); S1−O1−C4, 114.6(6); C2−C1−C3, 116(1); O1−C4−C1, 110.5(9).

occupancy (O2 and O2′) so as to give a pair of enantiomers. This disorder might have lowered the accuracy of the S=O bond distance (1.31(1) Å; generally, S=O is in the range 1.45−1.48 Å).[9,10]

When the $CDCl_3$ solution containing primarily **2a**, which was formed as described above, was allowed to stand, the amount of **2a** decreased and those of **3a** and **4a** increased (after 97 h: **2a**, 34%; **3a**, 52%; **4a**, 5%), indicating that **2a** isomerized to **3a**. Moreover, pure **3a** showed no tendency to undergo any transformation on standing in CD_2Cl_2 ([**3a**] = 1.30×10^{-2} M) at 40 °C for 6 days. We suggest that **2a** is the kinetically preferred product and **3a** is thermodynamically preferred and that **3a** is not a precursor to **4a**.

Pure **2b** was stable and unchanged in C_6D_6 at 40 °C for 73 h. In a polar solvent, however, **2b** was found to change to **3b** and **4b**, albeit much more slowly than **2a** (Scheme 1). Thus, when a CD_2Cl_2/CD_3CN (1/1) solution of **2b** (1.29×10^{-2} M) was allowed to stand at 40 °C for 79 h, formation of **3b** (5%) and **4b** (2%) was observed and 92% of **2b** remained unchanged. Interestingly, treatment of a CH_2Cl_2 solution of **2b** by silica gel column chromatography greatly promoted the transformation to give 28% of **4b** and 23% of a mixture of **2b**/**3b** (22/78).

We propose that the series of reactions above are rationalized by the intermediacy of the TMM−Pd intermediate formed by C−Cl or C−OS(O) cleavage (Scheme 2). In the reaction of **1** with $NaSO_2Ph$, the TMM−Pd intermediate arising from **1** is trapped by the O atom of the sulfinate anion to give **2** initially as the kinetically preferred product. **2** also generates the TMM−Pd intermediate which is trapped by the S atom of the sulfinate anion to yield the thermodynamically preferred product **3**. This is in line with the fact that sulfinate esters are known to undergo isomerization to sulfones when the nature of the alkyl moiety is such as to give rise to a comparatively stable carbocation.[8a,11] The generation of the cationic TMM−Pd species during the isomerization of **2** to **3** is supported by the observation that **2b** was unchanged in C_6H_6 while the trans

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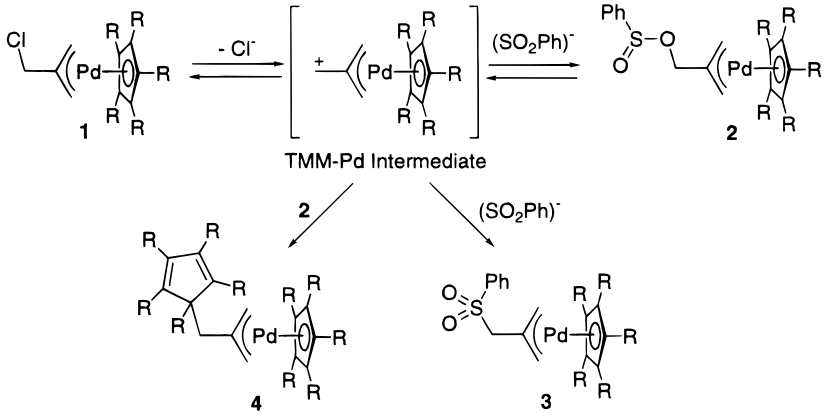
Scheme 2



formation proceeded in CD_2Cl_2/CD_3CN. Furthermore, the cyclopentadienyl ligand of **2** may also have trapped the TMM−Pd intermediate to yield **4**. This process is analogous to that of the decomposition of **1a** into **4a** and **7**.[6] However, we have not been able to detect a possible byproduct analogous to **7**, $[Pd\{\eta^3\text{-}CH_2C(CH_2OS(O)Ph)\text{-}CH_2\}]^+(SO_2Ph)^-$.

Finally, it is remarkable that the electron-donating cyclopentadienyl ligand plays a key role in the O-alkylation of the (2-(chloromethyl)ally)palladium complex. Thus, the reaction of **8** having two N-donors of pyrazolylborate, with $NaSO_2Ph$ in CD_2Cl_2, afforded exclusively the S-alkylated complex **9** in 61% NMR yield after 8 days. No O-alkylated complex was seen throughout the reaction. This reaction is explained by an S_N2 process similar to the reaction of alkyl halides with $(SO_2Ph)^-$, since the pyrazolylborate ligand is not as electron-donating as the cyclopentadienyl group.

