Butoxycarbonylation of aryl halides catalyzed by a silica-supported poly[3-(2-cyanoethylsulfanyl)propylsiloxane palladium] complex
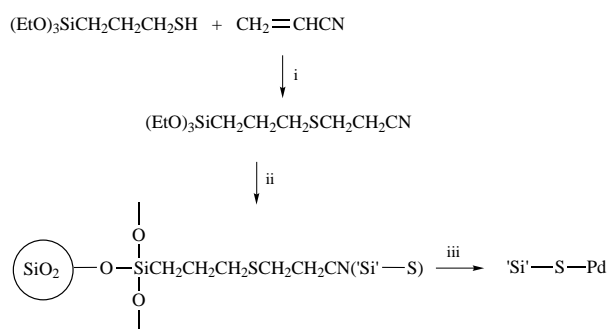
Ming-Zhong Cai,[a] Cai-Sheng Song[b] and Xian Huang*,[a]

[a] Department of Chemistry, Hangzhou University, Hangzhou, 310028, PR China
[b] Department of Chemistry, Jiangxi Normal University, Nanchang, 330027, PR China

Aryl bromides and iodides react with carbon monoxide and *n*-butyl alcohol at 100 °C and atmospheric pressure in the presence of tri-*n*-butylamine and a catalytic amount of a silica-supported sulfur palladium complex to form esters in moderate to good yields.

The carbonylation of aryl halides in the presence of palladium catalysts is a very versatile reaction and an important synthetic route because it has the advantage of proceeding smoothly under low pressures of carbon monoxide. For example, the syntheses of carboxylic acids,[1,2] esters,[3] acid fluorides,[4] amides[5] and aldehydes[6] have been reported to be readily achieved with an atmospheric pressure of CO in good to high yields. However, in most cases, homogeneous catalysts such as $Pd(OAc)_2$, $Pd(PPh_3)_2Cl_2$ are used and it is difficult to recover them from the products. Polymer-supported metal complexes are currently attracting great interest because they combine the advantages of homogeneous and heterogeneous catalyzed processes. Reddy *et al.*[7] reported that a polymer-anchored phosphine palladium complex with a P:Pd ratio of 0.895 catalyzed ethoxycarbonylation of organic halides in ethanol, but the activity of the catalyst was moderate and decreased gradually with repeated use. It is known that catalysts containing phosphine ligands are unstable.[8] Furthermore, the procedure for preparing the polymer-bound phosphine palladium complex is rather complicated; the non-crosslinked poly(chloromethylstyrene) is not commercially available, and the chloromethylation requires the use of carcinogenic chloromethyl methyl ether. To our knowledge, no Heck carbonylation catalyzed by a polymer-bound sulfur palladium complex has been reported. We prepared a silica-supported poly[3-(2-cyanoethylsulfanyl)propylsiloxane palladium] complex ('Si'–S–Pd) from 3-(1,1,1-triethoxysilyl)propane-1-thiol and fused silica *via* hydrolysis, followed by treatment with palladium chloride in acetone under a nitrogen atmosphere (Scheme 1).

$$(EtO)_3SiCH_2CH_2CH_2SH \ + \ CH_2{=}CHCN$$

$$\downarrow i$$

$$(EtO)_3SiCH_2CH_2CH_2SCH_2CH_2CN$$

$$\downarrow ii$$

SiO₂—O—SiCH₂CH₂CH₂SCH₂CH₂CN('Si'—S) $\xrightarrow{iii}$ 'Si'—S—Pd

Scheme 1 *Reagents and conditions:* i, CH_3CH_2ONa; ii, SiO_2, H_2O, toluene; iii, $PdCl_2$, CH_3COCH_3

X-Ray photoelectron spectroscopy (XPS) of the polymeric palladium complex showed that the binding energy (337.5 eV) of $Pd^{II} 3d_{\frac{5}{2}}$ in the polymeric palladium catalyst was lower than the binding energy (338.3 eV) of $Pd^{II} 3d_{\frac{5}{2}}$ in $PdCl_2$. This result suggests

Table 1 Butoxycarbonylation of aryl halides[a]

