Palladium Nanoparticles on Graphite Oxide as Catalyst for *Suzuki–Miyaura*, *Mizoroki–Heck*, and *Sonogashira* Reactions

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Pd^{2+}-Exchanged graphite oxide (GO) serves as a precatalyst for the formation of Pd-nanoparticles which are then deposited on the highly functionalized carbonaceous support. This versatile, air-stable, and ligand-free system was applied successfully to *Suzuki–Miyaura* couplings of some aryl chlorides and to the *Mizoroki–Heck* as well as the *Sonogashira* reaction showing relatively high activities and good selectivities. Like with other ligand-free supported systems, the reaction proceeded dominantly by a homogeneous mechanism, but attack of an aryl iodide to Pd-nanoparticles can be excluded as substantial contribution to the entire catalytic process. Beside its straightforward preparation and its stability in air, the system combines the advantages of both homogeneous and heterogeneous catalysis.

Introduction. – Since the pioneering advances in graphene chemistry [1][2], graphite oxide (GO) [3–9] and chemically derived graphenes (CDG) [10–12] have been under thorough investigation as new materials, *e.g.*, for nanoelectronic applications [13–17] and polymer nanofillers [18–22]. However, in the past, only a limited number of publications have dealt with the synthesis of transition metals and their clusters supported by GO or CDG [23–26] and their applications [27–32]. The preparation of GO can be accomplished either by controlled chemical or by electrochemical oxidation of graphite *via* its nitrate or hydrogensulfate salts [33–37]. Different models have been published characterizing the structure of this nonstoichiometric hygroscopic material [38–43]. The formation of functional groups during oxidation enables sorption and intercalation of ions and molecules [40][44–46]. This behavior of GO and its high specific surface area of *ca.* 400 m^2 g^{-1} makes it a versatile material for catalytic applications preventing for example the aggregation and hence deactivation of the catalytic species [6][47] and thus, this system would be an interesting alternative for unsupported nanoparticles and Pd/C, both of which have been extensively investigated for its use in C–C coupling procedures [48–53]. In a previous publication, we have reported on the formation of different Pd/GO and Pd/CDG catalysts and their use in the *Suzuki–Miyaura* coupling of aryl bromides [54]. In these studies, it was found that Pd^{2+}-exchanged GO was the most active catalyst among the investigated new catalytic materials showing turnover frequencies (TOFs) of up to 39000 h^{-1}. *In situ* reduction of Pd^{2+} afforded highly dispersed and uniform Pd-

nanoparticles of 4 ± 1 nm in diameter. As a result, this allowed for good recyclability in combination with a low leaching of < 1 ppm. Here, we have extended the scope of application to a number of aryl chlorides in *Suzuki–Miyaura* couplings as well as to *Mizoroki–Heck* reactions and a number of *Sonogashira* couplings.

Results and Discussion. – The catalyst synthesis was carried out according to our previously reported procedure [54]. The widened distance of 0.8 nm between the highly functionalized graphitic layers is responsible for the high surface area of the GO support. This morphology was confirmed by SEM (scanning electron microscope) and WAXS (wide-angle X-ray scattering) measurements (*Fig. 1*).

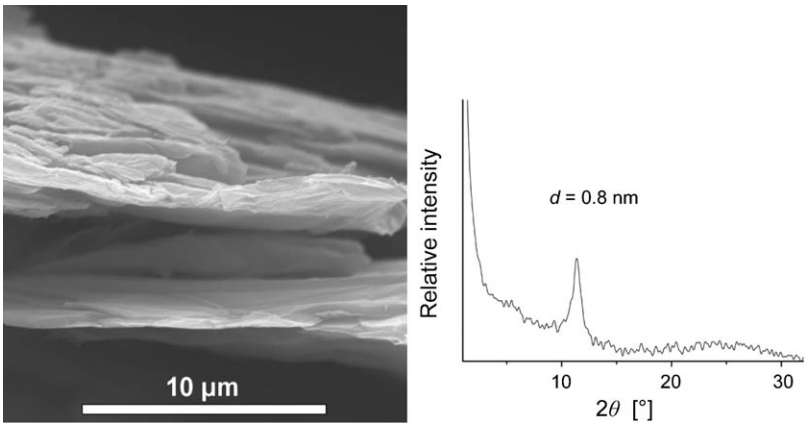
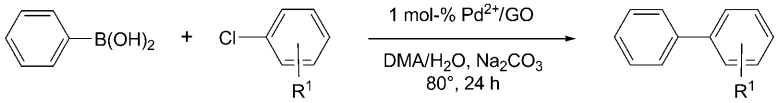