Experimental Section

All manipulations were carried out under argon by the use of standard vacuum-line techniques. Solvents were dried by standard methods and distilled prior to use. 3-Chloro-2-(chloromethyl)-1-propene and $NaSO_2Ph$ were obtained from Aldrich Chemical Co., Ltd., and used without further purification. **1a** and **7** were prepared according to the reported methods.[3,6] ^1H NMR spectra were recorded on a JEOL JNM-GSX-270 (270 MHz) spectrometer. Chemical shifts in the ^1H NMR are referenced to residual protons of the solvents. All NMR experiments were carried out in sealed NMR tubes.

Synthesis of $[Pd(\eta^3\text{-}CH_2C(CH_2Cl)CH_2)(\eta^5\text{-}C_5Ph_5)]$ (1b). LiC_5Ph_5 was prepared in situ by dropwise addition of *n*-BuLi in hexane (1.6 M; 0.3 mL, 0.48 mmol) to C_5Ph_5H (206 mg, 0.461 mmol) in dried THF (10 mL) at room temperature. To the solution of LiC_5Ph_5 was added **7** (95 mg, 0.411 mmol), and the mixture was stirred for 5 min. Solvents were removed in vacuo, the residue was extracted with C_6H_6, the solution was filtered to remove the salts, and the filtrate was evaporated under reduced pressure. Recrystallization of the residue from C_6H_6/hexane yielded **1** as purple crystals. Yield: 204 mg (77%). ^1H NMR ($CDCl_3$): δ 2.68 (s, 2H), 3.59 (s, 2H), 4.06 (s, 2H), 6.9−7.1 (m, 25H). Anal. Calcd for $C_{39}H_{31}ClPd$: C, 73.02; H, 4.87. Found: C, 73.07; H, 5.06.

Synthesis of $[Pd(\eta^3\text{-}CH_2C(CH_2OS(O)Ph)CH_2)(\eta^5\text{-}C_5Ph_5)]$ (2b). To a solution of **1** (451 mg, 0.70 mmol) in CH_2Cl_2 (40 mL) was added $NaSO_2Ph$ (222 mg, 1.35 mmol), and the mixture was stirred for 3 days. Excess $NaSO_2Ph$ and NaCl were removed by filtration, and solvents were removed in vacuo. The residue was extracted with C_6H_6, the solution filtered to remove the salts, and the filtrate evaporated under reduced pressure. Recrystallization of the residue from C_6H_6/hexane yielded the product as purple crystals. Yield: 327 mg (62%). ^1H NMR (CD_2Cl_2): δ 2.62 (s, 1H), 2.64 (s, 1H), 3.48 (d, J = 2.7 Hz, 1H), 3.57 (d, J = 2.7 Hz, 1H), 4.01 (d, J = 11.9 Hz, 1H), 4.55 (d, J = 11.9 Hz, 1H), 6.8−7.1 (m, 25H), 7.4−7.6 (m, 5H). Anal. Calcd for $C_{45}H_{36}O_2SPd$: C, 72.37; H, 4.86. Found: C, 72.28; H, 4.92.

Table 1. Crystallographic Data for 2b

empirical formula	$C_{45}H_{36}O_2SPd$
fw	687.18
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
a, Å	10.674(3)
b, Å	17.117(5)
c, Å	10.032(3)
α, deg	98.18(3)
β, deg	95.67(2)
γ, deg	93.31(3)
V, Å^3	1800.6(10)
Z	2
D_{calc}, g/cm^3	1.267
λ(Mo Kα), Å	0.710 69
μ(Mo Kα), cm^{-1}	6.04
temp, °C	23.0
$2\theta_{max}$, deg	55.1
no. of observns	5217 ($I > 3.00\sigma(I)$)
least-squares weights	$w^{-1} = \sigma^2(F_o)$
R	0.067
R_w	0.084

Synthesis of 2-(Chloromethyl)-3-(phenylsulfonyl)propene (5). To a MeOH solution (60 mL) of 3-chloro-2-(chloromethyl)-1-propene (3.64 g, 29.1 mmol) was added $PhSO_2Na$ (4.78 g, 29.1 mmol), and the mixture was refluxed for 24 h. MeOH was removed under reduced pressure, and the residue was extracted with H_2O (50 mL)/CH_2Cl_2 (2 × 30 mL). The CH_2Cl_2 extract was dried ($MgSO_4$), and the solvent was removed. Recrystallization of the residue from Et_2O/hexane yielded the product as pale yellow crystals. Yield: 3.65 g (55%). ^1H NMR ($CDCl_3$): δ 3.96 (s, 2H), 4.22 (s, 2H), 5.03 (s, 1H), 5.45 (s, 1H), 7.57 (m, 2H), 7.68 (m, 1H), 7.88 (m, 2H). Anal. Calcd for $C_{10}H_{11}ClO_2S$: C, 52.06; H, 4.81. Found: C, 52.26; H, 4.79.

Synthesis of $[Pd(\eta^3\text{-}CH_2C(CH_2SO_2Ph)CH_2)(Cl)]_2$ (6). This compound was prepared from **5** in a manner similar to that for **7**.[3] Yield: 35%. ^1H NMR (DMSO-d_6): δ 3.34 (s, 2H), 3.97 (s, 2H), 4.43 (s, 2H), 7.69 (m, 2H), 7.80 (m, 1H), 7.93 (m, 2H). Anal. Calcd for $C_{10}H_{11}ClO_2SPd$: C, 35.66; H, 2.99. Found: C, 35.88; H, 3.24.

