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LETTER

Novel cyclic trinuclear palladium(II) complex containing dimetallated benzene

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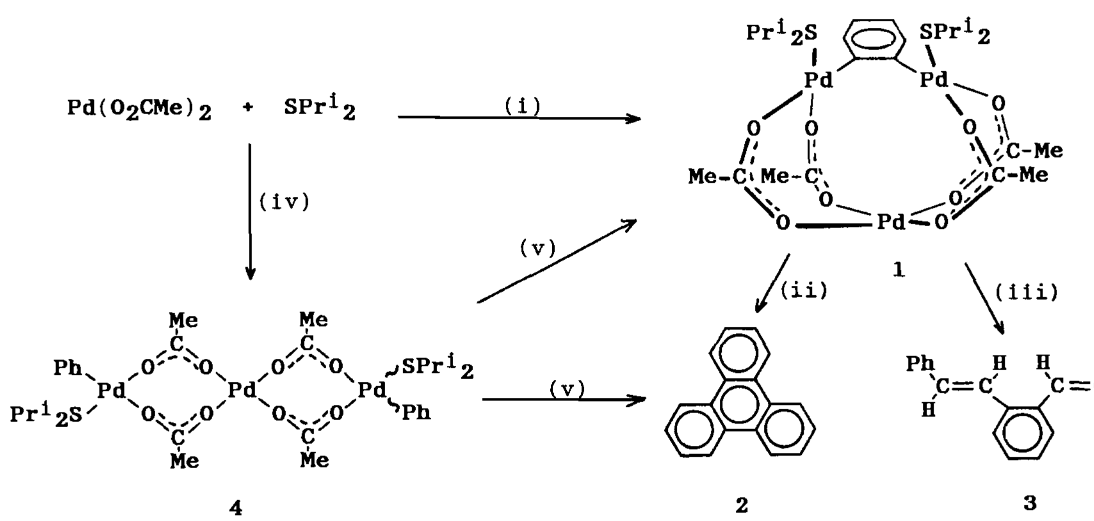
We have recently reported that the palladium(II) acetate–dialkyl sulfide system directly activated aromatic C–H bonds to give diaryltripalladium(II) complexes $[(\mathrm{R_2S})\mathrm{ArPd}(\mu\text{-}\mathrm{O_2CMe})_2\mathrm{Pd}(\mu\text{-}\mathrm{O_2CMe})_2\mathrm{PdAr}(\mathrm{SR_2})]$ [1–3]. In the presence of diisopropyl sulfide as an additive, palladium(II) acetate directly activated benzene C–H bonds at 70 °C to yield $[(\mathrm{Pr^i_2S})\mathrm{PhPd}(\mu\text{-}\mathrm{O_2CMe})_2\mathrm{Pd}(\mu\text{-}\mathrm{O_2CMe})_2\mathrm{PdPh}(\mathrm{SPr^i_2})]$ [2]. However, when the above reaction was performed at 90 °C, it was found that another arylpalladium(II) species was obtained. In this letter we wish to describe the isolation and some reactivity of the novel arylpalladium(II) complex of $[\mathrm{Pd_3}(\mu\text{-}\mathrm{C_6H_4})(\mu\text{-}\mathrm{O_2CMe})_4(\mathrm{SPr^i_2})_2]$ having a cyclic tripalladium structure with a dimetallated benzene molecule.