Fig. 1. *SEM Picture* (left) *and the X-ray diffraction pattern* (right) *display the layered nature of Pd/GO at the microscale and at the nanoscale*

When 1-chloro-4-nitrobenzene was coupled to phenylboronic acid in the presence of 1 mol-% of Pd^{2+}/GO under the same conditions as for the reaction of aryl bromides (1 mol-% of Pd^{2+}/GO, H_2O/EtOH, 80°) [54], only 8% of the desired 4-nitro-1,1′-biphenyl was formed. However, switching to the solvent system *N*,*N*-dimethylacetamide (DMA)/H_2O 20:1 led to an increased conversion of 90%. As previously reported, the solvent effect on the efficiency of the coupling may be related to the reductive homocoupling pathway with the alcohol and/or boronic acid as reducing agent [55]. The use of the nonreducing solvent DMA avoided this problem. Application of the modified reaction conditions in combination with the use of Pd^{2+}/GO enabled the *Suzuki–Miyaura* coupling of different aryl chlorides with moderate to good conversions. The results are summarized in *Table 1*. As expected, the nature and position of the substituents had an influence on the reactivity of the substrate. The high conversion and good selectivity of the less reactive 2-chlorobenzaldehyde might be caused *via* a directing effect of the aldehyde O-atom by complexation of palladium (*Table 1*, *Entry 8*). Moreover, ester groups are stable under the applied conditions, and ethyl 4-chlorobenzoate (*Entry 10*) was coupled in good yield and with high selectivity. By doubling the amount of Pd to 2 mol-%, almost all conversions were enhanced significantly but at the expense of selectivity. The TEM (transmission electron

Table 1. Suzuki–Miyaura *Couplings of Phenylboronic Acid and Different Aryl Chlorides in the Presence of Pd^{2+}/GO*



Entry	R^1	Conversion[a])[b]) [%]	Selectivity[a])[b])[c])
1	4-NO_2	90 (95)	1:42 (1:1)
2	2-NO_2	67 (87)	1:8 (1:10)
3	3-NO_2	28 (45)	1:3 (1:1)
4	4-CF_3	88 (100)	1:23 (1:31)
5	2-CF_3	57 (58)	1:11 (1:18)
6	3-CF_3	82 (96)	0:1 (0:1)
7	4-CHO	51 (60)	1:11 (1:4)
8	2-CHO	95	1:6
9	3-CHO	43	1:4
10	4-CO_2Et	78 (99)	1:61 (1:16)
11	4-COMe	8 (34)	1:1 (1:4)

[a]) Conversion and selectivity determined by GC/MS. [b]) Results in parenthesis were obtained with 2 mol-% of Pd. [c]) Molar ratio homocoupling product/*Suzuki–Miyaura* product.

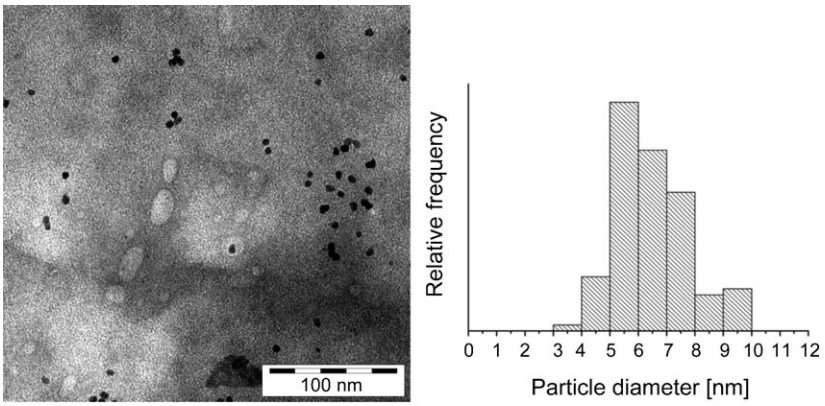


Fig. 2. *TEM Picture* (left) *and size distribution* (right) *of Pd-nanoparticles on GO generated* in situ *during the* Suzuki–Miyaura *coupling*

microscope) pictures of the catalyst after the reaction showed a narrow size distribution of the Pd-nanoparticles of 6.6 ± 1.3 nm (*Fig. 2*).

