# Activation of Benzene Carbon–Hydrogen Bonds by Palladium(II) Acetate–Dialkyl Sulphide Systems

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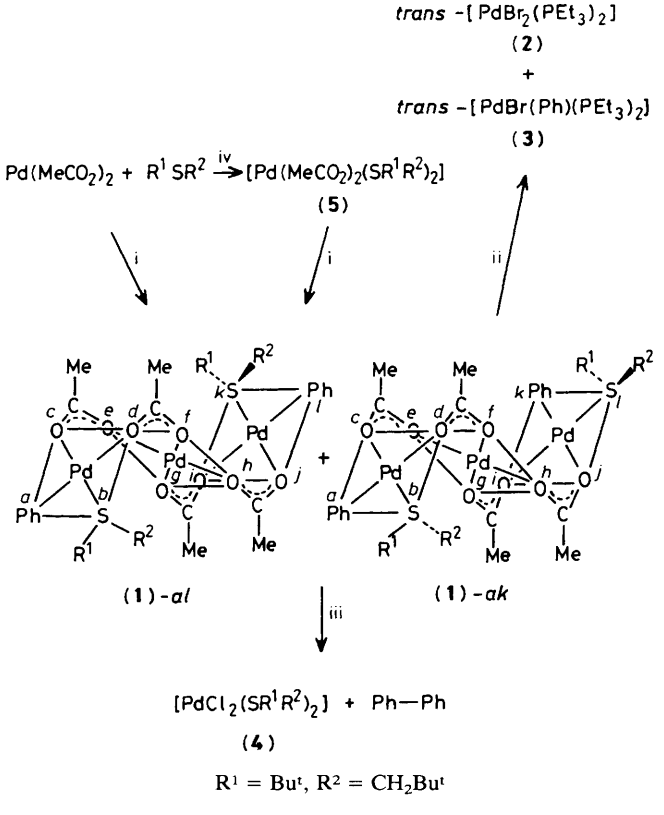
Benzene is directly activated by palladium(II) acetate–dialkyl sulphide systems at 70 °C to afford acetato-bridged diphenyltripalladium(II) complexes $[(R_2S)PhPd(\mu\text{-}MeCO_2)_2Pd(\mu\text{-}MeCO_2)_2PdPh(SR_2)]$, which are regarded as intermediate species in the catalytic arylation of alkenes and carbonylation of arenes by palladium(II) acetate.

Although the thalliation[1] and mercuriation[2] of arenes are well established reactions, the activation of arene C–H bonds by transition metals is a subject undergoing current research in organometallic chemistry. It is of considerable interest that aryl compounds are metallated directly by an [Rh(octaethylporphyrinato)]Cl–Ag salt system[3] and by co-ordinatively unsaturated species which are photochemically generated from dihydridometal complexes such as $[W(\eta^5\text{-}C_5H_5)_2H_2]$[4] and $[Ir(\eta^5\text{-}C_5Me_5)H_2(PMe_3)]$.[5] In addition, it has been reported that $H_2PtCl_6$ activates the C–H bond of arenes in $CF_3CO_2H$–$H_2O$.[6] Here, we report a novel C–H bond activation of benzene by palladium(II) acetate–dialkyl sulphide systems and the characterization of the diphenyltripalladium(II) species.

Palladium(II) acetate reacted with t-butyl neopentyl sulphide in benzene at 70 °C for 90 min to give yellow-brown crystals of (**1**) (29%). In the i.r. spectrum of (**1**), a ν(C–H) frequency of the benzene ring was newly observed at 3040 cm$^{-1}$, together with the bands due to bridging acetato ligands at 1570, 1555, 1410, and 1395 cm$^{-1}$. The molecular weight was determined to be 1055 by osmometry in benzene at 42 °C (calc. for $C_{38}H_{62}O_8Pd_3S_2$; 1030.28). On the basis of these results, the n.m.r. data,† and elemental analysis (C,H,O,Pd,S), (**1**)