A benzene solution (20 $\mathrm{cm^3}$) containing palladium(II) acetate (500 mg, 2.23 mmol) and diisopropyl sulfide (176 mg, 1.49 mmol)was heated in an oil bath at 90–95 °C for 1 h (Scheme 1). After reprecipitation with hexane and purification by silica gel column chromatography, yellow crystals (**1**: 84 mg, 13%) were obtained. ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta = 1.05$ (6H, d, $J = 6.8$ Hz, $\mathrm{SCHC}H_3$), 1.62 (6H, d, $J = 6.8$ Hz, $\mathrm{SCHC}H_3$), 2.00 (12H, s, $\mathrm{O_2CC}H_3$), 3.10 (1H, hept, $J = 6.8$ Hz, $\mathrm{SC}H\mathrm{CH_3}$), 3.46 (1H, hept, $J = 6.8$ Hz, $\mathrm{SC}H\mathrm{CH_3}$), and AA'BB' pattern centered at 6.56 and 6.68 (4H, m. $\mathrm{C_6}H_4$); ^{13}C NMR ($\mathrm{CDCl_3}$) $d = 20.88$ ($\mathrm{SCHCH_3}$), 24.87 ($\mathrm{O_2CCH_3}$), 25.15 ($\mathrm{SCHCH_3}$), 44.92 ($\mathrm{SCHCH_3}$), 49.24 ($\mathrm{SCHCH_3}$), 124.19 (2,5-C of *o*-phenylene), 132.16 (3,4-C of *o*-phenylene), 153.75 (1,6-C of *o*-phenylene) and 180.54 ($\mathrm{O_2CCH_3}$).

Thermal decomposition of **1** in refluxing benzene for 21 h gave triphenylene (**2**, 37% yield), which was yielded by the couplings of three *o*-phenylene groups. Moreover, the reaction of **1** with styrene afforded 1,6-di[(*E*)-styryl]benzene (**3**) in 65% yield. It was reported previously that a diphenyltripalladium(II) complex $[(\mathrm{Bu^i_2S})\mathrm{PhPd}(\mu\text{-}\mathrm{O_2CMe})_2\mathrm{Pd}(\mu\text{-}\mathrm{O_2CMe})_2\mathrm{PdPh}(\mathrm{SBu^i_2})]$ produced (*E*)-stilbene in good yield [2]. Taking this fact into consideration, it was strongly suggested that **1** contained a dipalladated *o*-phenylene group. On the basis of these results and elemental analysis, **1** was assigned to the novel cyclic tripalladium(II) complex containing the dimetallated benzene molecule.



Scheme 1. (i) 90–95 °C in benzene; (ii) heated in refluxing benzene; (iii) with styrene; (iv) 70 °C in benzene; (v) heated in refluxing benzene; see text.

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Thermal reaction of the diphenyltripalladium(II) complex [(Pr$^i{}_2$S)PhPd(μ-O$_2$CMe)$_2$Pd(μ-O$_2$CMe)$_2$-PdPh(SPr$^i{}_2$)] (**4**) [2] was investigated in refluxing benzene for 1 h. After the reaction, volatile materials were removed and ^{1}H NMR was measured. It was found that the residue contained biphenyl, **1**, **2** and unreacted **4** in 87%, 6%, 3% and 4% yields, respectively, in molar ratios. Furthermore, benzene was detected by GLC analysis of the reaction mixture of **4** in mesitylene at 90 °C. Accordingly, the above thermal reaction showed that 82% of **4** was decomposed to produce biphenyl, 14% of **4** was converted to **1** (60% of which was successively decomposed to afford **2**), and 4% of **4** remained unchanged in these reaction conditions. The formation of **1** during the thermal reaction of **4** liberating the benzene molecule indicated that **4** itself cyclized intramolecularly to produce **1**.

Further studies on the X-ray crystallographic analysis of **1**, and the synthesis and reactivity of the novel cyclic tripalladium(II) complexes containing dimetallated aromatic compounds are currently in progress.

References

1 Y. Fuchita, K. Hiraki, Y. Kamogawa and M. Suenaga, *J. Chem. Soc., Chem. Commun.*, (1987) 941.

2 Y. Fuchita, K. Hiraki, Y. Kamogawa, M. Suenaga, K. Tohgoh and Y. Fujiwara, *Bull. Chem. Soc. Jpn.*, *62* (1989) 1081.

3 Y. Fuchita, M. Kawakami and K. Shimoke, *Polyhedron*, in press.