While the *Suzuki–Miyaura* reaction is the method of choice for the synthesis of biarenes, the *Mizoroki–Heck* coupling is the preferred procedure for coupling alkenes to organic compounds bearing a suitable leaving group [56]. Pd/C has been applied to this coupling reaction already back in 1973 and is since then regarded as the most important heterogeneous catalyst [48][51][57][58]. To investigate the scope of reactions catalyzed by the novel heterogeneous system Pd/GO, we applied 0.1 mol-

% of Pd^{2+}/GO to *Mizoroki–Heck* couplings of butyl acrylate (= butyl prop-2-enoate) with a number of aryl bromides (*Table 2*). The transformations with activated aryl bromides (*Entries 1–9*) as well as nonactivated aryl bromides (*Entries 10–16*) led, after extractive workup and column chromatography, to the desired substituted olefin derivatives in good yields. In addition, the selectivity of these reactions was high, resulting in $>99\%$ of the (*E*)-configured forms.

The *Sonogashira* reaction is the preferred method for the coupling of sp^2-hybridized C-atoms of aryl, heteroaryl, and vinyl halogenides with sp-hybridized C-atoms of terminal alkynes [59][60]. Pd/C has often been used as heterogeneous catalyst for these reactions under different reaction conditions [49][53][61–63], the most common being Pd/C, CuI, and PPh_3 in Et_3N/DMF [64]. To demonstrate the versatility of the Pd/GO system, amine-, copper-, and phosphine-free conditions were applied. Phenylacetylene was coupled with different aryl iodides, and the results are shown in *Table 3*. Depending on the electronic nature of the substituents, moderate to good conversions to the desired products could be observed. In contrast, 4-methyl iodobenzoate could only be converted by 25%, whilst a partial saponification of the starting material was observed. TEM Pictures of the catalyst after the reaction showed an extremely narrow size distribution of the Pd-nanoparticles of 2.9 ± 0.5 nm on GO (*Fig. 3*).

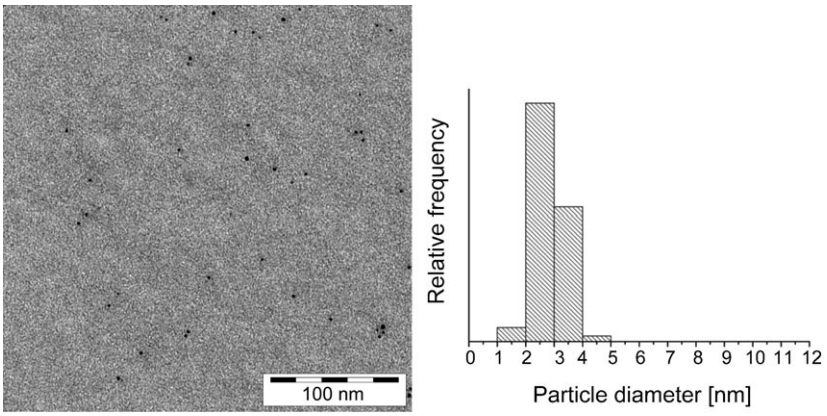
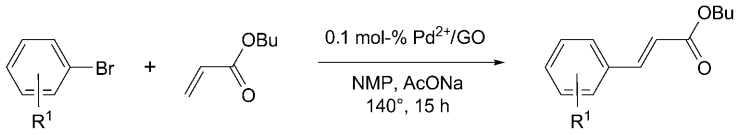


Fig. 3. *TEM Picture* (left) *and size distribution* (right) *of Pd-nanoparticles on GO generated* in situ *during the* Sonogashira *coupling*

During the last decade, the elucidation of the mechanism of heterogeneous C–C couplings mediated by Pd has been an area of high activity. There is strong evidence for a dissolution/redeposition process taking place during the reaction [65][66]. At the beginning of the reaction, leaching of Pd ions and atoms is often very high but diminishes while the reaction progresses, resulting in low values after complete conversion. For *Heck* reactions, it was postulated that the reactions are not catalyzed by nanoparticles but rather take place by an attack of the arylating agent on the Pd-atoms at the outer rim of the nanoparticles [67][68]. These data were substantiated by reactions employing a two-compartment membrane reactor [69][70].