Entry	R–X	t/h	Product (yield, %)[b]
1	C_6H_5I	25	$C_6H_5CO_2Bu^n$ (88)
2	$4\text{-}CH_3OC_6H_4I$	30	$4\text{-}CH_3OC_6H_4CO_2Bu^n$ (82)
3	$4\text{-}CH_3C_6H_4I$	25	$4\text{-}CH_3C_6H_4CO_2Bu^n$ (87)
4	$4\text{-}ClC_6H_4I$	25	$4\text{-}ClC_6H_4CO_2Bu^n$ (91)
5	$4\text{-}CH_3O_2CC_6H_4I$	25	$4\text{-}CH_3O_2CC_6H_4CO_2Bu^n$ (90)
6	$4\text{-}NO_2C_6H_4I$	25	$4\text{-}NO_2C_6H_4CO_2Bu^n$ (84)
7	$4\text{-}ClC_6H_4Br$[c]	40	$4\text{-}ClC_6H_4CO_2Bu^n$ (56)
8	$4\text{-}CH_3O_2CC_6H_4Br$[c]	40	$4\text{-}CH_3O_2CC_6H_4CO_2Bu^n$ (54)
9	$4\text{-}NO_2C_6H_4Br$[c]	40	$4\text{-}NO_2C_6H_4CO_2Bu^n$ (45)
10	$C_6H_5CH_2Br$	30	$C_6H_5CH_2CO_2Bu^n$ (27)
11	$1\text{-}C_{10}H_7Br$[c]	72	$1\text{-}C_{10}H_7CO_2Bu^n$ (34)

[a] Reactions were carried out at 100 °C with 1 atm of CO, 3 mmol of aryl halide, 0.04 mmol of palladium catalyst, and 3.5 mmol of tri-*n*-butylamine in 2 ml of *n*-butyl alcohol. [b] Yields are of isolated, pure products. [c] 0.06 mmol PPh_3 was added.

that a coordination bond between S and Pd is formed. In this paper we report its catalytic properties in the butoxycarbonylation of aryl halides with carbon monoxide in *n*-butyl alcohol at 1 atm pressure (Scheme 2).

$$RX \ + \ CO \ + \ Bu^nOH \ \xrightarrow{i} \ RCO_2Bu^n$$

Scheme 2 *Reagents and conditions:* i, 'Si'–S–Pd (1.5 mol%), Bu^n_3N

The initial experiment was carried out with iodobenzene adding 1.5 mol% 'Si'–S–Pd as catalyst. The polymeric palladium(II) complex was reduced by the carbon monoxide in the reaction mixture. We used *n*-butyl alcohol as the alcohol and tri-*n*-butylamine as the base, since they boil well above the reaction temperature used. The butoxycarbonylation reaction at 100 °C required 25 h to go to completion and *n*-butyl benzoate was obtained in 88% yield. When 1.5 mol% $Pd(OAc)_2$ was used, *n*-butyl benzoate was obtained in 70% yield under comparable conditions.[3] This polymeric palladium catalyst not only has higher catalytic activity in the butoxycarbonylation of iodobenzene than $Pd(OAc)_2$, but also can be recovered by simple filtration. The activity of the recovered catalyst was tested after two recycles and it was found that the yield of *n*-butyl benzoate decreased by only 2 and 3% after each recycle, respectively.

The reaction is suitable for a variety of functional groups on the aryl halides; both strongly electron donating and withdrawing substituents can be present. The butoxycarbonylation of various aryl iodides has been achieved with good to high yields. These results are summarized in Table 1. The substituent effects in the aryl iodides appeared to be less significant than in the aryl bromides. Aryl bromides did not react unless they were strongly activated with electron withdrawing substituents and in the presence of a catalytic amount of PPh_3. A similar observation was also made by Heck[3] using $Pd(OAc)_2$ as catalyst in butoxycarbonylation of aryl bromides. We found that adding 2 mol% PPh_3 caused activated aryl bromides to react and produce esters in moderate yields. However, the butoxycarbonylation of aryl

bromides with electron donating substituents was very slow even in the presence of PPh$_3$ and only trace amounts of products were obtained. Benzyl bromide also reacted with CO and *n*-butyl alcohol without PPh$_3$, but the yield was low. In the presence of a catalytic amount of PPh$_3$, the butoxycarbonylation of 1-bromonaphthalene gave an ester after 72 h in low yield. Table 1 contains one example of particular interest: the butoxycarbonylation of methyl *p*-iodobenzoate gave a 90% yield of *n*-butyl methyl terephthalate with none of the symmetrical esters being formed.