Synthesis of $[Pd(\eta^3\text{-}CH_2C(CH_2SO_2Ph)CH_2)(\eta^5\text{-}C_5H_5)]$ (3a). This compound was prepared from **6** in a manner similar to that for **1a**.[6] Yield: 55%. ^1H NMR ($CDCl_3$): δ 2.24 (s, 2H), 3.40 (s, 2H), 3.71 (s, 2H), 5.72 (s, 5H), 7.57 (m, 2H), 7.68 (m, 1H), 7.89 (m, 2H). Anal. Calcd for $C_{15}H_{17}O_2SPd$: C, 48.99; H, 4.66. Found: C, 49.22; H, 4.54.

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Synthesis of [Pd(η^3-$CH_2C(CH_2SO_2Ph)CH_2$)(η^5-C_5Ph_5)] (3b). This compound was prepared from **6** in a manner similar to that for **1b**. Yield: 37%. ^{1}H NMR (CD_2Cl_2): δ 2.57 (s, 2H), 3.29 (s, 2H), 3.75 (s, 2H), 6.85−7.0 (m, 25H), 7.57 (m, 2H), 7.69 (m, 1H), 7.85 (m, 2H). Anal. Calcd for $C_{45}H_{36}O_2SPd$: C, 72.37; H, 4.86. Found: C, 72.95; H, 5.12.

Synthesis of [Pd(η^3-$CH_2C(CH_2C_5Ph_5)CH_2$)(η^5-C_5Ph_5)] (4b). A CH_2Cl_2 solution (0.5 mL) of **2b** (158 mg, 0.211 mmol) was subjected to flash column chromatography with silica gel (Wako gel C-300, 12 g), yielding **4b** (63 mg, 28%, R_f 0.54) and a **2b**/**3b** mixture (22/78) (36 mg, 23%, R_f 0.45). Recrystallization with C_6H_6/hexane gave purple crystals of **4b**. Yield: 42 mg (19%). ^{1}H NMR (CD_2Cl_2): δ 2.51 (s, 2H), 3.23 (s, 2H), 3.24 (s, 2H), 6.7−7.3 (m, 50H). Anal. Calcd for $C_{74}H_{56}Pd$: C, 84.51; H, 5.37. Found: C, 84.38; H, 5.87.

Synthesis of [Pd{η^3-$CH_2C(CH_2Cl)CH_2$}(BPz_4)] (8). To a suspension of **7** (266 mg, 1.15 mmol) in CH_2Cl_2 (5 mL) was added $KBPz_4$ (391 mg, 1.23 mmol) at room temperature, and the mixture was stirred for 5 min. KCl was removed by filtration, and the yellow solution was concentrated. Recrystallization from CH_2Cl_2/hexane yielded yellow crystals of **8**. Yield: 377 mg (69%). ^{1}H NMR (CD_2Cl_2): δ 2.91 (s, 2H), 3.73 (s, 2H), 3.77 (s, 2H), 6.26 (t, J = 2.4 Hz, 4H), 6.97 (d, J = 2.4 Hz, 4H), 7.64 (d, J = 0.8 Hz, 4H). Anal. Calcd for $C_{16}H_{18}BClN_5Pd$: C, 40.43; H, 3.82; N, 24.14. Found: C, 40.48; H, 3.70; N, 23.58.

Synthesis of [Pd(η^3-$CH_2C(CH_2SO_2Ph)CH_2$)(BPz_4)] (9). This compound was prepared from **6** in a manner similar to that for **8**. Yield: 75%. ^{1}H NMR ($CDCl_3$): δ 2.84 (s, 2H), 3.30 (s, 2H), 3.48 (s, 2H), 6.23 (t, J = 2.4 Hz, 4H), 6.98 (br s, 4H), 7.60 (m, 6H), 7.71 (m, 1H), 7.86 (m, 2H). Anal. Calcd for $C_{22}H_{23}BN_8O_2SPd$: C, 45.50; H, 3.99; N, 19.29. Found: C, 45.15; H, 3.96; N, 18.92.

X-ray Structure Determination for 2b. A crystal (0.2 × 0.2 × 0.2 mm) suitable for X-ray diffraction was mounted on a glass fiber. The data were obtained on a Rigaku AFC-5R diffractometer with graphite-monochromated Mo Kα radiation. The calculation was carried out with the TEXSAN crystallographic software package of Molecular Structure Corp. The structure was solved by direct methods and refined by full-matrix least-squares procedures, the function minimized being $\sum w(|F_o| - |F_c|)^2$. The non-hydrogen atoms were refined anisotropically. The crystallographic data are summarized in Table 1.

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Supporting Information Available: Figures giving additional views and tables of positional and thermal parameters and bond lengths and angles for **2b** (17 pages). Ordering information is given on any current masthead page.

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