Table 2. Mizoroki–Heck *Couplings in the Presence of* Pd^{2+}*/GO*



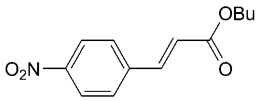
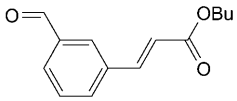
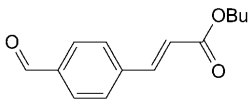
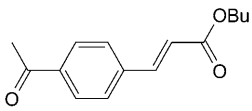
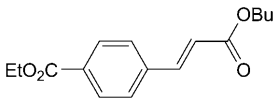
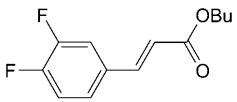
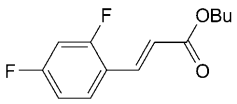
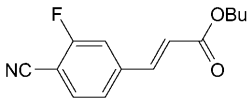
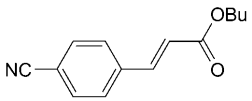
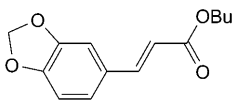
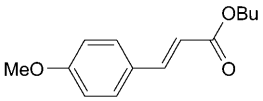
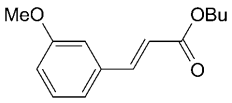
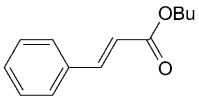
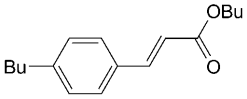
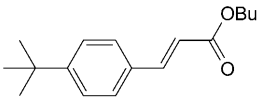
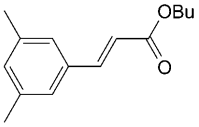
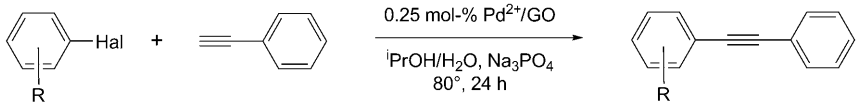
Entry	Product	Conversion[a]) [%]	Yield [%]
1		> 95	86
2		> 95	83
3		> 95	81
4		> 95	93
5		> 95	85
6		> 95	81
7		> 95	89
8		> 95	91
9		> 95	89
10		92	85

Table 2 (cont.)

Entry	Product	Conversion[a]) [%]	Yield [%]
11		88	79
12		92	87
13		80	74
14		86	80
15		89	81
16		79	73

[a]) Conversion determined *via* GC/MS.

Table 3. Sonogashira *Couplings in the Presence of* Pd^{2+}*/GO*



R	Hal	Conversion[a]) [%]
H	I	95
4-Br	I	73
3-Br	I	> 95
2-MeO	I	69
4-CO_2Me	I	25
4-Ac	I	93
4-Ac	Br	< 5

[a]) Conversion determined *via* GC/MS.

The reported data are in accordance with our observations for C–C coupling reactions in the presence of GO-supported Pd-nanoparticles as catalytic system. During the reactions, up to 49% of the applied Pd-concentration was leaching into solution. However, after completion of the reaction, a maximum of 3 ppm was detected in the reaction media. To establish that in our system, a soluble Pd-species is responsible for the catalysis, we carried out filtration experiments where we observed a continuation of the reaction, indicative of a soluble catalytic species. In addition, we performed a so-called three-phase test [71][72] in which we subjected a solid-phase-bound aryl iodide to [63][64] a *Mizoroki–Heck* coupling as well as to a *Sonogashira* coupling. The experiments were carried out under comparable conditions and in the presence as well as in the absence of a soluble substrate. In all experiments, more than 90% conversion of the solid-phase-bound aryl iodide was observed. Since the solid-phase-bound aryl iodide is unable to attack nanoparticles on GO, a proposed substantial contribution of this catalytic pathway [68][69] to the entire catalytic process can thus be ruled out.