In conclusion, the silica-supported poly[3-(2-cyanoethylsulfanyl)propylsiloxane palladium] complex is an efficient catalyst for butoxycarbonylation of aryl halides. This polymeric palladium catalyst not only has higher catalytic activity than Pd(OAc)$_2$, but also can be reused without loss of activity. The present method has the advantages of ease of handling, separation of the products and reuse of the catalyst.

Experimental †

Synthesis of 3{[3-(1,1,1-triethoxysilyl)propyl]sulfanyl}propanenitrile

To a mixture of 3-(1,1,1-triethoxysilyl)propane-1-thiol (11.90 g, 50 mmol) and sodium ethoxide (0.07 g, 1.03 mmol) at 0 °C was added dropwise acrylonitrile (3.97 g, 75 mmol). After being stirred for 1 h, the mixture was warmed to room temperature and stirred for 20 h. The reaction mixture was diluted with diethyl ether (60 cm³) and filtered. The filtrate was washed with 5% AcOH (10 cm³), 10% aqueous sodium hydrogen carbonate (10 cm³) and water (3 × 10 cm³) and dried over CaCl$_2$. After concentration under reduced pressure, the residue was distilled *in vacuo* to give the title compound (10.20 g, 70%), bp 142–144 °C/26.6 Pa (Found: C, 49.25; H, 8.36; N, 4.93; S, 10.69. C$_{12}$H$_{25}$NO$_3$SSi requires C, 49.48; H, 8.59; N, 4.81; S, 10.99%); ν_{max}(film)/cm^{-1} 2930, 2860, 2260, 1080, 1190, 780; δ_H(90 MHz, CDCl$_3$, Me$_4$Si) 0.62 (t, *J* 8.2, 2 H), 1.16 (t, *J* 7.0, 9 H), 1.43–1.85 (m, 2 H), 2.43–2.76 (m, 6 H), 3.75 (q, *J* 7.0, 6 H); *m/z* 291 (M$^+$, 28%) and 163 (100).

Syntheses of 'Si'–S and 'Si'–S–Pd

Toluene (120 cm³) and fused silica (5.00 g) were placed in a flask equipped with a magnetic stirrer and reflux condenser. After stirring for 10 min, 3{[3-(1,1,1-triethoxysilyl)propyl]sulfanyl}-propanenitrile (5.00 g) was added and the mixture was heated to reflux for 48 h under nitrogen. Distilled water (30 cm³) was added and after refluxing for another 48 h, the product was allowed to cool, then filtered and dried at 200 °C *in vacuo* for 5 h. The resulting white powder was washed with acetone (3 × 20 cm³), followed by drying to give 6.80 g of 'Si'–S. The sulfur content was determined to be 6.02 wt% by elemental analysis.

A mixture of 'Si'–S (2.00 g) and PdCl$_2$ (0.22 g, 1.20 mmol) in acetone (50 cm³) was heated to reflux under nitrogen for 72 h. The product was allowed to cool, then filtered. The resulting yellow powder was washed with distilled water (3 × 10 cm³) and acetone (3 × 10 cm³) and then dried *in vacuo* to afford 2.04 g of 'Si'–S–Pd. The sulfur and palladium content were 4.89 wt% and 4.45 wt%, respectively.

Typical procedure for the butoxycarbonylation of aryl halides with CO

Into a 50 cm³ flask, fitted with a magnetic stirrer, gas inlet tube and reflux condenser, were placed 'Si'–S–Pd (0.01 g, 0.04 mmol). The atmosphere was replaced with carbon monoxide. Iodobenzene (0.61 g, 3 mmol), Bu$^n_3$N (0.65 g, 3.5 mmol) and *n*-