**Scheme 1.** i, benzene, 70 °C; ii, $PEt_3$, LiBr; iii, LiCl; iv, benzene, 5—10 °C.

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† *Spectroscopic data* for (**1**): $^1H$ n.m.r. ($C_6D_6$) δ 8.14 [*o*-H, d, 2H, $^3J$(HH) 7.7 Hz], 8.05 [*o*-H, d, 2H, $^3J$(HH) 7.7 Hz], 6.95—7.5 (*m,p*-H, m, 6H]; δ($CH_2$) *ca.* 3.5 (4H, br); δ($CH_3CO_2$) 1.93 (s, 3H), 1.84 (s, 3H), 1.74 (s, 3H), 1.63 (s, 3H); δ($CCH_3$) 1.46 (s, 9H), 1.39 (s, 9H), 1.31 (s, 18H); $^{13}C\{^1H\}$ n.m.r. ($C_6D_6$) δ(Me*C*$O_2$) 183.6, 183.1, 182.8, 182.3; δ($C_6H_5$) 140.7 (i-C), 140.3 (i-C), 129.0 (*o*-C), 128.6 (*o*-C), 127.5 (*m*-C), 127.0 (*m*-C), 124.0 (*p*-C); δ(S*C*$Me_3$) 50.5, 50.4; δ (S*C*$H_2$) 45.4, 45.3; δ($SCH_2$*C*$Me_3$) 31.7; δ(C*C*$H_3$) 30.0, 29.9, 29.7, 29.4; δ(*C*$H_3CO_2$) 24.0, 23.9, 23.4, 22.6.

was assigned as the diphenyltripalladium(II) complex, $[(\mathrm{Bu^tSCH_2Bu^t})\mathrm{PhPd}(\mu\text{-}\mathrm{MeCO_2})_2\mathrm{Pd}(\mu\text{-}\mathrm{MeCO_2})_2\mathrm{PdPh}(\mathrm{Bu^tSCH_2Bu^t})]$. The n.m.r. data indicate that (**1**) consists of two geometrical isomers, *al* and *ak* (Scheme 1), in a population ratio of 1:1, as in the case of a trinuclear acetato-bridged cyclopalladated complex of *N*,*N*-dimethylneopentylamine.[7] It was also found that palladium(II) acetate, when treated in a similar way with benzene in the presence of diethyl, di-isopropyl, or di-isobutyl sulphide, afforded the corresponding diphenyltripalladium(II) complexes analogous to (**1**).

An acetone solution of (**1**) and $\mathrm{PEt_3}$ was stirred at room temperature, and then lithium bromide was added to afford both *trans*-$[\mathrm{PdBr_2(PEt_3)_2}]$ (**2**) (61%) and *trans*-$[\mathrm{PdBr(Ph)(PEt_3)_2}]$ (**3**) (14%). These data confirm that (**1**) contains phenylpalladium moieties as well as a '$\mathrm{Pd(MeCO_2)_2}$' moiety. The reaction of (**1**) with lithium chloride did not afford a phenylpalladium species but an adduct $[\mathrm{PdCl_2(Bu^tSCH_2Bu^t)_2}]$ (**4**) (41%).[‡] However, biphenyl was detected in 70% yield based on (**1**) by g.l.c. analysis of the reaction mixture.

The reaction of palladium(II) acetate and t-butyl neopentyl sulphide, carried out in benzene at 5—10 °C, produced a mononuclear addition complex $[\mathrm{Pd(MeCO_2)_2(Bu^tSCH_2Bu^t)_2}]$ (**5**) (19%).[§] When (**5**) was heated in benzene at 70 °C for 2 h, (**1**) was formed in 46% yield.

The complex (**1**) reacted with styrene in tetrahydrofuran (THF) at room temperature to produce *trans*-stilbene (94%). When carbon monoxide was bubbled through a THF solution of (**1**) at room temperature and the reaction mixture treated with sodium hydrogen carbonate and hydrochloric acid, benzoic acid was obtained in 64% yield. These facts are important in elucidating the mechanisms for arylation of alkenes[8] and carbonylation of arenes by palladium(II) acetate.[9,10] In conclusion, it has been found that the benzene molecule is directly activated by palladium(II) acetate–dialkyl sulphide systems to afford diphenyltripalladium(II) complexes.

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[‡] $^1$H N.m.r. ($\mathrm{CDCl_3}$); δ($\mathrm{CH_2}$) 2.8br, δ($\mathrm{CH_3}$) 1.41s, 1.14s.

[§] $^1$H N.m.r. ($\mathrm{CDCl_3}$); δ($\mathrm{CH_2}$) 2.4br, δ($\mathrm{CH_3CO_2}$) 1.91s, δ($\mathrm{CH_3}$) 1.51s, 1.25s. I.r.: ν($\mathrm{CO_2}$) 1610, 1275 cm$^{-1}$.

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