Conclusions. – In summary, immobilization of Pd^{2+} on graphite oxide (GO) followed by *in situ* reduction afforded an active catalyst of GO-supported Pd-nanoparticle clusters for ligand-free *Suzuki–Miyaura* couplings of aryl chlorides and for *Mizoroki–Heck* as well as *Sonogashira* reactions. The catalyst could be readily prepared and easily handled as it is stable in air. A low leaching of Pd was observed after completion of the reaction, and the catalytic system could easily be recovered. Filtration experiments and a three-phase test supported a homogeneous mechanism but the latter approach established that an attack of the aryl iodide on the surface of the nanoparticles can be ruled out as significant contribution to the entire catalytic process.

Experimental Part

General. All reagents were purchased from commercial sources (*Aldrich*, *Fluka*, *Acros*, *ABCR*, and *Alfa Aesar*). HPLC Analysis: *Agilent-1100* system with a *Zorbax Eclipse XDB-C$_8$* column (4.6 × 150 mm, *Agilent*). M.p.: *Electrothermal IA 9000*; uncorrected. NMR Spectra: *Bruker-AM-400* spectrometer; at 400 (^{1}H) and 100.6 MHz (^{13}C); $CDCl_3$ soln.; δ in ppm rel. to $CHCl_3$ (δ(H) 7.26, δ(C) 77.23) as an internal reference, *J* in Hz. CI-MS: *Finnigan MAT312* with NH_3 as gas (0.4 mbar, 220°, 250 eV, 1 mA, 2 kV); in *m*/*z* (rel. %). EI-MS: *Finnigan MAT8200* (230°, 70 eV, 1.0 mA, 3 kV); in *m*/*z* (rel. %). Elemental analyses: *Vario EL* (*Elementaranalysensysteme GmbH*).

The characterization of the coupling products is given only for compounds **5**–**8** and **15** that are not reported in the literature. However, all data can be requested from the corresponding author.

Catalyst Synthesis. Graphite oxide (GO) was synthesized according to the method of *Hummers* and *Offeman* [35][48]. The ion exchange with Pd, *i.e.*, the adsorption of Pd^{2+} ions by the functionalized GO was achieved by dispersing GO (2.5 g) in H_2O (200 ml). Subsequently, $[Pd(AcO)_2]$ (250 mg, 1.1 mmol) was added, and the mixture was vigorously sonicated for 5 min and stirred overnight. After centrifugation and several washings with H_2O and acetone, the Pd^{2+}/GO was dried *in vacuo* at 40° and gently powdered through a 150 μm mesh regaining a H_2O content of 4.5%. The powder density was roughly estimated to be 0.3 g cm^{-3}, and the Pd-content amounted to 3.4% as verified by atomic-absorption spectrometry (AAS; digestion of the samples in hot *aqua regia* followed by analysis with an atomic-absorption spectrometer *Vario 6*, *Jena Analytics*). Nanoparticles were characterized by transmission electron microscopy (TEM) in suspension on a 200 μ mesh Cu grid and as a microtome cut of the samples embedded in epoxy resin with a *LEO CEM 912* operating at 120 kV. The particle size was determined

counting at least 200 particles from different images by means of iTEM computer software from *Olympus-SIS*. The morphology of the materials was observed *via* environmental scanning electron microscopy (ESEM) in an *Electroscan ESEM 2020*. An acceleration voltage of 23 kV was applied, and the samples were coated with gold/palladium prior to analyses. The wide-angle X-ray scattering (WAXS) measurements were carried out on a *Siemens-D-5000* diffractometer at 40 kV and 30 mA with CuK_α radiation in the 2θ range from 1° to 100° (step size 0.0156°, step time 1 s, transmission rotation and detection by a *Braun PSD ASA S*). Interplanar distances were calculated with the *Bragg* equation.

For a detailed characterization of the GO, see [54].

Suzuki *Reactions of Aryl Chlorides in DMA/H_2O: General Procedure.* A pressure tube was charged with phenylboronic acid (67 mg, 0.55 mmol, 1.1 equiv.), Na_2CO_3 (106 mg, 1 mmol, 2 equiv.), the chloro-substituted benzene (0.5 mmol, 1 equiv.), and Pd^{2+}/GO (16.0 mg, 5 μmol, 1 mol-%). A DMA/H_2O 20:1 mixture (3 ml) was added. The vessel was closed, evacuated, and flushed with Ar, and the procedure was repeated 4×. Finally, the mixture was stirred in an oil bath at 100° for the given time, followed by the sampling (10 μl) for GC/MS analysis. After cooling to r.t., the mixture was filtered over a small column of silica gel/kieselgur and the column washed with CH_2Cl_2 (10 ml). The product was extracted into the org. phase (2 × 10 ml CH_2Cl_2) and the combined org. phase dried ($MgSO_4$) and concentrated. In some cases, purification of the crude product by column chromatography (SiO_2, 2.5 × 13 cm, cyclohexane/AcOEt 4:1) was necessary.