butyl alcohol (2 cm³) were added by syringe and a slow stream of CO was passed into the flask. The mixture was stirred at 100 °C for 25 h. The reaction mixture was cooled and dissolved in diethyl ether (60 cm³). The 'Si'–S–Pd was separated from the mixture by filtration, washed with distilled water (2 × 10 cm³), ethanol (2 × 10 cm³) and diethyl ether (2 × 10 cm³) and reused in the next run. The ethereal solution was washed with 20% aqueous hydrochloric acid (2 × 10 cm³), saturated aqueous sodium hydrogen carbonate (10 cm³) and distilled water (3 × 10 cm³). The ethereal layer was dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was purified by preparative TLC on silica gel (light petroleum–ethyl acetate 19:1) to afford *n*-butyl benzoate [3] (0.47 g, 88%); ν_{max}(film)/cm^{-1} 3060, 2919, 2880, 1718, 1600, 1450, 1380, 1110, 700; δ_H(90 MHz, CCl$_4$, Me$_4$Si) 0.98 (t, *J* 7.5, 3 H), 1.17–1.84 (m, 4 H), 4.27 (t, *J* 6.0, 2 H), 7.13–7.60 (m, 3 H), 7.77–8.10 (m, 2 H).

n-Butyl 4-methylbenzoate.[9] ν_{max}(film)/cm^{-1} 3050, 2940, 2860, 1710, 1600, 1450, 1380, 1170, 840; δ_H(90 MHz, CDCl$_3$, Me$_4$Si) 0.97 (t, *J* 7.5, 3 H), 1.16–1.90 (m, 4 H), 2.39 (s, 3 H), 4.22 (t, *J* 6.0, 2 H), 7.12 (d, *J* 9.0, 2 H), 7.81 (d, *J* 9.0, 2 H).

n-Butyl 4-methoxybenzoate.[3] ν_{max}(film)/cm^{-1} 3050, 2920, 2870, 1710, 1600, 1450, 1380, 1260, 1100, 845; δ_H(90 MHz, CCl$_4$, Me$_4$Si) 0.93 (t, *J* 7.5, 3 H), 1.06–1.83 (m, 4 H), 3.75 (s, 3 H), 4.16 (t, *J* 6.0, 2 H), 6.83 (d, *J* 9.0, 2 H), 7.89 (d, *J* 9.0, 2 H).

n-Butyl 4-chlorobenzoate.[10] ν_{max}(film)/cm^{-1} 3070, 2930, 2860, 1715, 1590, 1455, 1380, 1170, 845; δ_H(90 MHz, CCl$_4$, Me$_4$Si) 0.92 (t, *J* 7.5, 3 H), 1.10–1.83 (m, 4 H), 4.18 (t, *J* 6.0, 2 H), 7.30 (d, *J* 9.0, 2 H), 7.86 (d, *J* 9.0, 2 H).

n-Butyl 4-nitrobenzoate.[11] ν_{max}(KBr)/cm^{-1} 3050, 2940, 2860, 1715, 1600, 1525, 1450, 1350, 1100, 870; δ_H(90 MHz, CDCl$_3$, Me$_4$Si) 0.98 (t, *J* 7.5, 3 H), 1.19–1.87 (m, 4 H), 4.26 (t, *J* 6.0, 2 H), 7.34 (d, *J* 9.0, 2 H), 7.92 (d, *J* 9.0, 2 H).

n-Butyl methyl terephthalate.[3] ν_{max}(film)/cm^{-1} 3060, 2930, 2860, 1718, 1500, 1440, 1100, 870; δ_H(90 MHz, CDCl$_3$, Me$_4$Si) 0.93 (t, *J* 7.5, 3 H), 1.15–1.85 (m, 4 H), 3.83 (s, 3 H), 4.20 (t, *J* 6.0, 2 H), 7.84 (s, 4 H).

n-Butyl 2-phenylacetate.[3] ν_{max}(film)/cm^{-1} 3060, 2940, 2870, 1725, 1600, 1450, 1060, 700; δ_H(90 MHz, CCl$_4$, Me$_4$Si) 0.93 (t, *J* 7.5, 3 H), 1.10–1.71 (m, 4 H), 3.51 (s, 2 H), 4.02 (t, *J* 6.0, 2 H), 7.05–7.42 (m, 5 H).

n-Butyl 1-naphthoate.[3] ν_{max}(film)/cm^{-1} 3050, 2930, 2870, 1710, 1590, 1450, 1060, 1010, 780; δ_H(90 MHz, CCl$_4$, Me$_4$Si) 0.95 (t, *J* 7.5, 3 H), 1.12–1.86 (m, 4 H), 4.23 (t, *J* 6.0, 2 H), 7.23–7.52 (m, 3 H), 7.56–8.15 (m, 3 H), 8.61–8.95 (m, 1 H).

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† *J* Values are given in Hz.