Mizoroki–Heck *Reaction* (synthesis of **5**–**8** and **15**): *General Procedure.* A *Schlenk* tube was evacuated thoroughly and flushed with Ar prior to the addition of the aryl bromide (1 mmol, 1 equiv.), AcONa (99 mg, 1.2 mmol, 1.2 equiv.), Pd^{2+}/GO (3.1 mg, 1.0 μmol, 0.1 mol-%), and NMP (=1-methylpyrrolidin-2-one; 2.4 ml). The mixture was stirred at 120° during 2 min before the addition of butyl prop-2-enoate (164 μl, 1.15 mmol, 1.15 equiv.). Thereafter, the mixture was stirred at 140° during 15 h followed by withdrawal of an aliquot for GC/MS analysis (10 μl). After cooling to r.t., the mixture was diluted with H_2O (8 ml) and extracted with toluene (3 × 8 ml). The combined extract was washed with H_2O (3 × 8 ml) and brine (8 ml), dried ($MgSO_4$), and concentrated, and the crude product purified by flash chromatography (SiO_2, 3 × 13 cm, cyclohexane/AcOEt 4:1).

*Ethyl 4-[(1*E*)-3-Butoxy-3-oxoprop-1-en-1-yl]benzoate* (**5**): R_f (cyclohexane/AcOEt 4:1) 0.24. ^{1}H-NMR: 0.97 (*t*, *J* = 7.4, Me); 1.40 (*t*, *J* = 7.1, *Me*CH_2O, overlapped with δ(H) 1.44); 1.44 (*sext.*, *J* = 7.5, 2 H); 1.66–1.73 (*m*, 2 H); 4.22 (*t*, *J* = 6.7, O*C*$H_2$$CH_2$); 4.39 (*t*, *J* = 7.1, MeCH_2O); 6.52 (*d*, *J* = 16.0, H–C(2′)); 7.57 (J_{app} = 8.1, 2 arom. H); 7.69 (*d*, *J* = 16.1, H–C(1′)); 8.05 (J_{app} = 8.3, 2 arom. H). ^{13}C-NMR: 13.7; 14.3; 19.2; 30.8; 61.2; 64.6; 120.6; 127.9; 130.1; 131.7; 138.6; 143.2; 165.9; 166.6. EI-MS: 276 (26, M^+), 231 (15, $[M - OEt]^+$), 219 (37, $[M - Bu]^+$), 203 (47, $[M - OBu]^+$, $[M - CO_2Et]^+$), 192 (78), 175 (71, $[M - CO_2Bu]^+$), 102 (35), 44 (100). Anal. calc. for $C_{16}H_{20}O_4$: C 69.54, H 7.30; found: C 69.28, H 7.39.

*Butyl (2*E*)-3-(3,4-Difluorophenyl)prop-2-enoate* (**6**): R_f (cyclohexane/AcOEt 4:1) 0.42. ^{1}H-NMR: 0.97 (*t*, *J* = 7.4, Me); 1.44 (*sext.*, *J* = 7.5, 2 H); 1.65–1.75 (*m*, 2 H); 4.21 (*t*, *J* = 6.7, CH_2O); 6.35 (*d*, *J* = 16.0, H–C(2)); 7.17 (*dd*, *J* = 8.5, 7.8, 1 arom. H); 7.23–7.27 (*m*, 1 arom. H); 7.34 (*ddd*, *J* = 11.1, 7.5, 2.1, 1 arom. H); 7.57 (*d*, *J* = 16.0, H–C(3)). ^{13}C-NMR: 13.7; 19.2; 30.8; 64.7; 116.2; 117.7; 119.5; 124.7; 131.7; 142.2; 149.3; 151.8; 152.7; 166.6. ^{19}F-NMR (235 MHz): −136.7; −134.4. EI-MS: 240 (13, M^+), 183 (97, $[M - Bu]^+$), 167 (100, $[M - OBu]^+$), 139 (30, $[M - CO_2Bu]^+$), 119 (33).

*Butyl (2*E*)-3-(2,4-Difluorophenyl)prop-2-enoate* (**7**): R_f (cyclohexane/AcOEt 4:1) 0.31. ^{1}H-NMR: 0.97 (*t*, *J* = 7.4, Me); 1.44 (*sext.*, *J* = 7.5, 2 H); 1.65–1.73 (*m*, 2 H); 4.22 (*t*, *J* = 6.7, CH_2O); 6.48 (*d*, *J* = 16.2, H–C(2)); 6.85 (*m* (='*ddd*'), J_{app} = 10.8, 8.6, 2.4, 1 arom. H); 6.88–6.93 (*m*, 1 arom. H); 7.52 (*ddd*, *J* = 8.6, 8.6, 6.3, 1 arom. H); 7.73 (*d*, *J* = 16.2, H–C(3)). ^{13}C-NMR: 13.7; 19.2; 30.8; 64.6; 104.6; 112.0; 120.5; 130.2; 136.1; 160.4; 162.7; 165.1; 166.8. ^{19}F-NMR (235 MHz): −106.2; −109.9. EI-MS: 240 (14, M^+), 183 (77, $[M - Bu]^+$), 167 (100, $[M - OBu]^+$), 139 (30, $[M - CO_2Bu]^+$), 119 (38).

*Butyl (2*E*)-3-(4-Cyano-3-fluorophenyl)prop-2-enoate* (**8**): R_f (cyclohexane/AcOEt 4:1) 0.29. ^{1}H-NMR: 0.96 (*t*, *J* = 7.4, Me); 1.41 (*sext.*, *J* = 7.5, 2 H); 1.65–1.72 (*m*, 2 H); 4.21 (*t*, *J* = 6.7, CH_2O); 6.51 (*d*, *J* = 16.0, H–C(2)); 7.34 (*dd*, *J* = 9.5, 1.5, 1 arom. H); 7.39 (*dd*, *J* = 8.0, 1.5, 1 arom. H); 7.59 (*d*, *J* = 16.1, H–C(3)); 7.63 (*dd*, *J* = 8.2, 6.4, 1 arom. H). ^{13}C-NMR: 13.7; 19.2; 30.7; 65.0; 113.5; 115.0; 123.3; 124.2; 133.9; 140.9; 141.6; 161.9; 164.6; 165.9. ^{19}F-NMR (235 MHz): −105.8. EI-MS: 247 (12, M^+), 190 (43, $[M - Bu]^+$), 174 (100, $[M - OBu]^+$), 192 (78), 146 (34, $[M - CO_2Bu]^+$), 126 (26), 44 (29).

*Butyl (2*E*)-3-[4-(*tert*-Butyl)phenyl]prop-2-enoate* (**15**): R_f (cyclohexane/AcOEt 4:1) 0.69. ^{1}H-NMR: 0.97 (*t*, *J* = 7.3, Me); 1.33 (*s*, Me_3C); 1.44 (*m* (='*sext.*'), J_{app} = 7.4, 2 H); 1.69 (*m* (='*quint.*'), J_{app} = 7.1, 2 H); 4.20 (*t*, *J* = 6.7, CH_2O); 6.40 (*d*, *J* = 15.9, H–C(2)); 7.40 (m_c, 2 arom. H); 7.47 (m_c, 2 arom. H); 7.67 (*d*, *J* = 16.0, H–C(3)). ^{13}C-NMR: 13.8; 19.2; 30.8; 31.2; 34.9; 64.4; 117.4; 125.8; 127.9; 131.8; 144.4; 153.8; 167.3. EI-MS: 260 (29, M^+), 245 (100, $[M - Me]^+$), 203 (11, $[M - Bu]^+$), 187 (13, $[M - OBu]^+$). Anal. calc. for $C_{17}H_{24}O_2$: C 78.42, H 9.29; found: C 78.24, H 9.48.

Sonogashira *Reactions in ^{i}PrOH/H_2O: General Procedure.* Aryl iodide (0.51 mmol, 1 equiv.), phenylacetylene (=ethynylbenzene; 66 µl, 0.6 mmol, 1.2 equiv.), $Na_3PO_4 \cdot 12\,H_2O$ (357 mg, 1 mmol, 2 equiv.), Pd^{2+}/GO (4.0 mg, 0.125 µmol, 0.25 mol-%), and ^{i}PrOH/H_2O (1 ml) were placed in a *Schlenk* tube under Ar and stirred at 80° during 24 h followed by withdrawal of an aliquot (10 µl) for GC/MS analysis. After cooling to r.t., the mixture was diluted with H_2O (8 ml) and extracted with Et_2O (3 × 8 ml). The combined extract was washed with H_2O (3 × 8 ml) and brine (8 ml), dried ($MgSO_4$), and concentrated, and the crude product purified by flash chromatography (SiO_2, 3 × 12 cm, cyclohexane/AcOEt 6:1).

Solid-Supported Aryl Iodide on Novasyn TGR *Resin.* To an ice-cooled soln. of 4-iodobenzoic acid (126 mg, 0.51 mmol) in THF (2.5 ml) and CH_2Cl_2 (2.5 ml), DMF (10 µl) and oxalyl chloride (0.1 ml, 1.2 mmol, 2.3 equiv.) were added and stirred overnight at r.t. The solvent was then evaporated and the residue dissolved in THF (2.5 ml) and MeCN (2.5 ml). Separately, the *Novasyn TGR* resin (0.5 g) was dried by co-concentration with MeCN (3 × 10 ml). The resin was then suspended in MeCN/pyridine 1:1 (20 ml) for 1 h. The previously synthesized soln. of 4-iodobenzoyl chloride was added, and the mixture was shaken overnight at r.t. The resin was then filtered, washed with MeCN (3 × 15 ml) and dried under reduced pressure: solid-supported aryl iodide.

Three-Phase Test: Mizoroki–Heck *Reaction* (analogously for the *Suzuki–Miyaura* and *Sonogashira* reactions). In a glass tube, NMP (1.3 ml) was added to the solid-supported aryl iodide (*ca.* 50 mg), butyl prop-2-enoate (82 µl, 0.58 mmol, 1.15 equiv.), 4-iodoacetophenone (123.1 mg, 0.5 mmol, 1 equiv.), and AcONa (50 mg, 0.6 mmol, 1.2 equiv.). After 1 h, Pd^{2+}/GO (1.6 mg, 0.5 µmol, 0.1 mol-%) was added. The suspension was shaken at 140°. After 24 h, a small sample (25 µl) was taken and added to MeCN (950 µl + 25 µl of AcOH) for HPLC analysis. From this sample, the ratio of 4-iodoacetophenone to butyl (2*E*)-3-(4-acetylphenyl)prop-2-enoate was determined and the conversion calculated. The mixture was cooled to r.t. and filtered. The resin and graphite oxide were washed with H_2O (2 × 2 ml) and AcOEt (2 × 2 ml). MeCN/CF_3COOH 1:1 (1 ml) was added to the mixture of resin and Pd and shaken at r.t. for 1 h. The mixture was then filtered. From the filtrate, the ratio of 4-iodobenzamide to 4-[(*E*)-3-butoxy-3-oxoprop-1-en-1-yl]benzamide was determined by HPLC. Hence, the conversion of the solid-supported aryl iodide was calculated.

Filtration Experiment: Heck *Reaction* (analogously for the *Suzuki–Miyaura* and *Sonogashira* reactions). In a glass tube (∅ 2 cm), NMP (2.3 ml) was added to Pd^{2+}/GO (3.1 mg, 1.0 µmol, 0.1 mol-%), AcONa (99 mg, 1.2 mmol, 1.2 equiv.), butyl prop-2-enoate (164 µl, 1.15 mmol, 1.15 equiv.), and ethyl 4-bromobenzoate (163 µl, 1.0 mmol, 1 equiv.). Then the suspension was stirred at 140°. After 10 and 30 min, small probes (20 µl) were taken and given in HPLC vessels with MeCN (950 µl + 30 µl of AcOH) for analysis. Then, the hot mixture was filtered off. The soln. was further stirred at 140°. After 1, 5, and 24 h, small probes (20 µl) were taken and placed into HPLC vessels containing MeCN (950 µl + 30 µl of AcOH) for analysis. From these probes, the conversion was calculated by GC/MS.

The same reaction was carried out without filtration of the catalyst.

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